# CLASSICAL PARTIAL CHARGE CALCULATIONS

by

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# INTRODUCTION

The primary goal of scientists worldwide is the prediction of the future. Whether their work is aimed at predicting the future by experience with empirical data, through calculations, or a combination of the two, this goal is foremost in the scientist's mind.

Some of the many phenomena a chemist might wish to predict or better explain involve the polarity of the chemical bond. This polarity is caused by the unequal sharing of electrons in a chemical bond. If a chemist could get a good quantitative handle on this unequal sharing of electrons, he might be able to predict or better explain such things as thermal stability, bond strength, bond type, relative acid/base strength, and bond length. Many aspects of nuclear magnetic resonance (NMR), electron spectroscopy for chemical analysis (ESCA), as well as many other spectrophotometric precedures, could also be linked to this unequal sharing of electrons in a chemical bond. A theoretical calculation that leads directly to bond polarity is the calculation of the partial charges of the atoms involved in that bond.

The purpose of this study is to develop such a calculation. Further, it is desired that this calculation be of simple nature, one that could easily be carried out with simple mathematics and possibly with the aid of a hand-held calculator.

Basically, there are two pathways used to calculate partial charge: classical calculations involving electronegativity, and wave mechanics. As most wave mechanical calculations require an extensive understanding of the field and employ substantial time on a larger size computer, the latter type of calculation has been ruled out for this study, as it does

not meet the criterion specifying that this calculation be of simple nature. Therefore, this study is concerned with the classical type of calculation involving electronegativity.

This study begins with a review of some of the many electronegativity scales that have been proposed in the past, proceeds to the partial charge calculations that have been derived from these scales, developing two new types along the way, and concludes by testing these calculations on a series of phosphorus oxide cage compounds synthesized for this purpose. Along with the review of the various electronegativity scales, this study compares and contrast these scales allowing the designation of the "best" scale. The partial charge calculations are compared with the aid of a computer , not because the calculations are complex, but rather to allow the numerous calculations to be evaluated and compared as fully possible with many different types of molecules. The synthetic methods for the preparation of the compounds for which these calculations were tested are discussed along with the presentation of the ESCA data that was determined for these synthesized compounds.

As mentioned, a computer was employed. To fully utilize a computer with minimal human intervention, a method for introducing absolute chemical structure into a computer was required. A linear line notation that was developed to meet this need is presented. This novel line notation has the capability of fully describing all aspects of 3-dimensional chemical structure.

# CHAPTER I

## ELECTRONEGATIVITY

Electronegativity: "The power of an atom in a molecule to attract electrons to itself"

Linus Pauling, 1932

Linus Pauling, in 1932, was the first to define a scale of "relative electronegativity values"[1]. Much of his earlier work[2-8] was concerned with bonding, bond radii, and bond energy. The concept of electronegativity arose from a need to readily distinguish or define the difference between an ionic and a covalent bond. Pauling's original values for electronegativity were assigned to a scale representing a "degree of electronegativity" based on bond dissociation energies. Originally, this scale was used to alter the wave function, representing the bond between unlike atoms, allowing the addition of an ionic term to the normal covalent one.

Many have addressed themselves to this concept of electronegativity[9-14] and there have been many reviews written on the subject as well as numerous different and abstract methods for deriving electronegativity values.

### Pauling Electronegativity Scale

Pauling based his scale for electronegativity on "excess bond energy"[1]. Pauling had noticed that the difference in bond dissociation energy (D) between two atoms and the average of the two pure covalent bond energies of both atoms was always positive.

$$\Delta = D_{A-B} - \frac{D_{A-A} + D_{B-B}}{2} \qquad \text{(equation I.1)}$$

$$\Delta > 0$$

The term $\Delta$ was defined to be the polar term in the A-B bond and $\frac{D_{A-A} + D_{B-B}}{2}$ as the covalent term. Pauling, observing that $\Delta$'s were not additive, based electronegativity on the square roots of the $\Delta$'s.

$$\Delta = 23.06\ (X_A - X_B)$$

$$\Delta X = (X_A - X_B) = 0.208\sqrt{\Delta} \qquad \text{(equation I.2)}$$

In this equation $X_A$ and $X_B$ were the assigned values of electronegativity for atoms A and B respectively. Pauling, wishing to express $\Delta X$ in electron volts and noting that the unit of bond dissociation energy, derived from heats of formation and combustion, was kilocalories, introduced a conversion factor of 23.06 eV's/Kcal. In later investigations[15-17], Pauling's values for electronegativity were correlated with dipole moment giving the scale some empirical credibility.

Mulliken Electroaffinity Scale

In 1934, Mulliken[18,19] defined electroaffinity as the average of the ionization potential and the electron affinity for the particular atom.

$$X_{Mulliken} = \frac{(I.B + E.A)}{2} \qquad \text{(equation I.3)}$$

This scale was largely empirical, but agreed with chemical facts and also corresponded with Pauling's scale. Originally, Mulliken[18] had defined his scale in terms of Linear Combination of Atomic Orbital (LCAO)

coefficients. Mulliken also presented a theoretical derivation of Pauling's original empirical equation. The difference in philosophy between Mulliken and others in this new field was that Mulliken's scale was based on ground state molecular orbitals whereas others chose to define their scales in terms of atomic orbitals.

Hinze and Jaffe[20-23] presented a different point of view by changing the basis of Mulliken's scale from ground state ionization potentials and electron affinities to variable valence state ionization potentials and electron affinities. These values were determined by a linear combination of the appropriate spectroscopic energy states.

Allred-Rochow Electronegativity Scale

Allred and Rochow[24] derived a scale assuming that electronegativity could be directly related to electrostatic charge between the nucleus and the electrons of an atom.

$$X_{\text{Allred-Rochow}} \propto \frac{Ze^2}{r^2} \qquad \text{(equation I.4)}$$

Where Z is the effictive nucular charge as defined by Slater's screening rules, e the charge on an electron, and r, the colvalent radius of the atom as detremined by Pauling's work in 1932[1].

Sanderson Electronegativity Scale

Sanderson defined electronegativity in a rather abstract manner[25-29]. The values in this electronegativity scale were defined in terms of relative electron density. Sanderson defined a stability ratio (SR):

$$X_{Sanderson} = SR = \frac{D}{Di}$$

$$D = \frac{3Z}{4\pi r^3} \qquad \text{(equation I.5)}$$

Di was defined as the electron density of an isoelectric inert atom, determined by interpolation between real values, which was needed to correct the average electron density (D) for variations in Z that were unrelated to chemical reactivity. An SR value of 1 was theoretically the most stable.

Sanderson found linear relationship between electronegativity, determined by his scale, and experimental electron affinities for halogens. He also established that a linear relationship existed between acid/base strength and SR for that particular atom.

Miscellaneous Scales

Gordy[30] based a scale on the relationship

$$X_{Gordy} \ \alpha \ \frac{Ze}{r} \qquad \text{(equation I.6)}$$

Gordy chose to define Z in a rather peculiar manner. An assumption was made that any electron in the valence shell would shield with a factor of 0.5, while all other electrons of the atom would shield with a factor equal to 1.0. He noted that a plot of $X_{Pauling}$ versus (n+1)/r, n = number of electron in the valence shell and r = the single bond covalent radius, would yield a linear plot.

Bellugue and Dandel[31] modified Pauling's scale where $(X_A - X_B)$ was a function of partial formal charge on an atom rather than a function of the neutral atom.

$$(X_A - X_B) = 0.208\sqrt{\Delta} + m(\delta_A^+ + \delta_B^-) \qquad \text{(equation I.7)}$$

where m is the degree of ionicity and $\delta_A^+$ and $\delta_B^-$ are the change in electronegativity in atom A and B respectively, upon the acquisition of a unit charge.

Iczkowski and Margrave[32] derived a relationship

$$X_{\text{Iczkowski and Margrave}} = \frac{-dE}{dN}, \qquad \text{(equation I.8)}$$

N is defined as the net change in charge such that $N \rightarrow 0$ for a neutral atom, $N \rightarrow -1$ for a negative atom, and $N \rightarrow +1$ for a positive atom; dE is the energy accompanying such a change in charge. Upon close examination, this work is similar to some of Mulliken's work.

Liu[33] derived an empirical equation similar to Gordy's,

$$X_{\text{Liu}} = 0.313\ (n + 2.6)/r^{2/3} \qquad \text{(equation I.9)}$$

Cottrell and Sutton[34] based two scales on the following observations.

$$X_{\text{Pauling}} \ \alpha \ \frac{(n+1)}{2r}$$
$$X_{\text{Pauling}} \ \alpha \ \frac{(n+1)}{\sqrt{r}} \qquad \text{(equation I.10)}$$

Others[35] based their schemes on a combination of what they believed to be the best values of the above mentioned scales.

## Comparison of Electronegativity Scales

The following discussion is a comparison of the four major types of electronegativity schemes: (1) Pauling's scale; representative of those scales that are derived empirically from thermodynamic data, (2)

Allred-Rochow's scale; representative of those scales that are derived theoretically from coulombic forces, (3) a Mulliken scale as modified by Hinze and Jaffe using valence shell ionization potentials and electron affinities, and (4) Sanderson's unique description for electronegativity defined as the relative electron density or stability ratio.

Figure 1 is a relative comparison of atomic number versus the difference in electronegativities derived from these four scales[12]. All four of these scales have been converted to a relative Pauling scale to enable the variations, arising from the methods from whence each were derived, to be examined. Table 1 tabulates this comparison by: (1) the equations used to derive electronegativity. (2) the theoretical/empirical basis, (3) the equation used to convert the scheme to a relitive Pauling scale, and (4) the notable influence on each individual scale. The ordinate axis of this graph is the simple algebraic difference between the two stated scales, i.e., $X_{Pauling} - X_{Sanderson}$, $X_{Pauling} - X_{Allred\text{-}Rochow}$, $X_{Pauling} - X_{Mulliken\text{-}Jaffe}$, $X_{Sanderson} - X_{Allred\text{-}Rochow}$, $X_{Sanderson} - X_{Mulliken\text{-}Jaffe}$, and $X_{Allred\text{-}Rochow} - X_{Mulliken\text{-}Jaffe}$. If a value for electronegativity for a particular scale is undefined (e.g. inert gases for Pauling's scale), the graphs involving that scale are not plotted at that point.

The graphs exemplify many interesting features that are a function of the theoretical/empirical of each scale. Every graph dealing with Pauling electronegativity values showed a dependence of a pseudo crystal field stabilization energy nature (atomic numbers 21 to 30, and 39 to 48). Sanderson's scale always seemed to fluctuate most as a shell of an atom neared filling (this is particularly noticeable at atomic numbers 2,10,

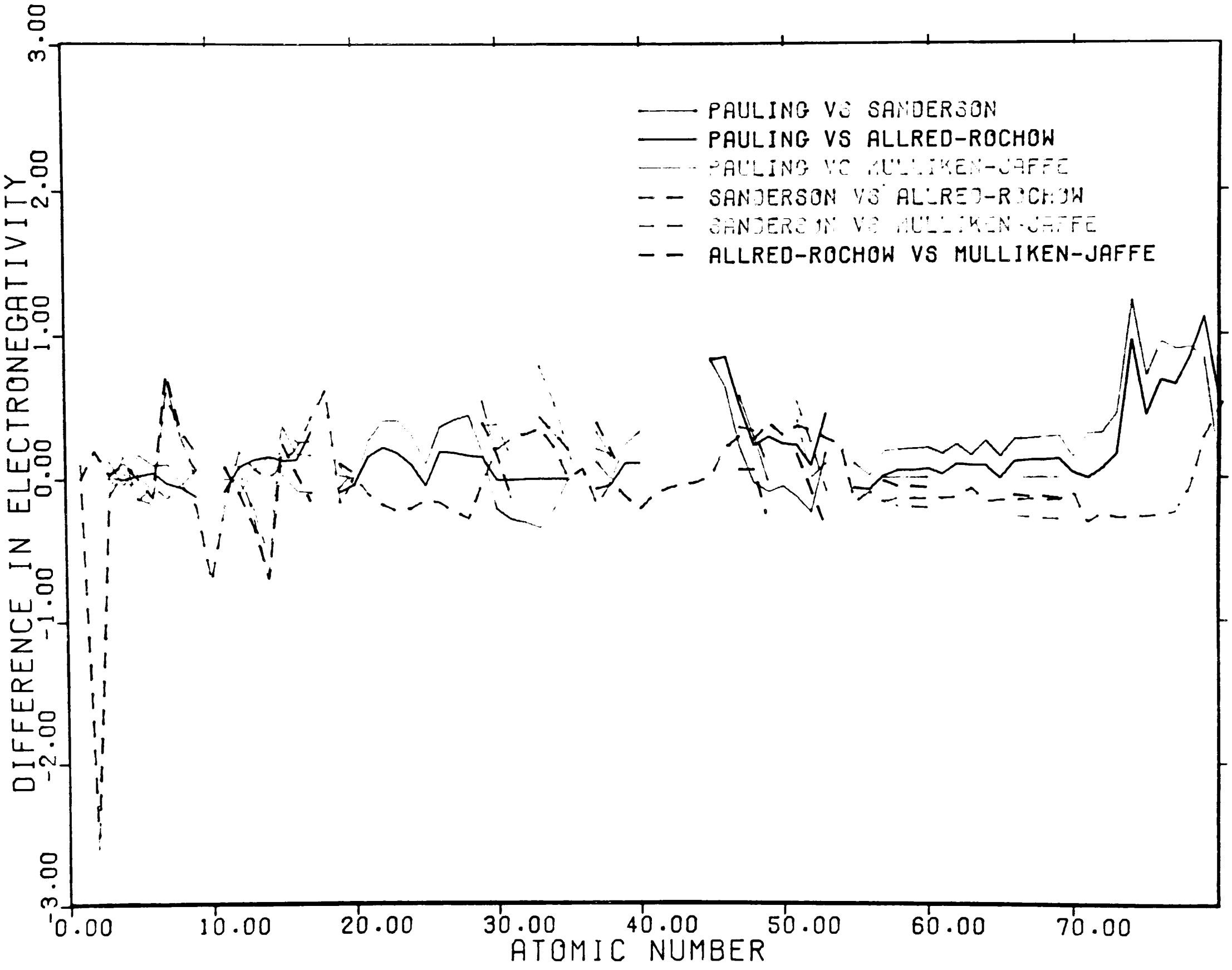

PAULING VS SANDERSON
PAULING VS ALLRED-ROCHOW
PAULING VS MULLIKEN-JAFFE
SANDERSON VS ALLRED-ROCHOW
SANDERSON VS MULLIKEN-JAFFE
ALLRED-ROCHOW VS MULLIKEN-JAFFE
DIFFERENCE IN ELECTRONEGATIVITY
3.00
2.00
1.00
0.00
-1.00
-2.00
-3.00
0.00
10.00
20.00
30.00
40.00
50.00
60.00
70.00
ATOMIC NUMBER

TABLE 1

COMPARISON OF ELECTRONEGATIVITY SCALES

| | Pauling | Mulliken-Jaffe | Allred-Rochow | Sanderson |
|---|---|---|---|---|
| Electronegativity As A Function Of | $D_{AB} - \frac{D_{AA} + D_{BB}}{2}$ | $\frac{I.E. + E.A.}{2}$ | $\frac{Ze^2}{r^2}$ | $\frac{D}{D_i}$ |
| Empirical/Theoretical Basis | thermodynamic bond dissociation energy | valence shell ionization energy and electron affinity | Coulomb's law | "compactness" (relative electron density) |
| Equation For Conversion To Pauling Scale | | $X_p = \frac{X_m}{2.8}$ | $X_p = \frac{0.359Z}{r^2} + 0.744$ | $X_p = (0.21X_s + 0.77)^2$ |
| Notable Influences | CFSE Z = 21 to 30, 39 to 48(?) | ½ filled orbitals Z = 7,15,33 | | filled shells Z = 2,10,18,36 |

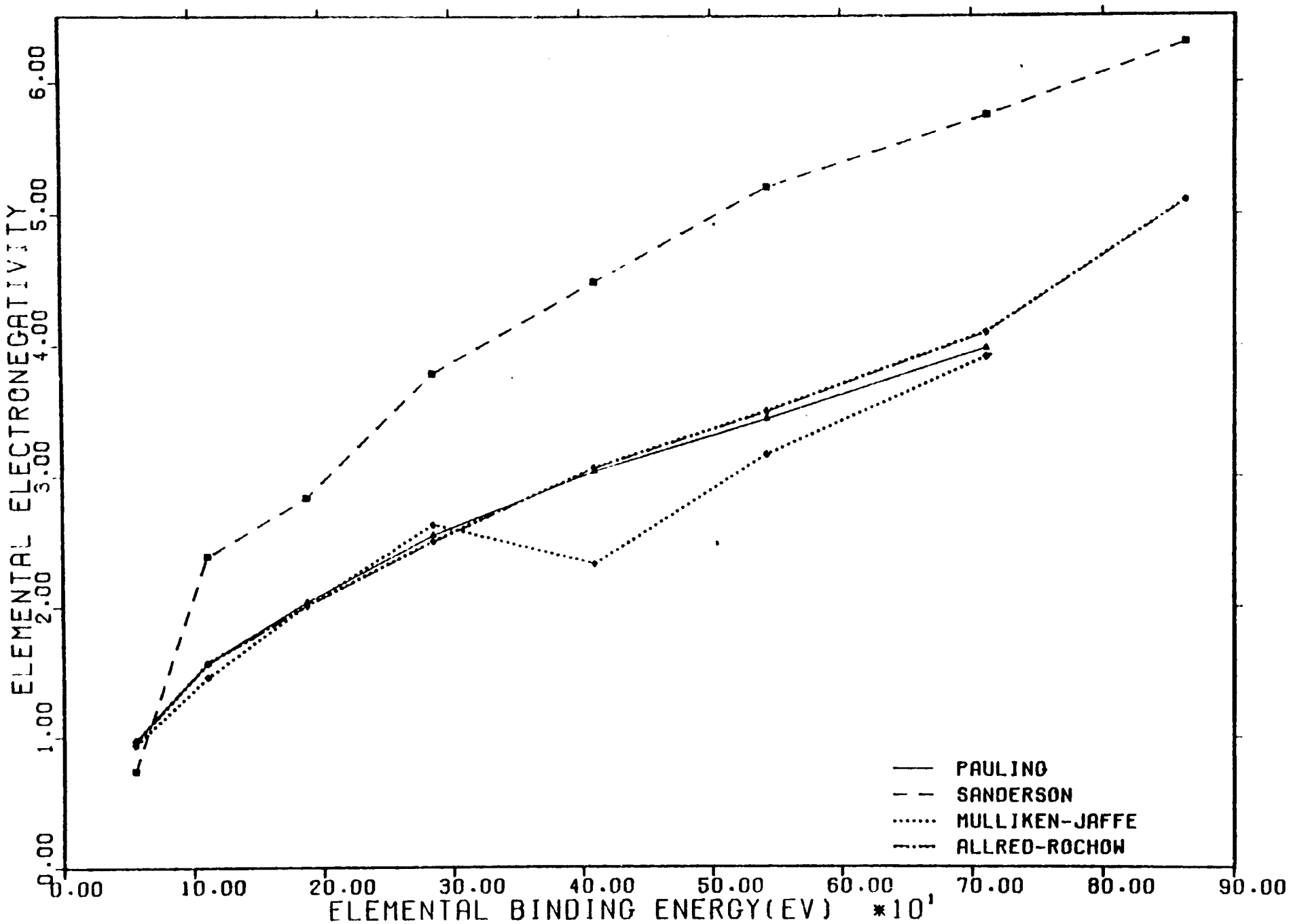



Fig. 2. Graph of core electron binding energy versus elemental electronegativity for the elements of the second period.

18, and 36). Differences between Mulliken-Jaffe and other definitions for electronegativity seemed most predominant when a shell aproached a half filld state. Overall, all four scales are in good agreement considering the wide range of methods used to derive these scales.

A need arose to test the "goodness" of a particular scale empirically. There have been attempts to measure partial charge by many methods. Two attempts used in the past to measure partial charge have been correlations with NMR data and dipole moment data[15-17,36]. Both of these methods have been ruled out for this work. Both NMR and dipole moment are influenced by many diverse phenomenon preventing the determination of the particular factor(s) due to electronegativity. Recently, electron spectroscopy for chemical analysis (ESCA) has been developed[34-40]. This measurement of the binding energies of core electrons most closely measures the factors that are influenced primarily by electronegativity[41-43].

To further compare these four basic types of electronegativity scales, figure 2 compares elemental core electron binding energies for the second row elements to their respective electronegativities as determined by each scale. If the assumption that ESCA is a measure of electronegativity factors is correct, then graphs of this type should show a correlation between ESCA data and electronegativity. Figure 2 supports this assumption. Further, the scales can be ranked from best to worst by this method. Figure 2 shows that Pauling's orginal values fit this criterion best, with Allred-Rochow's a close second. Sanderson's values do not fit the data as well and a Mulliken-Jaffe scale would need the most adjustments to fit this assumption.

# CHAPTER II

## PARTIAL CHARGE

Partial charge calculations are the logical extension to electronegativity. It is through these calculations that bond length, ionic/covalent character, stability and the like can be predicted or explained. Yet, few of the proposed electronegativity scales have proceeded to this extension.

### Pauling Ionicity

Pauling was perhaps the first to formulate what he referred to as ionicity[1-7,15-17]. He derived an equation which employed the difference in electronegativity ($\Delta X$) to facilitate the calculation of partial charge.

$$\text{ionicity} = 1.0 - e^{-c(\Delta X)} \qquad \text{(equation II.1)}$$

where c is an empirical constant. Pauling's "best value" for c was determined to be 0.25. Figure 3 is a graph of the difference in electronegativity ($\Delta X$) and ionicity as calculated by equation II.1 (with c = 0.25) for $\Delta X$ values between 0.0 and 4.0. Two notable characteristics about this calculation are that: (1) it does not account for a unit charge or greater (it is highly debatable, for example, whether or not a charge greater than 1 exists in scandium fluoride, $ScF_3$, or in magnesium oxide, MgO) and, (2) that it can only account for a diatomic system. The last characteristic is disastrous as this equation deals with the polarity of only one bond, ignoring all others in the compound.

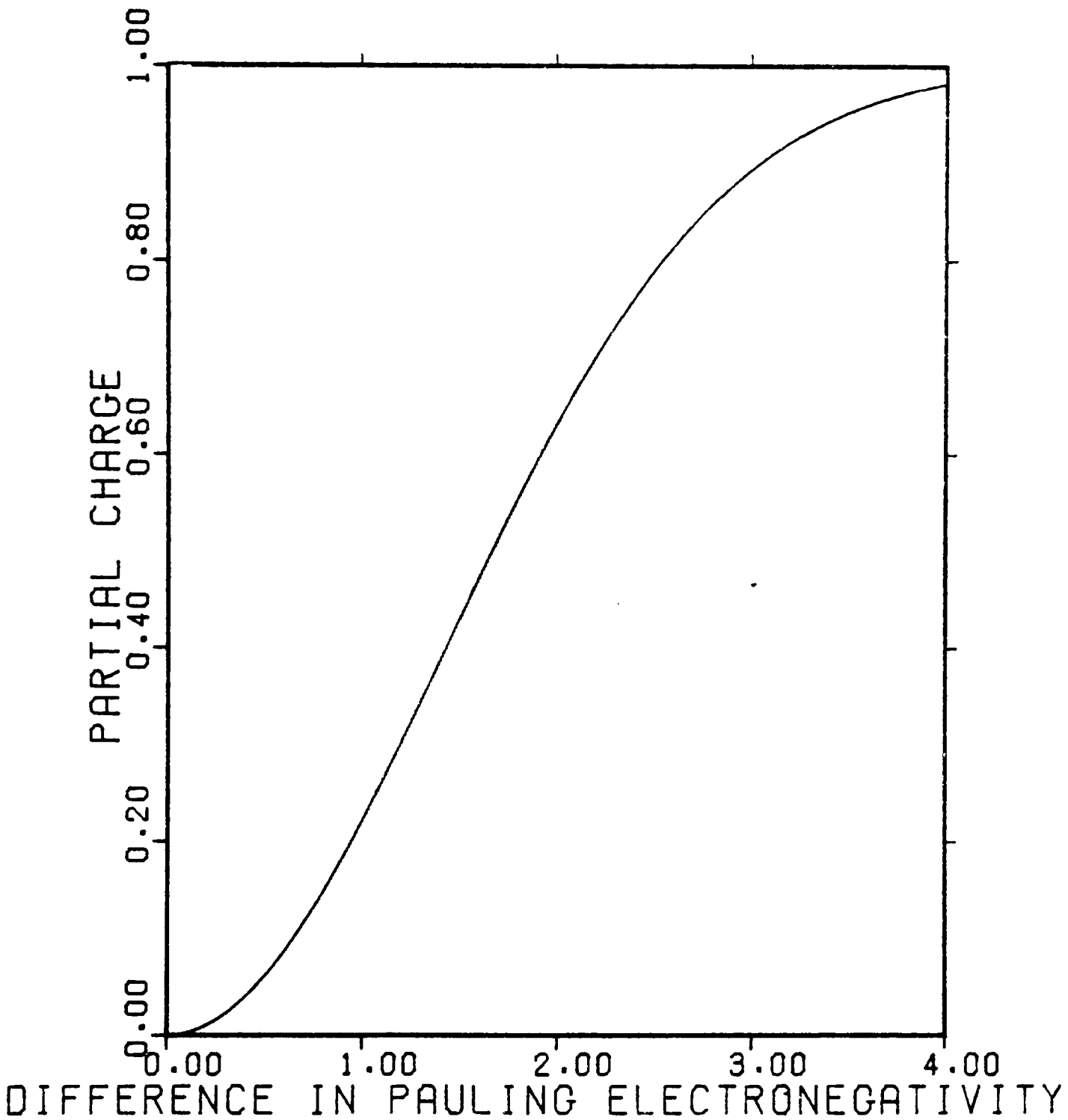



Fig. 3. Behavior of Pauling Ionicity.

Sanderson Electronegativity Equalization

Sanderson was another of the few to extend his electronegativity scheme to include partial charge calculations. He, in fact, has probably been the leader in this field with calculations correlating partial charge with bond length and acid/base strength. Sanderson[25-29,44] introduced the concept of "Electronegativity Equalization" that states, in part, that the electronegativities of the atoms in a molecule will equilibrate. This was the first time that electronegativity had been thought of as a dynamic property rather than a static one. Sanderson then defined the partial charge of an atom as a function of the difference between the elemental electronegativity and that of the new electronegativity, the equilibrium electronegativity. His original equation dealt with the difference between the stability ratio (SR) for the entire molecule and the SR for the atom for which the partial charge is being calculated.

$$\text{Partial Charge } (\delta) = \frac{n(SR_{molc})}{\Delta SR} - \frac{n(SR_{element})}{\Delta SR} \quad \text{(equation II.2)}$$

where n = valence of the atom
$\Delta SR$ = change in electronegativity per unit charge acquired

$SR_{molc}$ is calculated by Sanderson's scheme as the geometric mean of all the atoms in the molecule. Such that

$$SR_{molc} = \sqrt[n]{\Pi_n S_n}$$

$$\delta_{element} = \frac{\sqrt[n]{\Pi_n S_n} - S_{elemental}}{2.08\ S_{element}} \quad \text{(equation II.3)}$$

The denominator in equation II.3 is a factor which correlates the difference between elemental electronegativity and equilibrium electronegativity to partial charge. The most notable characteristic in this type of calculation is that atoms of the same type are treated equally (for example, all hydrogens in ethanoic acid).

Miscellaneous Schemes

There were a few others to introduce new ideas in this field. Smyth[36], in a paper that closely followed Pauling's original ideas, proposed two modifications of ionicity: (1) c = 0.156 in equation II.1 and (2)

$$\text{ionicity} = 1.6\ (\Delta X) + 0.35\ (\Delta X)^2 \qquad \text{(equation II.4)}$$

Other types of calculations have dealt with molecular orbital theory[45]. $\lambda$ was proposed to have described the polarity of the orbital in the equation

$$\psi_{molc} = \psi_{covalent} + \lambda\psi_{ionic} \qquad \text{(equation II.5)}$$

Jolly and Perry[39], as previously mentioned, attempted to correlate binding energies of core electrons with partial charge as calculated in the following manner.

$$\delta_n = F_n + \sum_i q_{n\rightarrow i} \qquad \text{(equation II.6)}$$

where $F_n$ is the formal charge on atom n and the summation of $q_{n\rightarrow i}$ represents the total amount of charge transferred from atom n to all other atoms in the molecule. This last term in equation II.6 is very hard to ascertain and as a result is the major downfall of this

particular system. Both of these partial charge calculations (molecular orbital and Jolly and Perry) were discarded for two reasons. First, and most important, neither can meet the criterion for a simple calculation and, secondly, the results for such calculations were not as successful as those discussed in this work.

Comparison of Partial Charge Calculations

To allow comparison of a Pauling type of calculation with other types, it became necessary to adapt a Pauling type of calculation to molecules containing more than one bond. This was accomplished by averaging the partial charges, calculated for each bond involving the atom for which the partial charge was sought.

$$\delta_n = \frac{\sum_i [1.0 - e^{-0.25(X_n - X_i)^2}]}{i} \quad \text{(equation II.7)}$$

i = number of atoms bonded to atom n

Figures 4 and 5 (Pauling partial charge) and figures 6 and 7 (Sanderson partial charge) are two examples of each partial charge calculation for two sets of data, nitrogen and phosphorus (see appendix IIa). To more fully compare the schemes in this paper, several data sets were examined. There were six data sets, one for each of the following type of atoms: phosphorus, oxygen, sulfur, fluorine and nitrogen. In general, the sulfur, fluorine, and nitrogen data sets contain smaller molecules, while the data sets containing phosphorus, oxygen, and carbon contain larger molecules. The oxygen and carbon data sets contained the most number of molecules, fluorine and sulfur the fewest, and phosphorus and nitrogen somewhere in between. To better compare the two types of

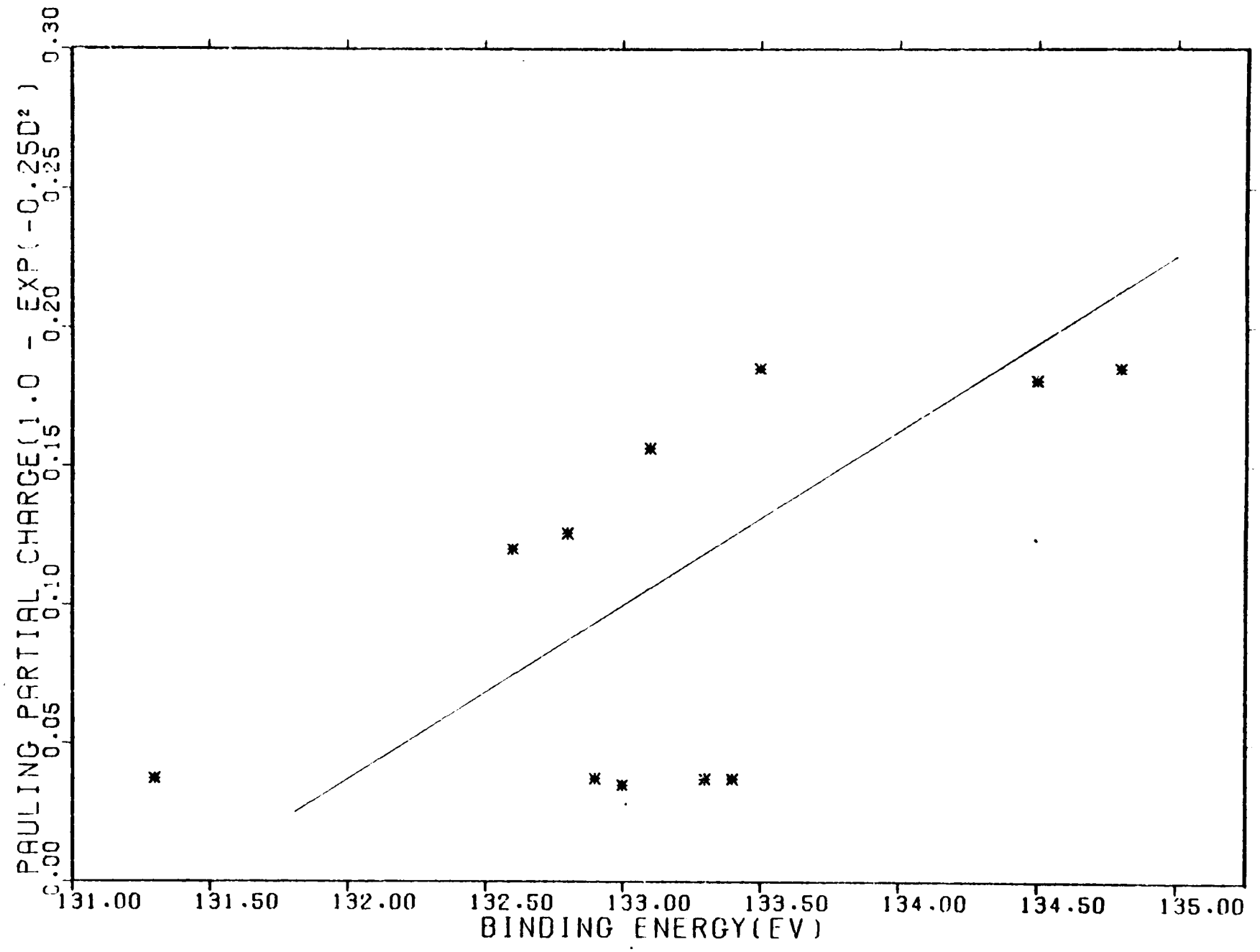



Fig. 4. Graph of binding energy versus Pauling partial charge for phosphorus data set.

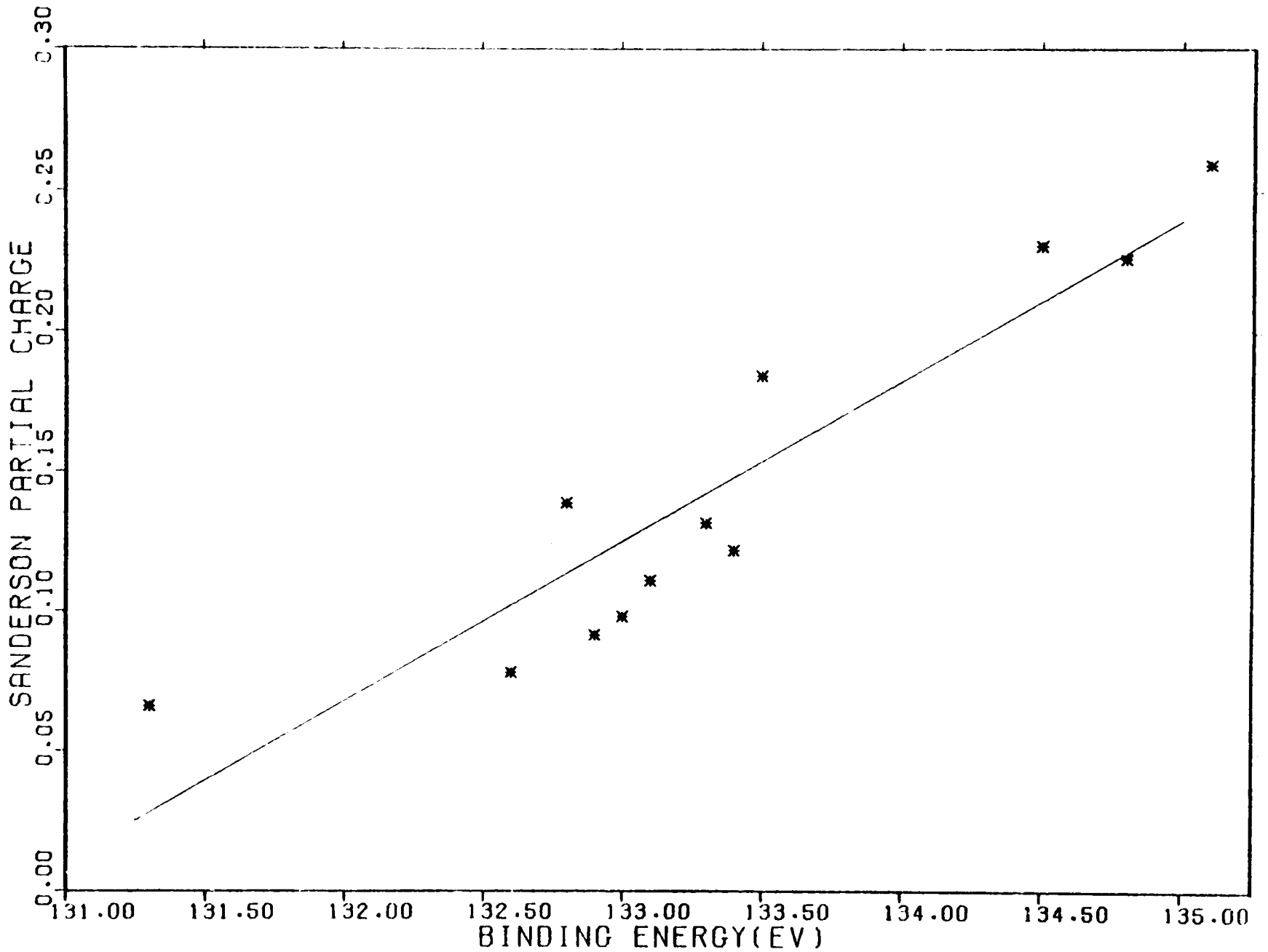



Fig. 6. Graph of binding energy versus Sanderson partial charge for phosphorus data set.

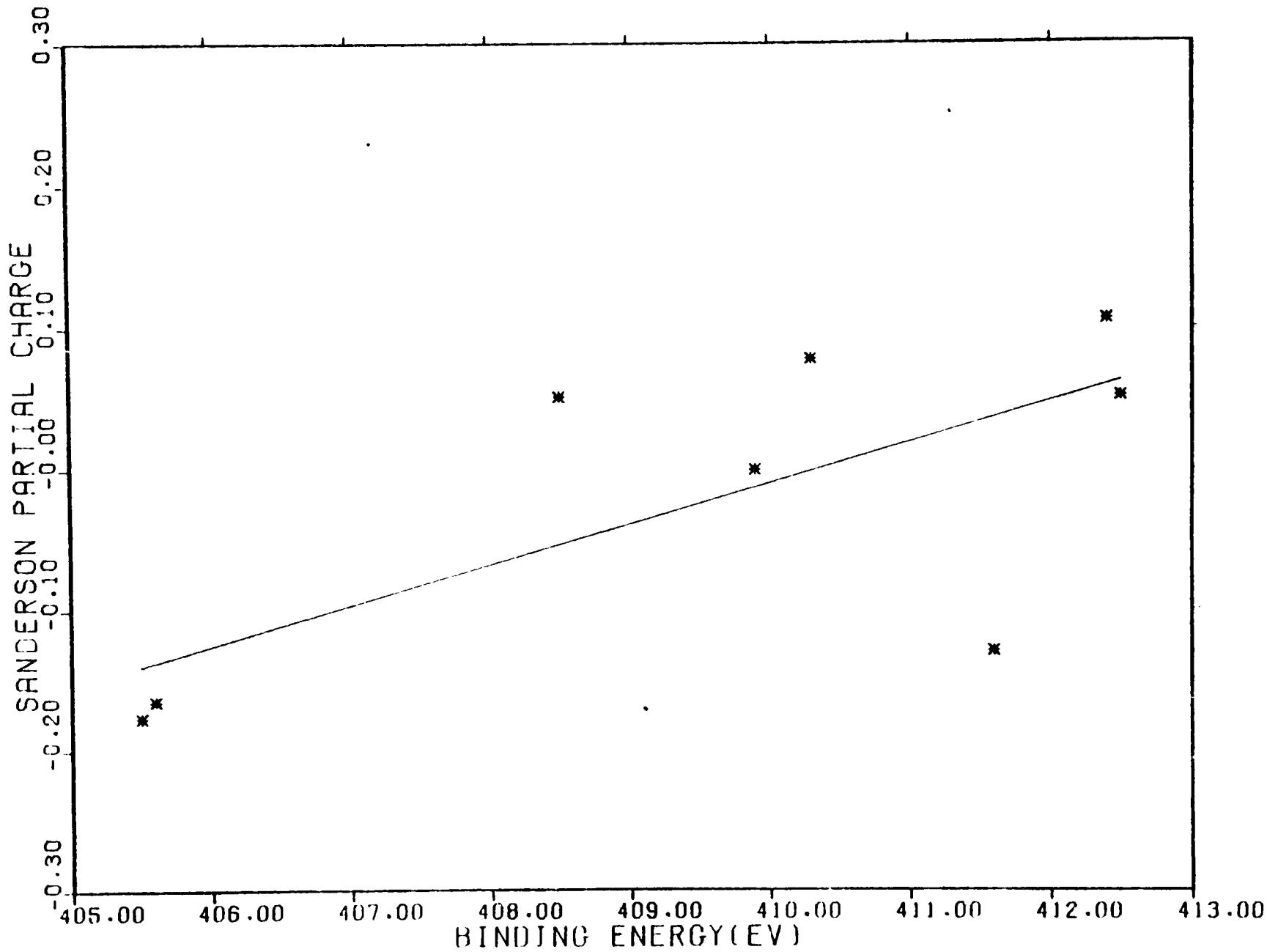



Fig. 7. Graph of binding energy versus Sanderson partial charge for nitrogen data set.

schemes, Pauling's and Sanderson's, the six data sets were examined. The correlation coefficients resulting from a least squares fit of graphs of partial charge versus binding energy, analogous to figures 4-7, are tabulated in table 2. One can immediatly notice a general trend. The data sets containing smaller molecules, sulfur, fluorine, and nitrogen are better described by a Pauling type of calculation. The larger molecules, in general, are described best by a Sanderson type of calculation. This is precisely what was expected. As previously mentioned, Pauling type calculations consider only one bond at a time. With the alterations made to accomodate multiple bonds, this type of calculation can be considered a complete localization of partial charge. On the other hand, the Sanderson type of calculation is completely delocalized partial charge as it treats all atoms in a molecule equally.

To best exploit the difference between the Pauling type of partial charge (complete localization and unchanging values for electronegativity) and the Sanderson type (complete delocalization with the concept of dynamic electronegativity values), several permutations of these schemes were calculated attempting to show that perhaps a "happy medium" existed. This is the most philisophically correct as an atom cannot "feel" other atoms at an infinite distance nor can adjacent atoms be ignored. These permutations were simple linear combinations of the two types of schemes. The correlation coefficients for these combinations are shown in table 3. With oxygen and carbon (these two contained the larger molecules and the most data of the six data sets, allowing for a maximum consistency within the particular data set), a maximum correlation at about 30% - 40% Pauling and 70% - 60% Sanderson was noted.

TABLE 2

CORRELATION COEFFICIENTS FOR PAULING AND SANDERSON TYPE CALCULATIONS

| Type of Caluclation | Data Set | | | | | |
|---|---|---|---|---|---|---|
| | P | O | S | F | C | N |
| Sanderson | 0.9222 | 0.6793 | 0.9632 | 0.5329 | 0.9213 | 0.6880 |
| Pauling $[1.0 - e^{-0.25\Delta x^2}]$ | 0.7279 | 0.5808 | 0.9854 | 0.7848 | 0.9705 | 0.9095 |
| Pauling $[1.0 - e^{-0.16\Delta x^2}]$ | 0.7297 | 0.5702 | 0.9886 | 0.7861 | 0.9657 | 0.9080 |
| Pauling $[0.16\Delta X + 0.035\Delta X^2]$ | 0.7125 | 0.6051 | 0.9562 | 0.7870 | 0.9738 | 0.9409 |

TABLE 3

LINEAR COMBINATION OF PAULING AND SANDERSON TYPE OF PARTIAL CHARGE CALCULATIONS

| %Pauling | %Sanderson | Data Set P | O | S | F | C | N |
|---|---|---|---|---|---|---|---|
| 100 | 0 | 0.7125 | 0.6051 | 0.9562 | 0.7870 | 0.9738 | 0.9409 |
| 90 | 10 | 0.7477 | 0.6548 | 0.9571 | 0.2650 | 0.9872 | 0.9216 |
| 80 | 20 | 0.7811 | 0.6889 | 0.9579 | 0.0083 | 0.9885 | 0.9216 |
| 70 | 30 | 0.8144 | 0.7091 | 0.9586 | 0.2586 | 0.9910 | 0.9038 |
| 60 | 40 | 0.8384 | 0.7182 | 0.9594 | 0.3552 | 0.9901 | 0.8810 |
| 50 | 50 | 0.8618 | 0.7194 | 0.9601 | 0.4146 | 0.9858 | 0.8841 |
| 40 | 60 | 0.8814 | 0.7154 | 0.9608 | 0.4543 | 0.9783 | 0.8240 |
| 30 | 70 | 0.8971 | 0.7082 | 0.9614 | 0.4826 | 0.9678 | 0.7914 |
| 20 | 80 | 0.9089 | 0.6992 | 0.9620 | 0.5037 | 0.9545 | 0.7575 |
| 10 | 90 | 0.9172 | 0.6893 | 0.9626 | 0.5200 | 0.9389 | 0.7228 |
| 0 | 100 | 0.9222 | 0.6793 | 0.9632 | 0.5329 | 0.9213 | 0.6880 |

As a Sanderson calculation is a complete delocalization of electronegativity, it was proposed that a maximum correlation might exist at a particular iteration in a scheme iterating out to Sanderson's equation for partial charge. This was accomplished by allowing each iteration to include one more coordination sphere than the one prior to it. The first iteration would include only the atoms directly bonded to the atom (primary or first coordination sphere) for which the partial charge was being calculated. The second iteration includes not only the atoms bonded directly to this atom, but those atoms bonded directly to the atoms in the primary coordination sphere as well. This definition was then extrapolated for the 3rd, 4th, and 5th iterations. The correlation coefficients for this iterative Sanderson calculation are tabulated in table 4. With four of these data sets (sulfur, fluorine, carbon, and nitrogen) a maximum correlation occurs at the first iteration, with the other two (phosphorus and oxygen) the maximum correlation occurred at a higher iteration, but it is noteworthy that a maximum correlation never occurred at infinite iterations (Sanderson's value).

Semi-Localized Partial Charge

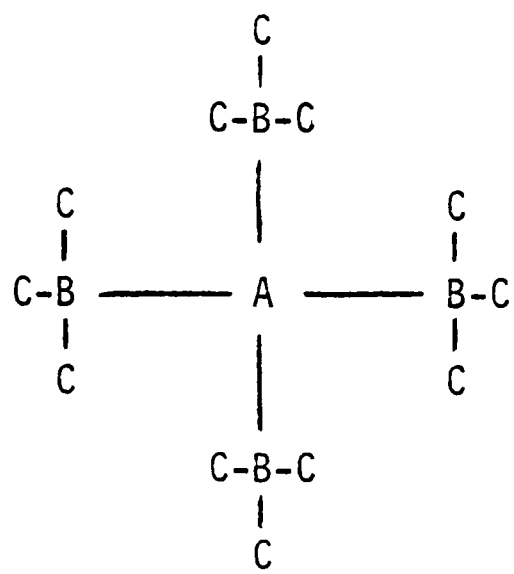
The data obtained in the iterative scheme described above, along with the facts obtained by the linear combination of a completely localized scheme (altered Pauling calculation) and a completely delocalized (Sanderson's calculation), leads to the conclusion that a semi-localized scheme, collaborated with the concept that electronegativity is a dynamic property rather than a static property, might best fit the data. This scheme would adjust the electronegativities of the atoms directly bonded to the atom for which the partial charge is sought considering the atoms

TABLE 4

CORRELATION COEFFICIENTS OF AN ITERATIVE SANDERSON SCHEME

| | Data Set | | | | | |
|---|---|---|---|---|---|---|
| Iteration | P | O | S | F | C | N |
| 1st | 0.9195 | 0.6425 | 0.9623 | 0.7857 | 0.9672 | 0.9473 |
| 2nd | 0.9094 | 0.6371 | 0.9632 | 0.0451 | 0.9650 | 0.9063 |
| 3rd | 0.9318 | 0.6904 | 0.9632 | 0.2175 | 0.9628 | 0.9006 |
| 4th | 0.9412 | 0.6905 | 0.9632 | 0.0450 | 0.9557 | 0.8825 |
| 5th | 0.9411 | 0.6948 | 0.9632 | 0.0530 | 0.9518 | 0.8701 |
| ∞ | 0.9222 | 0.6793 | 0.9632 | 0.5392 | 0.9213 | 0.6880 |

which are bonded to them before the partial charge is evaluated.




To illustrate this scheme the hypothetical molecule above will be used. The adjustment of the electronegativities of B sphere atoms would be accomplished first by averaging the effects of the C's with those of the B's allowing participation of C sphere atoms. The partial charge of A, $\delta_A$, was then calculated as a function of $\Delta$, the difference between the average B electronegativity and the electronegativity of A.

$$B_j = \frac{B_1^* + \sum_{j_i} (R_{j_i} C_{j_i})}{1 + \sum_{j_i} (R_{j_i})}$$

$$\Delta = A - \frac{A + \sum_i R_i B_j}{1 + \sum_i R_i} \qquad \text{(equation II.8)}$$

$$\delta_A = \frac{\Delta}{2.08 \sqrt{A}}$$

where: A, B, and C are the electronegativities of atoms A, B, and C
i is the number of atoms in the first coordination sphere of A
j is the number of atoms in the second coordination sphere of A
$j_i$ is the number of atoms in the first coordination sphere of $B_i$
$R_n$ is the multiple bond factor associated with atom n
(r = 1, single; 1.2, double, vide post)

For example, the calculation of the partial charge of the oxygen in ethanol ($CH_3CH_2OH$) would be accomplished as follows. The electronegativity of the carbon bonded directly to oxygen would be adjusted by the average of the electronegativities of one carbon and two hydrogens. Then Δ is calculated by taking the difference between the electronegativity of oxygen and the average of this adjusted electronegativity for the carbon bonded directly to oxygen and electronegativity of hydrogen (for the alcoholic proton).

$$\Delta = O - \frac{C + \frac{H + H + C}{3}}{2} + H \qquad \text{(equation II.9)}$$

where O, C, and H are the electronegativities of oxygen, carbon, and hydrogen.

There were many factors that could influence this calculation: (1) The function of Δ used to calculate the partial charge, (2) the scale of electronegativity, (3) the method of averaging, and (4) accounting for multiple bonds. Each of these factors were studied in detail by a comparison of the correlation coefficients calculated from the grapns of partial charge, as calculated with the various permutations of each of these factors, versus binding energy.

The two functions relating Δ to δ chosen for examination were a

Pauling type, the conventional concept that electronegativity is a static property of an atom, and Sanderson's electronegativity equalization, utilizing the concept of dynamic electronegativity. Table 5 lists the correlation coefficients of the graphs for each data set as calculated by either method. As the adjusted Pauling scheme used arithmetic averaging and Sanderson used geometric, both types of averaging were compared. This data is very decisive; an electronegativity equalization function yields substantially better results.

As shown in figure 2 and latter part of Chapter I, all of the various types of electronegativity scales were similar. As Sanderson's electronegativity equalization function was shown to be the best and Pauling's electronegativity scales was the most widely accepted, a comparison was made of the two scales as shown in table 6. Again, as Sanderson's calculations used geometric mean, this method of averaging was included as a factor in the comparison. This data is inconclusive. The highest correlation coefficient for each data set is scattered among both scales. Pauling's scale is most widely accepted, and it is already incorporated into most periodic charts. Thus, Pauling's scale was chosen, since the main criterion of this study was the design of an uncomplicated calculation (in this case an uncomplicated calculation was interpreted as not having to look up special values for electronegativity).

This method of averaging has been shown in each of the preceeding comparisons. There is a very close agreement between the arithmetic and geometric methods. Overall, arithmetic averaging is slightly better. Arithmetic averaging is also much simpler to calculate. For these reasons, arithmetic averaging has been chosen for the schemes proposed by this study.

TABLE 5

COMPARISON OF FUNCTIONS OPERATING ON $\Delta X$

| Type Calc. | $\int(\Delta X)$* | Data Set P | O | S | F | C | N | Average |
|---|---|---|---|---|---|---|---|---|
| $\Sigma$ | EE | 0.7956 | 0.4398 | 0.9612 | 0.6788 | 0.9683 | 0.8944 | 0.7897 |
| $\Sigma$ | P | 0.7877 | 0.4329 | 0.8925 | 0.7704 | 0.8169 | 0.8402 | 0.7568 |
| $\Pi$ | EE | 0.8089 | 0.4515 | 0.9609 | 0.6109 | 0.9648 | 0.8810 | 0.7797 |
| $\Pi$ | P | 0.7979 | 0.4358 | 0.8741 | 0.7079 | 0.7760 | 0.8546 | 0.7413 |

*EE = electronegativity equalization (equation II.3), P = Pauling type (equation II.1)

TABLE 6

EMPIRICAL COMPARISON OF PAULING'S AND SANDERSON'S ELECTRONEGATIVITY SCALES

| Scale* | Type Mean** | Data Set P | O | S | F | C | N | Average |
|---|---|---|---|---|---|---|---|---|
| P | Σ | 0.7956 | 0.4398 | 0.9612 | 0.6788 | 0.9683 | 0.8944 | 0.7897 |
| S | Σ | 0.8038 | 0.4655 | 0.9546 | 0.6177 | 0.9720 | 0.8978 | 0.7852 |
| P | Π | 0.8089 | 0.4515 | 0.9609 | 0.6109 | 0.9648 | 0.8810 | 0.7797 |
| S | Π | 0.8251 | 0.4798 | 0.9559 | 0.5420 | 0.9714 | 0.8871 | 0.7767 |

*P = Pauling electronegativity, S = Sanderson electronegativity scale
**Σ = arithmetic mean, Π = geometric mean

One factor, not discussed in any other partial charge scheme, is the consideration of double bonds. Double bonds were the only multiple bond encountered in this study so the original value for this factor was derived from the ratio of the coulombic forces as caused by the difference in bond length between a double and a single bond between the two atoms.

$$\text{Coulombic force} = \frac{k}{r^2}$$

$$r = \text{distance between charged species} \qquad \text{(equation II.10)}$$

$$\frac{F_2}{F_1} = \frac{k/r_2^2}{k/r_1^2} = \frac{r_1^2}{r_2^2} = 1.38$$

As this is only a starting approximation, it was assumed that the force constant was the same for a double as for a single bond. The values for $r_1$ and $r_2$ were typical single and double bond lengths for phosphorus.

$$\Delta = A - \frac{\sum_i \left(B_i - \frac{\sum_j C_j R}{j}\right) R}{i} \qquad \text{(equation II.11)}$$

Equation II.11 shows the alteration of equation II.8 incorporating the addition of the multiple bond factor, R. Table 7 tabulates the correlation coefficients for the graphs of partial charge, with varying values of R, versus binding energy. All variations of R yielded good results, with the best value equal to 1.16. Taking into account that Pauling's values for electronegativity are only to two significant figures, this factor was rounded to 1.2

In summary, Pauling's values for electronegativity gave the best results, as well as being readily available. An arithmetic mean was desired as it was the easiest to utilize. Equation II.12 shows the

$$\delta_X = \frac{\Delta}{2.08\sqrt{X_n}} \qquad \text{(equation II.12)}$$

function of $\Delta$ which gave the best results. A multiple bond factor of 1.2 was determined the most realistic. To illustrate the results of this scheme, partial charges of phosphorus and nitrogen in various molecules, as calculated by this semi-localized method, were graphed versus the binding energies for the atoms (figures 8 and 9).

Coordination Sphere Partial Charge

The coordination sphere partial charge is an attempt at a simpler scheme. It is an approximation of the semi-localized partial charge scheme and works well for approximations, but never yielding as high a correlation coefficient as the semi-localized scheme.

The calculation of the coordination sphere type involves adding the average of the first coordination sphere of the atom for which the partial charge is being calculated to the average of the second. The effects of the second coordination sphere were reduced by multiplying by an empirical factor.

$$\Delta = A - \frac{A + \sum_i R_i B_i + \Omega \sum_j R_j C_j}{1 + \sum_j R_j + \Omega \sum_j R_i} \qquad \text{(equation II.13)}$$

$$\delta_A = \frac{\Delta}{2.08\sqrt{A}}$$

where: A, B, and C are the electronegativities of atoms A, B, and C
i is the number of atoms in the first coordination sphere of A
j is the number of atoms in the second coordination sphere of A
$R_n$ is the multiple bond factor associated with atom n
$\Omega$ is the weighting factor for the second coordination sphere of A ( $\Omega$= 0.20)

TABLE 7

COMPARISON OF MULTIPLE BOND FACTORS

| | Data Set | | | | | | |
|---|---|---|---|---|---|---|---|
| R | P | O | S | F | C | N | Average |
| 1.38 | 0.7956 | 0.4398 | 0.9612 | 0.6788 | 0.9683 | 0.8944 | 0.7897 |
| 1.16 | 0.8356 | 0.4291 | 0.9626 | 0.6809 | 0.9698 | 0.8927 | 0.7951 |
| 1.50 | 0.7733 | 0.4440 | 0.9605 | 0.6778 | 0.9671 | 0.8946 | 0.7862 |

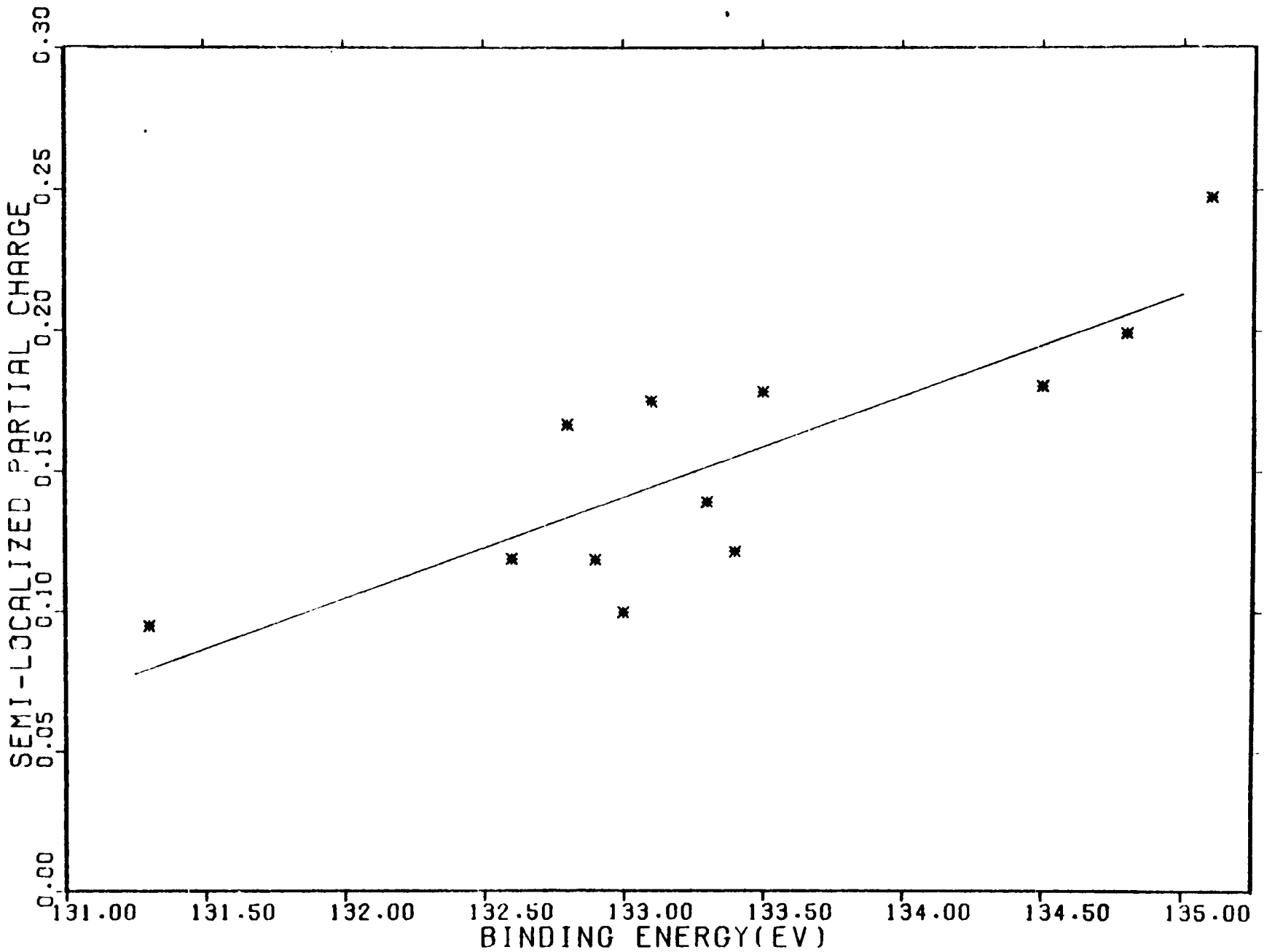



Fig. 8. Graph of binding energy versus semi-localized partial charge for phosphorus data set.

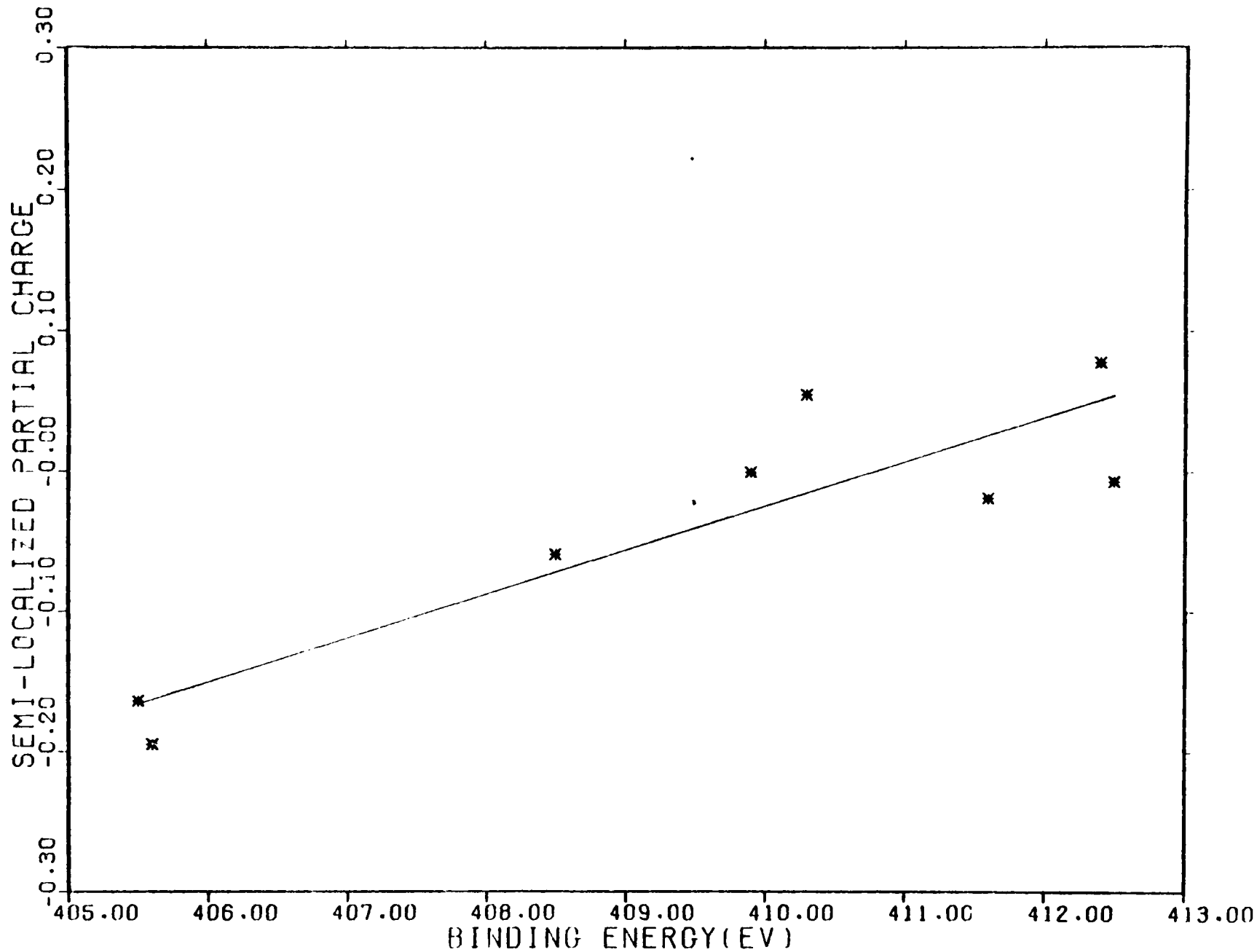



Fig. 9. Graph of binding energy versus semi-localized partial charge for nitrogen data set.

The weighting factor ($\Omega$) was chosen, as before, by comparisons of the various correlation coefficients obtained by calculations with various values of $\Omega$. Others[46], have used values between 0.10 and 0.33 for inductive factors of this nature. The other factors that influence this calculation, electronegativity scale, arithmetic and geometric averaging, were studied by the same procedure as was the semi-localized scheme. The results were similar: Pauling's scale was chosen and an arithmetic mean was the determined superior method of mean calculation. Figures 10 and 11 are examples of the graphs obtained by this calculation.

TABLE 8

COMPARISON OF THE WEIGHTING FACTOR IN A COORDINATION SPHERE TYPE OF CALCULATION

| | Data Set | | | | | | |
|---|---|---|---|---|---|---|---|
| Ω | P | O | S | F | C | N | Average |
| 0.333 | 0.8884 | 0.5214 | 0.9612 | 0.0125 | 0.9405 | 0.8637 | 0.6980 |
| 0.666 | 0.8556 | 0.4495 | 0.9612 | 0.5246 | 0.8817 | 0.6978 | 0.7284 |
| 0.166 | 0.8888 | 0.5754 | 0.9612 | 0.4621 | 0.9590 | 0.9079 | 0.7924 |
| 0.2 | 0.8899 | 0.5633 | 0.9612 | 0.3704 | 0.9565 | 0.8939 | 0.7725 |

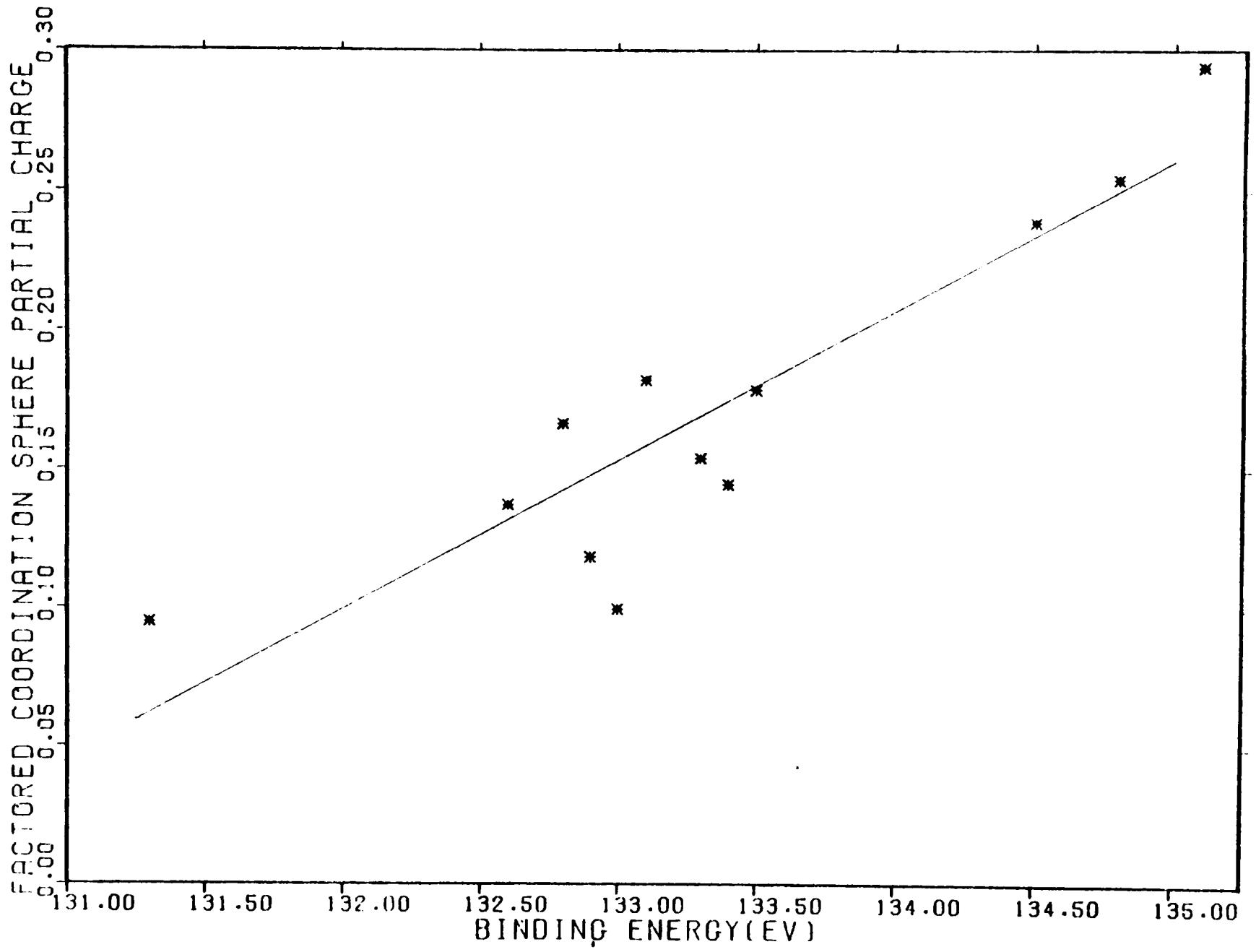



Fig. 10. Graph of binding energy versus coordination sphere partial charge for phosphorus data set.

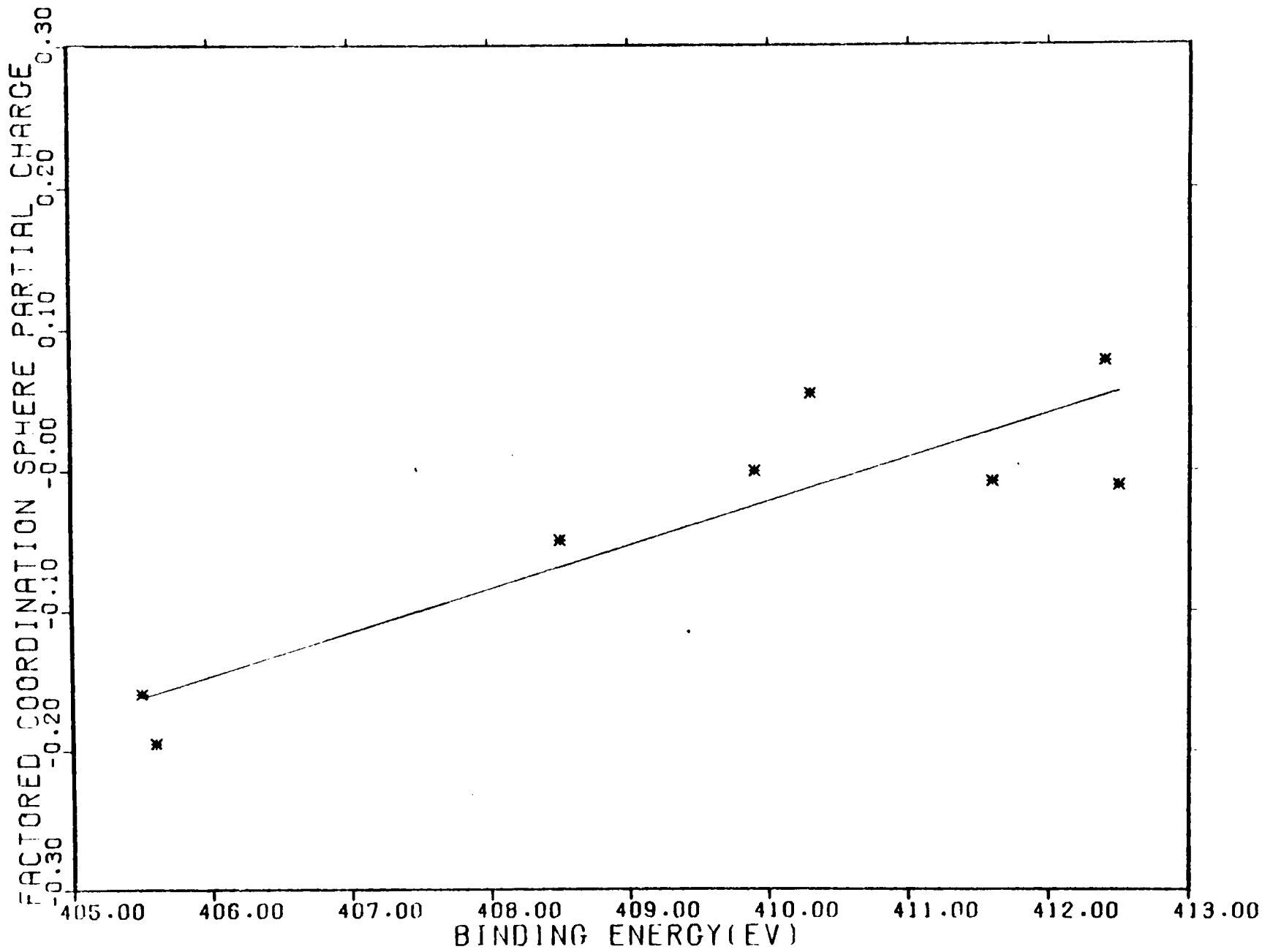



Fig. 11. Graph of binding energy versus coordination sphere partial charge for nitrogen data set.

# CHAPTER III

## EXPERIMENTAL APPLICATIONS OF PARTIAL CHARGE

To test the schemes proposed in Chapter II, empirical measurements of a series of phosphorus cage compounds were predicted and then measured. These measurements were the binding energies of phosphorus, oxygen and sulfur. This series of compounds showed that the partial charge is only a function of the next nearest neighbor and that partial charge can be used an as aid in the assignment of ESCA peaks. The series of compounds studies were $P_4O_6$, $P_4O_6S$, $P_4O_6S_2$, $P_4O_6S_3/P_4O_6S_4$, and $P_4O_6Se$. The backbone structure ($P_4O_6$) is shown in figure 12. The addition of sulfur (or selenium) occurs at the phosphorus site accordingly. The exact structure of these compounds is presented along with the binding energies in table 10.

### Experimental Procedures

Phosphorus and tetraphosphorus decasulfide ($P_4S_{10}$) were purchased from Fisher Chemical Company, and the tetraphosphorus decaselinide ($P_4Se_{10}$) from Research Organic/Inorganic Chemical Corporation. All were used without further purification. The solvents used in the synthetic work were dried by distilling from and storing over calcium hydride, lithium aluminum hydride, or molecular sieve.

All of the compounds synthesized were air sensitive and required special techniques and apparatus. The synthesis of these compounds were carried with Schenk ware and Schenk ware techniques[47] under a dried nitrogen atmosphere. Purification was carried out by sublimation. The transferring of these compounds from one container to another, when

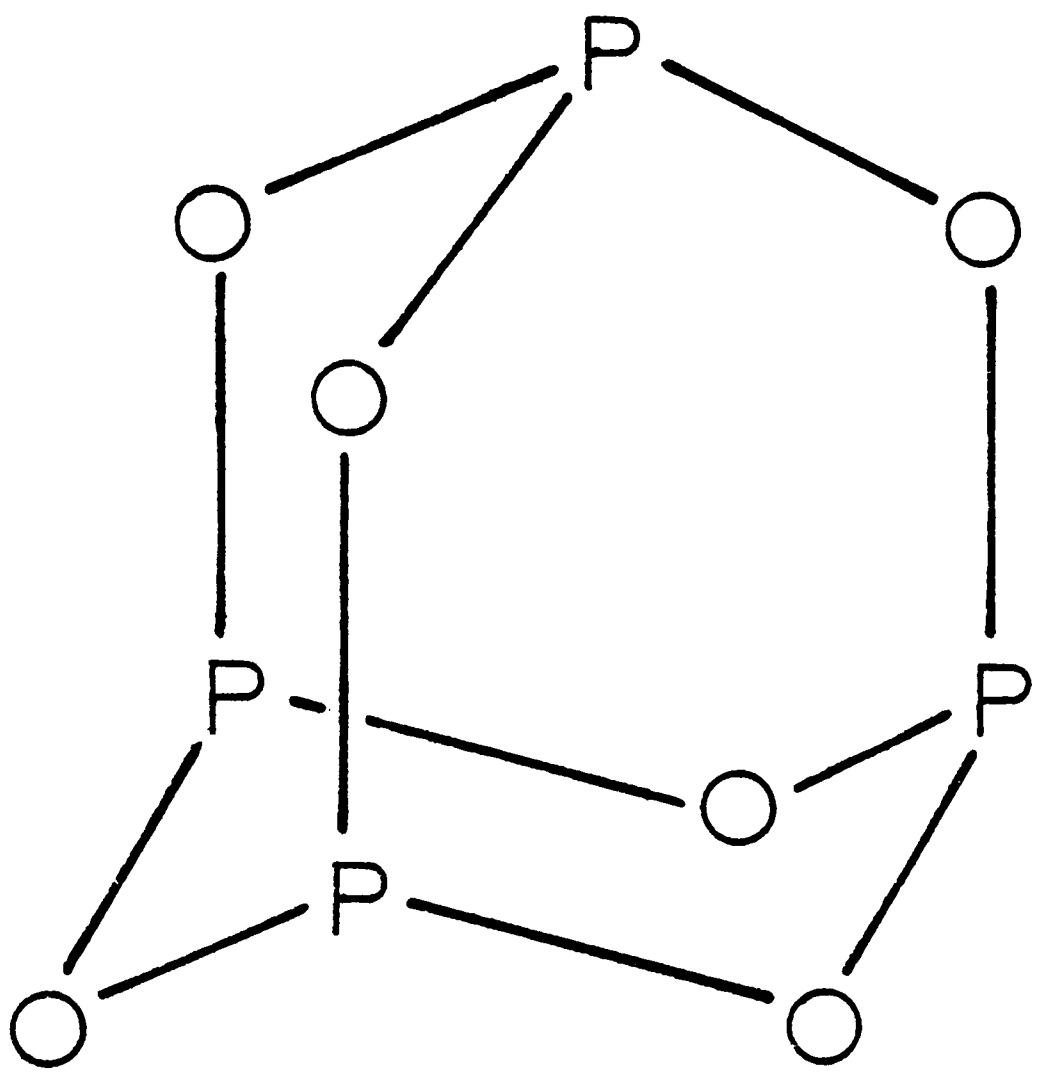



Fig. 12. Structure of $P_4O_6$.

Schenk ware could not be employed, was completed in a static helium atmosphere dry box using a sodium-potassium alloy (NaK) as oxygen and water scavengers. Nuclear magnetic resonance (NMR) samples were obtained by transferring the compounds to an NMR tube in the NaK dry box, injecting a suitable solvent into the tube through a rubber septum, freezing the sample with liquid nitrogen, and then sealing the tube under a vacuum of approximately $10^{-1}$ torr. Infrared (IR) sampling was accomplished by the preparation of a fluoro-mac mull in the NaK dry box.

$P_4O_6$

$$P_4 \text{ (white)} + O_2 \longrightarrow P_4O_6$$

The $P_4O_6$ was synthesized by the controlled combustion of white phosphorus with atmospheric oxygen. The technique and apparatus was modified slightly from those used by Walker[48]. The two traps filled with glass wool were replaced with a 15°-20° water cooled U-tube filled with 5 mm glass beads. The combustion was allowed to proceed through this trap (by turning off the coolant) to allow the phosphorus, which might have sublimed into it, to react. These modifications, besides making the apparatus easier to set-up and operate gave slightly better yields in less time, but increased contamination due to white phosphorus in the $P_4O_6$ trap. This problem was remedied by delaying the sublimation from the reaction trap to the storage vessel. This delay allowed the white phosphorus to be converted to red phosphorus, from which the $P_4O_6$ was readily sublimed.

$P_4O_6X_n$; X = S (n = 1 - 4), X = Se (n = 1)

$$P_4O_6 + P_4X_{10} \longrightarrow P_4O_6X_n$$

$P_4O_6S$, $P_4O_6S_2$, $P_4O_6S_3/P_4O_6S_4$, and $P_4O_6Se$ were all prepared by the above reaction under varying conditions. A particular ratio of $P_4O_6/P_4X_{10}$ was reacted at reflux under a dry nitrogen atmosphere in a suitable dried and degassed solvent with vigorous stirring. After the reaction was completed, the solution was allowed to cool and then filtered. The solvent was then drawn off and the resulting solid purified by sublimation at 55°-60° onto a 0° cold finger under $10^{-5}$ torr. The entire procedure was carried out under the proper inert conditions (Schenk ware and Schenk ware techniques, or in a dry box). Table 9 tabulates the exact conditions used to yield a particular product. It should be noted that $P_4O_6S_3$ and $P_4O_6S_4$ were prepared together and no attempt was made to separate them.

Instrumention

Infrared spectra were obtained (on a Perkin-Elmer model 457) and $^1H$ NMR and $^{31}P$ NMR spectra (on a Varian Associates NMR model XL-100-15 and a Brucker-90) for each sample. IR and NMR data were recorded soley to confirm the product and its purity. All spectra were in good agreement with those obtained by Walker[48] and Walker and Mills[49]. Electron Spectroscopy for Chemical Analysis (ESCA) data was accumulated by Dow Chemical, Freeport, Texas with a Hewlett Packard 5950A ESCA Spectrometer System. All reported ESCA data was referenced to a carbon 1s peak of 284.50 eV.

TABLE 9

EXPERIMENTAL CONDITIONS FOR THE SYNTHESIS OF $P_4O_6X_n$; X = S (n = 1-4), X = Se (n = 1)

| product | mole ratio ($P_4O_6/P_4X_{10}$) | solvent | reaction time |
|---|---|---|---|
| $P_4O_6S$ | 1/1 | toluene | 30 min. |
| $P_4O_6S_2$ | 1/1.5 | o-xylene | 2 hr. |
| $P_4O_6S_3/P_4O_6S_4$ (mixture) | 1/1.5 | o-xylene | 5-6 hrs. |
| $P_4O_6Se$ | 1/1 | o-xylene | 6 hr. |

Binding Energies

Partial charges were calculated for every atom in each compound by equation II.8. Theoretical binding energies were then calculated for all atoms (except selenium for which there was no reference data) by interpolation from graphs of binding energy versus partial charge (figure 8 and other similar to figure 8). These calculated partial charges and binding energies, along with the experimental binding energies and the structure for each compound are presented in table 10.

Experimental binding energies were obtained for each type of atom in these compounds and with the aid of the calculated partial charge, assignments made. Two examples of the ESCA spectrums obtained are figures 13, ESCA spectrum of $P_4O_6$: phosphorus region, and 14, ESCA spectrum of $P_4O_6$: oxygen region. This raw data was interpreted by calibrating with a carbon 1s peak of 283.87 eV. Partial charge can be, and was, used as an aid in assigning binding energies by the realization that an increase in the partial charge corresponds to an increase in the energy that is required to remove a core electron (bonding energy) from the atom. Table 11 statistically compares the calculated binding energies with the experimental, grouping the data by the calculated partial charge for each unique atom. This grouping assumes that binding energy and partial charge are directly dependent upon one another and that all atoms of one type with the same partial charge should yield identical binding energies.

As table 11 shows, the calculated binding energies for phosphorus and sulfur are in good agreement with the experimental. Oxygen, while in good agreement, did not give as favorable results. This was entirely expected from the poor correlations in the oxygen data set presented in

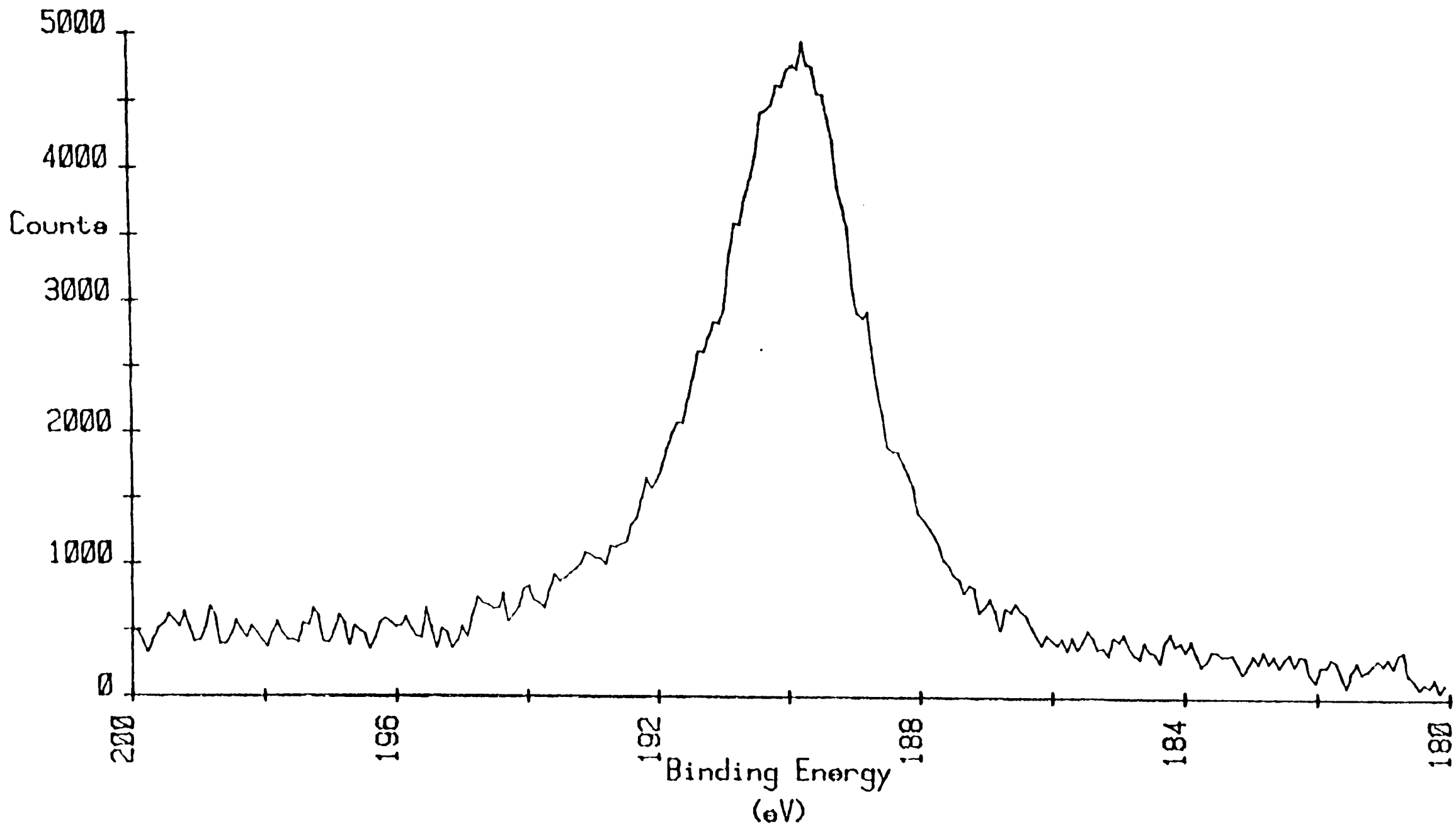



Fig. 13. ESCA spectrum of $P_4O_6$: phoshourus region.

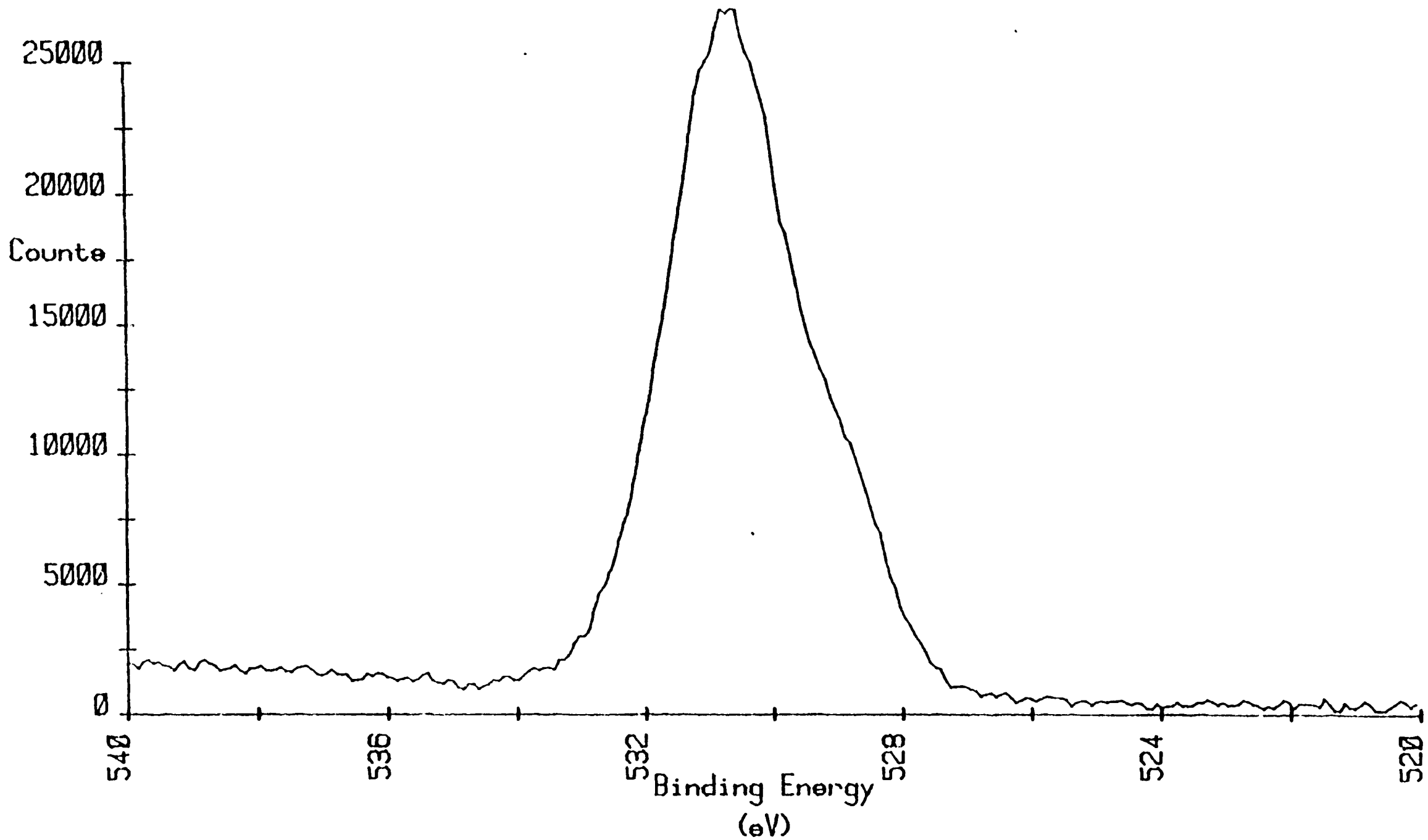



Fig. 14. ESCA spectrum of $P_4O_6$: oxygen region.

TABLE 10

STRUCTURE AND BINDING ENERGIES OF SOME PHOSPHORUS OXIDE CAGES

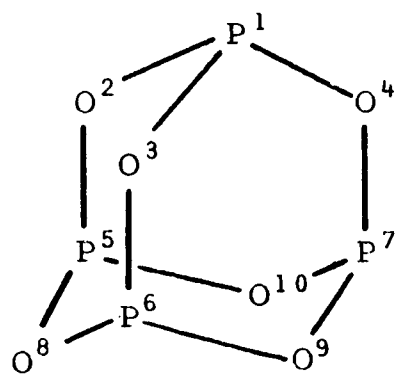
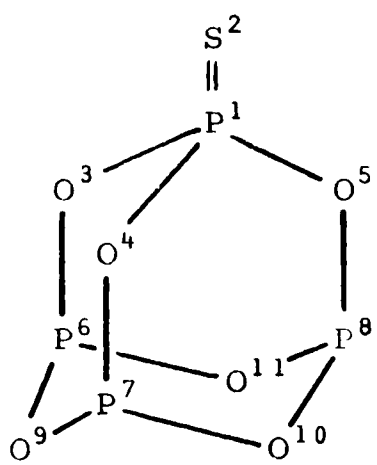
| structure | atom | atom number(s) | δ | calc'd b.e. | expt'l b.e. |
|---|---|---|---|---|---|
|  | P | 1,5,6,7 | +0.15 | 192.36 | 192.42 |
| | O | 2,3,4,8,9,10 | -0.07 | 532.89 | 531.45 |
|  | P | 1 | +0.16 | 192.61 | 193.19 |
| | S | 2 | +0.05 | 228.09 | 227.90 |
| | O | 3,4,5 | -0.08 | 532.65 | 532.65 |
| | P | 6,7,8 | +0.15 | 192.36 | 192.86 |
| | O | 9,10,11 | -0.07 | 532.89 | 532.90 |

TABLE 10 - continued

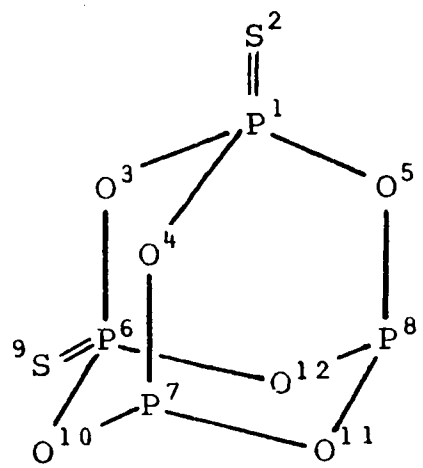
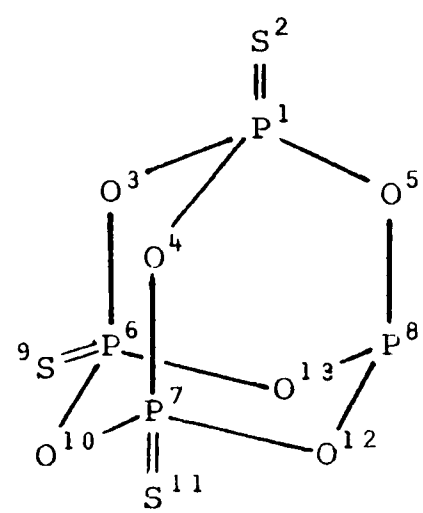
| structure | atom | atom number(s) | δ | calc'd b.e. | expt'l b.e. |
|---|---|---|---|---|---|
|  | P | 1,6 | +0.16 | 192.61 | 193.16 |
| | S | 2,9 | +0.05 | 228.09 | 227.71 |
| | O | 3 | -0.08 | 532.65 | 533.65 |
| | O | 4,5,10,12 | | | |
| | P | 7,8 | +0.15 | 192.36 | 192.42 |
| | O | 11 | -0.07 | 532.89 | 531.79 |
|  | P | 1,6,7 | +0.16 | 192.61 | 192.84 |
| | S | 2,9,11 | +0.05 | 228.09 | 227.78 |
| | O | 3,4,10 | -0.08 | 532.65 | 533.63 |
| | O | 5,12,13 | | | |
| | P | 8 | +0.15 | 192.36 | 192.28 |

TABLE 10 - continued

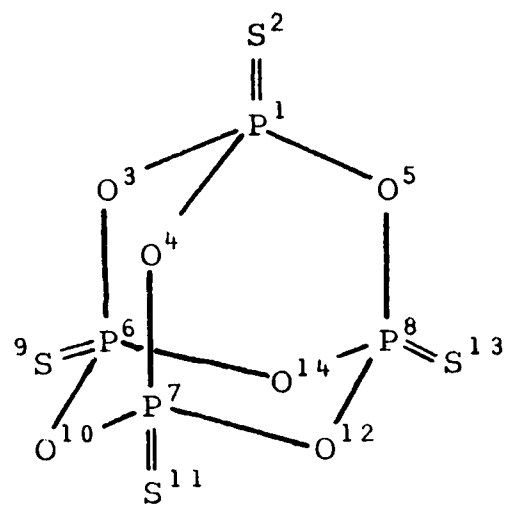
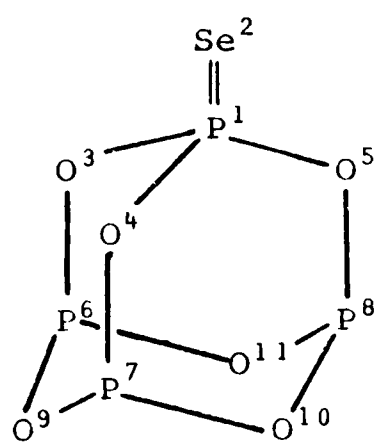
| structure | atom | atom number(s) | δ | calc'c b.e. | exp't b.e. |
|---|---|---|---|---|---|
|  | P | 1,6,7,8 | +0.16 | 192.61 | 192.84 |
| | S | 2,9,11,13 | +0.05 | 228.09 | 227.78 |
| | O | 3,4,5,10,12,14 | -0.08 | 532.65 | 533.63 |
|  | P | 1 | +0.14 | 192.23 | 191.93 |
| | Se | 2 | +0.09 | | 161.38($3p_3$) 55.10(3d) |
| | O | 3,4,5 | -0.08 | 532.65 | 533.00 |
| | P | 6,7,8 | +0.15 | 192.36 | 192.10 |
| | O | 9,10,11 | -0.07 | 532.89 | 533.44 |

TABLE 11

STATISTICAL COMPARISON OF CALCULATED AND EXPERIMENTAL BINDING ENERGIES

| atom/partial charge | observed b.e. | observed - average | observed - calculated |
|---|---|---|---|
| $\delta_P = 0.16$ | 193.19 | 0.13 | 0.58 |
| | 193.16 | 0.10 | 0.55 |
| | 192.84 | 0.22 | 0.23 |
| average | 193.06 | 0.15 | 0.45 |
| standard deviation of observed binding energies = 0.025 | | | |
| $\delta_P = 0.15$ | 192.42 | 0.00 | 0.06 |
| | 192.86 | 0.44 | 0.50 |
| | 192.42 | 0.00 | 0.06 |
| | 192.28 | 0.16 | 0.26 |
| | 192.10 | 0.32 | 0.26 |
| average | 192.42 | 0.18 | 0.19 |
| standard deviation of observed binding energies = 0.063 | | | |
| $\delta_P = 0.14$ | 191.93 | | 0.30 |

TABLE 11 - continued

| atom/partial charge | observed b.e. | observed - average | observed - calculated |
|---|---|---|---|
| $\delta_O$ = -0.08 | 533.98 | 0.60 | 1.33 |
| | 532.65 | 0.73 | 0.0 |
| | 533.65 | 0.27 | 1.00 |
| | 533.63 | 0.25 | 0.98 |
| | 533.00 | 0.38 | 0.35 |
| average | 533.38 | 0.45 | 0.73 |
| standard deviation of observed binding energies = 0.235 | | | |
| $\delta_O$ = -0.07 | 531.45 | 0.94 | 1.44 |
| | 532.90 | 0.50 | 0.01 |
| | 531.79 | 0.60 | 1.10 |
| | 533.42 | 1.05 | 0.55 |
| average | 532.40 | 0.77 | 0.77 |
| standard deviation of observed bindong energies = 0.651 | | | |

TABLE 11 - continued

| atom/partial charge | observed b.e. | observed - average | observed - calculated |
|---|---|---|---|
| $\delta_S = 0.05$ | 227.78 | 0.02 | 0.31 |
| | 227.71 | 0.09 | 0.38 |
| | 227.90 | 0.10 | 0.19 |
| average | 227.80 | 0.07 | 0.29 |

standard deviation of observed binding energies = 0.006

Chapter II and the fact that the standard deviation (a measure of data agreement within a group) of the observed binding energies is poorer for oxygen than that for the others. Oxygen characteristically gave poor correlations throughout this work, while the other types of atoms behaved in a more predictable manner. Both the fact that oxygen has such a high binding energy for its core electrons (therefore the greater the experimental error in data acquisition[50]) and the bond orders of oxygen are the most diverse (from a simple single bond to a bond order of 2½ for NO) probably contribute to this observation.

The characterization of the phosphorus cage compounds has demonstrated one of the many uses for partial charge calculations as well as proving the semi-localized partial charge calculation presented in Chapter II. A partial charge calculation, not only aids in the assignments of experimental binding energies, but with further manipulation can produce a theoretical binding energies that are in very good agreement with the real ones.

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# APPENDIX

I. Computer Based Line Notation for 3-Dimensional Chemical Structure

IIa. Binding Energies

IIb. Correlation Coefficients of Various Partial Charge Schemes

# APPENDIX I

## COMPUTER BASED LINE NOTATION FOR 3-DIMENSIONAL CHEMICAL STRUCTURE

It was evident in the beginning of this study that a method for introducing absolute chemical structure into a computer would be required. The line notations devised in the past do not satisfactorily meet this need requiring the design of a computer based line notation for chemical structure.

Wiswesser[51,52,53], Hayward[54], Skolnik[55], Gremas[56], Wheland[57], Zatopleg[58], and Meyer and Wenke[59] are some line notations cited in the literature. Typically, these notations are designed to generate a unique representation of a compound or to introduce a structure into a computer. Those designed to generate a unique representation, Wiswesser, Hayward, Skolnik, and Gremas, are not, by any means, designed to work in reverse. Therefore, these types of notations were not used as it is extremely hard, at best, to break down this generated representation into a form that can be utilized with calculations involving 3-dimensional chemical structure. Others, such as Wheland, Zatopleg, and Meyer and Wenke, that were designed for such purposes, generally require vast amounts of storage or input to denote the structure, making then cumbersome, time consuming and inefficient for use with a computer.

The line notation devised generally requires one line of input, defines absolute chemical structure, and is general in design allowing representation of most any compound. There are two parts to this notation referred to as a "legend" and a "map". The map describes chemical

structure symbolically and the legend assigns the symbols in the map to specific elements.

Legend

The symbols in the map, which represent elements, are numbers that correspond to elements presented in the legend. That is, a 1 in the map refers to the first element in the legend, a 2, the second, and so forth. Therefore, the legend is simply a list of the elements in structure.

Examples

| Compound | Legend |
|---|---|
| water | OH |
| ethanol | CHO |
| carboxylic acids | CHO |

Map

The map utilizes the position of the symbols in the legend to denote chemical structure. A "1" in the map refers to the first element in the legend, a "2" in the map refers to the second element in the legend, a "3" the third, and so forth. To describe the substituents bonded to an atom, these numbers, that correspond to the substituents of an atom, are listed in the map. The substituent list for a particular atom is delimited with the special symbol "0" which is followed by the description of the remaining substituents of the next atom. This proceeds until the entire structure has been denoted. Beginning with an arbitrarily assigned central atom, the substituent atoms bonded directly to this atom are denoted, then the remaining substituent atoms bonded directly those atoms, and so on, in the order that they have been placed in the map. The symbol "E", following an assignment, is used to denote a multiple bond and the

symbol "F" to denote a repetition factor (thus, avoiding repetitious representations). Bridgeheads are denoted with the special symbols "A" through "D". In the following examples the first atom in the legend was assumed to be the central atom and atom numbers have been assigned for examplification purposes.

Example 1: $H_2O$ (water)

structure : $H^1-O^2-H^3$

legend : OH

map : $\begin{matrix} 2 & 2 \\ (H^1 & H^3 \text{ -atom}) \end{matrix}$

In this example oxygen was assumed to be the central atom. The map shows that the second atom in the legend is bonded to the oxygen and that there are two such atoms. (The map could also have been 2F, showing that H is repeated once, but this is only efficient for denoting the representation of a multi-atom substituents).

Example 2 : $C_2H_6O$ (ethanol)

structure : $$\begin{array}{ccccccccc} & & H^4 & & H^8 & & & & \\ & & | & & | & & & & \\ H^3 & - & C^1 & - & C^2 & - & O^6 & - & H^9 \\ & & | & & | & & & & \\ & & H^5 & & H^7 & & & & \end{array}$$

legend : CHO

Arbitrarily choosing carbon 1 to be the central atom, a partial map describing the atoms bonded to this carbon ($C^2$, $H^3$, $H^4$, and $H^5$) would be

map : $\begin{matrix} 1 & 2 & 2 & 2 \\ (C^2 & H^3 & H^4 & H^5\text{- atom}) \end{matrix}$

Delimiting (signal that there is no more atoms bonded to carbon 2) with the special symbol "0" and then adding to the map the description of the first atom in the map, (carbon 2) the map becomes

map : 1 2 2 2 0 3 2 2
($C^2H^3H^4H^5$ $O^6H^7H^8$- atom)

As the next three atoms in the map (hydrogens 3, 4, and 5) have nothing bonded to them (terminal atoms) one simply delimits these atoms with "0". Upon describing the next atom (oxygen 6) in the map, the map becomes

map : 1 2 2 2 0 3 2 2 0 0 0 0 2
($C^2H^3H^4H^5$ $O^6H^7H^8$ $H^9$ - atom)

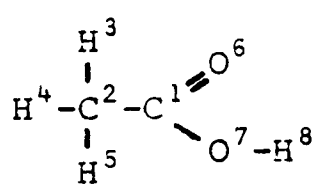
"0" can now be assumed for the balance of the map.

The representation of most compounds can be greatly simplified by assuming that there is a hydrogen bonded to those bonding positions of an element not assigned by the map (elimination all refers to hydrogen). This simplifies the map for ethanol to

map : 1 0 3
($C^2$ $O^6$ - atom)

Example 3 : $C_2H_4O_2$ (ethanoic acid)

structure :

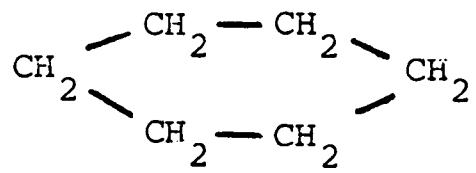



legend : COH

map : 2 E2 1
($O^6$ $O^7C^2$ - atom)

Carbon 1 was chosen as the central atom in example 3. Note the "E" in the map denoting the double bond between atoms 1 (carbon) and 6 (oxygen).

Example 4 : $C_6H_{12}$ (cyclohexane)

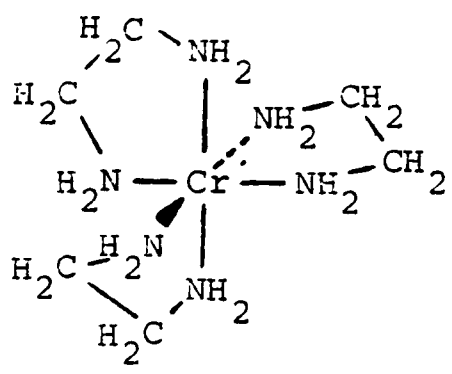
structure : 

legend : C

map : 1A010101010A

Any carbon in this example can serve as the central atom. Note the two "A"'s in the map used to close the ring. The first "A" sets up a bridgehead position and all subsequent "A"'s describe bonds to that bridgehead.

Example 5 : $Cr(en)_3$

structure : 

legend : CrNC

map : 2FFA0303020A

Chromium is the logical choice for the central atom. The "F" denotes that the preceeding assignment, and everything bonded to it, is repeated, in this case the -N-C-C-N- skeleton.

Example 6 : $P_4O_6S_4$

structure : see table 9

legend : POS

map : 3E222001010103E2A03E2B03E2C00B00C00A

Even this complex cage structure can be readily handled by this notation. Any phosphorus in this cage can serve as the central atom.

Because each atom designated in by the map is defined by a variable legend, this notation can be used to represent any chemical structure. The representations shown here use only a hexa-decimal symbol set (0-9, A-F), but there is no reason why this set could not be expanded as necessary to include any desired symbol. The notation can define any type of multiple bond, as many bridgeheads as necessary, as many atoms as needed, and, if one pre-defines a specific order for coding, stereochemistry as well.

## APPENDIX IIa

## BINDING ENERGIES (ESCA DATA)

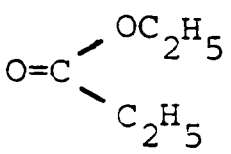
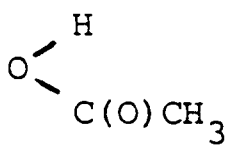
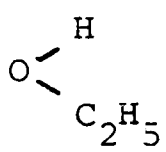
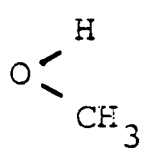
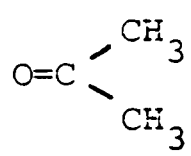
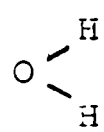
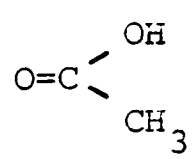
### Phosphorus Compounds

| compound | 2p binding energy (eV) |
|---|---|
| $(C_6H_5)_3P$ | 131.3 |
| $(C_6H_5)_3PO$ | 132.8 |
| $(C_6H_5)_3PS$ | 132.9 |
| $(C_6H_5)_3PSe$ | 133.0 |
| $(C_8H_{17})PO$ | 132.6 |
| $(C_6H_5O)_3PO$ | 134.9 |
| $(C_6H_5O)_3PS$ | 134.9 |
| $(C_6H_5O)_3PSe$ | 134.5 |
| $(C_6H_5S)_3P$ | 134.4 |
| $(C_6H_5S)_3PS$ | 133.3 |
| $(C_6H_5)_2P(O)OH$ | 133.5 |
| $(C_6H_5)_2P(O)N(CH_3)_2$ | 133.1 |

Source: T.A.Grutsch, M.V.Zeller, and T.T.Fehlner, Inorganic Chemistry, 12 (1973), 1431.

### Oxygen Compounds

| compound | 1s binding energy (eV) |
|---|---|
| $O{=}CHCH_3$ | 537.6 |
| $O(C_2H_5)(C(O)C_2H_5)$ | 537.6 |

| compound | 1s binding energy (eV) |
|---|---|
|  | 538.8 |
|  | 538.2 |
|  | 538.6 |
|  | 538.9 |
|  | 539.0 |
| $O{=}SF_2$ | 539.4 |
|  | 539.7 |
|  | 540.0 |
| O=C=O | 540.8 |
| ONN | 541.2 |
| ONO | 541.3 |
| OC | 542.1 |
| ON | 543.3 |
| $O_2$ | 543.1 |

Source: K.Siegbahn, ESCA Applied To Free Molecules, (Ansterdam: North-Holland Publishing Co., 1969), p. 124.

Sulfur Compounds

| compound | 2p binding energy (eV) |
|---|---|
| $CS_2$ | 169.8 |
| $H_2S$ | 170.2 |
| $SO_2$ | 174.8 |
| $SOF_2$ | 176.2 |
| $SF_6$ | 180.4 |

Source: Ibid., p. 126

Fluorine Compounds

| compound | 1s binding energy (eV) |
|---|---|
| $SOF_2$ | 693.6 |
| $CHF_3$ | 694.4 |
| $SF_6$ | 694.6 |
| $CF_4$ | 695.2 |

Source: Ibid., p. 129

Carbon Compounds

| compound | 1s binding energy (eV) |
|---|---|
| $H_3C-H$ | 290.7 |
| $H_3C-CH_2C(O)OC_2H_5$ | 290.8 |
| $H_3C-CH_2OH$ | 290.9 |
| $H_3C-C(O)CH_3$ | 291.2 |
| $H_3C-C(O)H$ | 291.3 |

APPENDIX IIa-continued

| compound | 1s binding energy (eV) |
|---|---|
| $H_3C-C(O)OH$ | 291.4 |
| $H_3C-OH$ | 292.3 |
| $H_2C(OH)(CH_3)$ | 292.3 |
| $H_2C(OC(O)C_2H_5)(CH_3)$ | 292.4 |
| $S=C=S$ | 293.1 |
| $O=C(CH_3)(CH_3)$ | 293.8 |
| $O=C(H)(CH_3)$ | 293.9 |
| $O=C(C_2H_5)(OC_2H_5)$ | 294.5 |
| $O=C(CH_3)(OH)$ | 295.4 |
| $OC$ | 295.9 |
| $CO_2$ | 297.5 |
| $CHF_3$ | 298.8 |
| $CF_4$ | 301.8 |

Source: Ibid., p. 119

Nitrogen Compounds

| compound | 1s binding energy (eV) |
|---|---|
| $H_2N(C_6H_5)$ | 405.5 |

APPENDIX IIa-continued

| compound | 1s binding energy (eV) |
|---|---|
| $NH_3$ | 405.6 |
| $\underline{N}NO$ | 408.5 |
| $N_2$ | 409.9 |
| NO | 410.3 |
| $O_2N(C_6H_5)$ | 411.6 |
| $NO_2$ | 412.4 |
| $N\underline{N}O$ | 412.5 |

Source: Ibid., p. 123

APPENDIX IIb

CORRELATION COEFFICIENTS OF VARIOUS PARTIAL CHARGE SCHEMES

The following data are the correlation coefficients obtained from a linear least squares analysis of plots between the ESCA data presented in appendix IIa versus the partial charge of the central atom in the molecule as calculated by the given equation with the indicated permutations or as described in the text of this paper

| TYPE OF CALCULATION | DATA SET P | O | S | F | C | N |
|---|---|---|---|---|---|---|
| SANDERSON $\left[ \delta = \frac{\sqrt[n]{\Pi_n S_n} - S_{elemental}}{2.08 \sqrt{S_{elemental}}} \right]$ | 0.9222 | 0.6793 | 0.9632 | 0.5329 | 0.9213 | 0.6880 |
| PAULING $[ 0.16\Delta X + 0.035\Delta X^2 ]$ | 0.7125 | 0.6051 | 0.9562 | 0.7878 | 0.9738 | 0.9409 |
| PAULING $[ 1.0 - e^{-0.25\Delta X^2} ]$ | 0.7279 | 0.5808 | 0.9854 | 0.7848 | 0.9705 | 0.9095 |
| PAULING $[ 1.0 - e^{-0.16\Delta X^2} ]$ | 0.7279 | 0.5702 | 0.9886 | 0.7861 | 0.9657 | 0.9080 |

APPENDIX IIb-continued

| TYPE OF CALCULATION | | DATA SET P | O | S | F | C | N |
|---|---|---|---|---|---|---|---|
| ITERATED SANDERSON (page 26) | iteration #1 | 0.9195 | 0.6425 | 0.9632 | 0.7857 | 0.9672 | 0.9473 |
| | #2 | 0.9094 | 0.6371 | 0.9632 | 0.04512 | 0.9650 | 0.9063 |
| | #3 | 0.9318 | 0.6904 | 0.9632 | 0.2175 | 0.9628 | 0.9006 |
| | #4 | 0.9412 | 0.6905 | 0.9632 | 0.04505 | 0.9557 | 0.8825 |
| | #5 | 0.9411 | 0.6948 | 0.9632 | 0.05300 | 0.9518 | 0.8701 |
| LINEAR COMBINATION OF PAULING AND SANDERSON (page 23 ) | | | | | | | |
| 90% Pauling | 10% Sanderson | 0.7477 | 0.6548 | 0.9571 | 0.2650 | 0.9872 | 0.9341 |
| 80% | 20% | 0.7811 | 0.6889 | 0.9579 | 0.00831 | 0.9885 | 0.9216 |
| 70% | 30% | 0.8114 | 0.7091 | 0.9586 | 0.2586 | 0.9910 | 0.9038 |
| 60% | 40% | 0.8384 | 0.7182 | 0.9594 | 0.3552 | 0.9901 | 0.8810 |
| 50% | 50% | 0.8618 | 0.7194 | 0.9601 | 0.4146 | 0.9858 | 0.8841 |
| 40% | 60% | 0.8814 | 0.7154 | 0.9608 | 0.4543 | 0.9783 | 0.8240 |
| 30% | 70% | 0.8971 | 0.7082 | 0.9614 | 0.4826 | 0.9678 | 0.7914 |
| 20% | 80% | 0.9089 | 0.6992 | 0.9620 | 0.5037 | 0.9545 | 0.7575 |
| 10% | 90% | 0.9172 | 0.6893 | 0.9626 | 0.5200 | 0.9389 | 0.7228 |

APPENDIX IIb-continued

Four factor were varied in the following equation. They were: (1) the scale, either Pauling's (P) or Sanderson's, used for the electronegativities of atoms A, B, and C (the atom for which the partial charge is being calculated, the atoms in the primary coordination, and in the secondary coordination sphere of this atom, respectively); (2) the type of mean, either arithmetic ($\Sigma$) or geometric ($\Pi$), $f'$; (3) the multipule bond factor, R; and (4) the function of $\Delta$ used to calculated partial charge, either equation II.1 or equation II.2 as given in chapter II of the paper, $f''$.

$$\Delta = A - \frac{A + f'_i R_i \dfrac{B_i + f'_{j_i}(R_{j_i} C_{j_i})}{1 + f'_{j_i}(R_{j_i})}}{1 + f'_i (R_i)}$$

$$\delta_A = f''(\Delta)$$

DATA SET

| scale | $f'$ | R | $f''$ | P | O | S | F | C | N | average | standard deviation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| P[1] | $\Sigma$ | 1.378 | II.2 | 0.7956 | 0.4398 | 0.9612 | 0.6788 | 0.9683 | 0.8944 | 0.7897 | $7.874 \times 10^{-2}$ |

APPENDIX IIb-continued

| scale | ∫' | R | ∫" | DATA SET P | O | S | F | C | N | average | standard deviation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $P^1$ | Π | 1.378 | II.2 | 0.8089 | 0.4515 | 0.9609 | 0.6109 | 0.9648 | 0.8810 | 0.7797 | $8.428 \times 10^{-2}$ |
| S | Σ | 1.378 | II.2 | 0.8038 | 0.4655 | 0.9546 | 0.6177 | 0.9720 | 0.8978 | 0.7852 | $8.060 \times 10^{-2}$ |
| S | Π | 1.378 | II.2 | 0.8251 | 0.4798 | 0.9559 | 0.5420 | 0.9714 | 0.8871 | 0.7767 | $8.775 \times 10^{-2}$ |
| S | Π | 1.50 | II.2 | 0.8061 | 0.4839 | 0.9537 | 0.5325 | 0.9697 | 0.8882 | 0.7723 | $8.968 \times 10^{-2}$ |
| P | Π | 1.50 | II.2 | 0.6874 | 0.4754 | 0.9636 | 0.7446 | 0.9723 | 0.8816 | 0.7875 | $7.571 \times 10^{-2}$ |
| $P^1$ | Π | 1.50 | II.2 | 0.7891 | 0.4559 | 0.9599 | 0.6082 | 0.6937 | 0.8816 | 0.7764 | $8.510 \times 10^{-2}$ |
| $P^1$ | Π | 1.378 | II.1 | 0.7979 | 0.4358 | 0.8741 | 0.7097 | 0.7760 | 0.8546 | 0.7413 | $8.848 \times 10^{-2}$ |
| $P^1$ | Σ | 1.50 | II.2 | 0.7733 | 0.4440 | 0.9605 | 0.6778 | 0.9671 | 0.8946 | 0.7862 | $7.968 \times 10^{-2}$ |
| $P^1$ | Σ | 1.15 | II.2 | 0.8356 | 0.4291 | 0.9626 | 0.6809 | 0.9698 | 0.8927 | 0.7951 | $7.810 \times 10^{-2}$ |
| $P^1$ | Σ | 1.378 | II.1 | 0.7877 | 0.4329 | 0.8925 | 0.7704 | 0.8169 | 0.8402 | 0.7568 | $8.167 \times 10^{-2}$ |
| P | Σ | 1.378 | II.1 | 0.7046 | 0.4434 | 0.9717 | 0.8351 | 0.8157 | 0.8402 | 0.7648 | $8.076 \times 10^{-2}$ |
| P | Σ | 1.15 | II.1 | 0.7516 | 0.4175 | 0.9631 | 0.8380 | 0.8049 | 0.8538 | 0.7715 | $8.134 \times 10^{-2}$ |
| P | Σ | 1.50 | II.1 | 0.6796 | 0.4420 | 0.9753 | 0.8836 | 0.8210 | 0.8839 | 0.7642 | $8.366 \times 10^{-2}$ |
| P | Σ | 1.50 | II.2 | 0.6725 | 0.4607 | 0.9626 | 0.7713 | 0.9734 | 0.8946 | 0.7892 | $7.727 \times 10^{-2}$ |
| P | Σ | 1.378 | II.2 | 0.6968 | 0.4559 | 0.9638 | 0.7731 | 0.9746 | 0.8944 | 0.7931 | $7.543 \times 10^{-2}$ |
| P | Σ | 1.15 | II.2 | 0.7429 | 0.4439 | 0.9660 | 0.7767 | 0.9762 | 0.8927 | 0.7997 | $7.307 \times 10^{-2}$ |
| P | Π | 1.15 | II.2 | 0.7532 | 0.4581 | 0.9681 | 0.7541 | 0.9745 | 0.8789 | 0.7978 | $7.189 \times 10^{-2}$ |
| P | Π | 1.378 | II.2 | 0.7103 | 0.4705 | 0.9651 | 0.7478 | 0.9734 | 0.8810 | 0.7913 | $7.400 \times 10^{-2}$ |

APPENDIX IIb-continued

| | | | | DATA SET | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| scale | ∫' | R | ∫" | P | O | S | F | C | N | average | standard deviation |
| S | Π | 1.15 | II.2 | 0.8597 | 0.4861 | 0.9602 | 0.5607 | 0.9737 | 0.8836 | 0.7873 | $8.210 \times 10^{-2}$ |
| P[1] | Π | 1.15 | II.2 | 0.8433 | 0.4407 | 0.9628 | 0.6164 | 0.9659 | 0.8789 | 0.7847 | $8.362 \times 10^{-2}$ |

[1]The Pauling value for the electronegativity of sulfur was set equal to 2.8.

APPENDIX IIb-continued

Three factors were varied in the following equation. They were: (1) the scale, either Pauling's (P) or Sanderson's (S), used for the electronegativities of atoms A, B, and C (the atom for which the partial charge was calculated, the atom(s) in the primary coordination sphere, and in the second coordination sphere of that atom, respectively); (2) the type of mean, either arithmetic ($\Sigma$) or geometric ($\Pi$), $\int$; and (3) the weighting factor of the secondary coordination sphere, $\Omega$.

$$\Delta = A - \frac{A + \int_i (R_i B_i) + \Omega \int_j (R_j C_j)}{1 + \int_i (R_i) + \Omega \int_j (R_j)}$$

$$\delta_A = \frac{\Delta}{2.08 \sqrt{A}}$$

DATA SET

| scale | $\int$ | $\Omega$ | P | O | S | F | C | N | average | standard deviation |
|---|---|---|---|---|---|---|---|---|---|---|
| P | $\Sigma$ | 0.333 | 0.8884 | 0.5214 | 0.9612 | 0.01254 | 0.9405 | 0.8637 | 0.6798 | $2.067 \times 10^{-1}$ |
| P | $\Sigma$ | 0.666 | 0.8556 | 0.4495 | 0.9612 | 0.5246 | 0.8817 | 0.6978 | 0.7284 | $1.095 \times 10^{-1}$ |

APPENDIX IIb-continued

| scale | $\int$ | $\Omega$ | DATA SET P | O | S | F | C | N | average | standard deviation |
|---|---|---|---|---|---|---|---|---|---|---|
| P | $\Sigma$ | 0.166 | 0.8888 | 0.5754 | 0.9612 | 0.4612 | 0.9590 | 0.9079 | 0.7924 | $8.228 \times 10^{-2}$ |
| P | $\Sigma$ | 0.200 | 0.8899 | 0.5633 | 0.9612 | 0.3704 | 0.9565 | 0.8939 | 0.7725 | $1.023 \times 10^{-1}$ |
| S | $\Sigma$ | 0.166 | 0.8996 | 0.6538 | 0.9546 | 0.5470 | 0.9589 | 0.9080 | 0.8203 | $5.789 \times 10^{-2}$ |
| S | $\Pi$ | 0.166 | 0.6781 | 0.5208 | 0.7928 | 0.7857 | 0.6838 | 0.2983 | 0.6226 | $1.691 \times 10^{-1}$ |
| P | $\Pi$ | 0.166 | 0.6617 | 0.5587 | 0.7928 | 0.7857 | 0.6644 | 0.3034 | 0.6278 | $1.660 \times 10^{-1}$ |