Relationship between the Atomic Structure and Electrochemistry. 1. Electric Force, Standard Reduction Potential $E^\circ$, and Standard Reaction Gibbs Free Energy $\Delta G^\circ$

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ABSTRACT: The relationship among the standard reaction Gibbs free energy $\Delta G^\circ$, the standard reduction potential $E^\circ$, and the atomic structure parameters of radius, nuclear charge, and isoelectronic orbitals $nl$ is accomplished through the attraction electric force $F_{\text{elec}}$. In relationship with $E^\circ$, it was necessary to define two new reference scales: $E_{\text{fl}}$ with a final state of $E^\circ$ in the element, which allowed to have a parabolic trend of $\Delta G^\circ$ versus $F_{\text{elec}}$ and $E^{\circ,\text{fl}}$ whose final state is the ion with a more negative charge (e.g., $-1, -2, -3$). The relationship with $\Delta G^\circ$ is related to the concept of chemical stability, and the relationship with $E^{\circ,\text{fl}}$ is more related to the concept of electronegativity. In relationship with $\Delta G^\circ$, it was necessary to predict the values of possible new cations and noncommon cations in order to find a better trend of $\Delta G^\circ$ versus $F_{\text{elec}}$ whose stability is analyzed by Frost diagrams of the isoelectronic series. This dependence of $\Delta G^\circ$ on $F_{\text{elec}}$ is split into two terms. The first term indicates the behavior of the minimum of $\Delta G^\circ$ for each isoelectronic orbital $nl$, while the second term deals with the parabolic trend of this orbital. For the minima of the configuration np$^5$, a hysteresis behavior of the minima of $\Delta G^\circ$ is found: an exponential behavior from periods 1 and 2 and a sigmoidal behavior from periods 5 and 4 to interpolate period 3. It is also found that the proximity of unfilled np or $(n + 1)s$ orbitals induces instability of the ion in configurations $ns^2/nd^2/4f^2$ and $nd^{10}/nd^2(n + 1)s^2$, respectively. On the contrary, the stability of the orbitals np$^6$ does not depend on the neighboring empty $(n + 1)s^0$ orbitals. Both phenomena can be explained by the stability of the configuration of noble gas np$^6$ and the nd$^{10}$(n + 1)$s^0$ configuration. We have also found that it is possible to increase the reduction potential $E^{\circ,\text{fl}}$ (macroscopic electronegativity), although the electric force $F_{\text{elec}}$ decreases because the orbital overlap influences the electronegativity.

INTRODUCTION

At present, the analysis of the electrochemical phenomena is currently made through the standard reduction potential $E^\circ(Z^\circ/Z^\text{fl})$, which is a macroscopic average variable used when an element is reduced from an oxidation state $n$ to an oxidation state $n'$ through the reaction of $(n - n')$ electrons. Thus, for instance, in cerium, in aqueous acidic solution at pH = 0

$$\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+} \quad E^\circ(\text{Ce}^{4+}/\text{Ce}^{3+}) = 1.76 \text{ V}$$

(1)

We can define the standard reduction potential relative to zero from the oxidation state $Z^\circ$ to the oxidation state $Z^\text{fl}$ named $E_{\text{fl}}(Z^\circ/Z^\text{fl})$ or simply $E_{\text{fl}}^\circ$. Thus, the standard reaction Gibbs free energy of the reduction potential $E_{\text{fl}}$ with respect to $Z^\circ$, $\Delta G_{0,\text{fl}}^\circ(Z^\circ/Z^\text{fl})$, or simply $\Delta G_{0,\text{fl}}^\circ$ is also evaluated in order to associate the macroscopic thermodynamic parameters to electrochemistry

$$\Delta G_{0,\text{fl}}^\circ = -nFE_{0}^\circ$$

(2)

where $F$ is the Faraday constant which is equivalent to 96,485 kJ/mol/V or eV/V and $n$ is the number of electrons transferred. Note that $n$ can be negative.

We also know that the standard reaction Gibbs free energy of oxidation $\Delta G_{0,\text{fl}}^\circ$ is the negative of $\Delta G_{0,\text{fl}}^\circ$. Thus

$$\Delta G_{0,\text{fl}}^\circ/F = -\Delta G_{0,\text{fl}}^\circ/F = nE_{0}^\circ$$

(3)

$\Delta G_{0,\text{fl}}^\circ/F$ has been selected because the stability of the cations is commonly plotted through the Gibbs free energy in the Frost diagrams, and its minimum indicates the highest cation stability. We also consider that the Frost diagrams with $\Delta G_{0,\text{fl}}^\circ/F$ provide a deep insight into the electrochemical behavior of the elements. For example, $\Delta G_{0,\text{fl}}^\circ/F$ indicates the importance of the metals in

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superconductivity alloys\(^1\) and hence (1) the great stability of La\(^{3+}\), Ba\(^{2+}\), and Y\(^{3+}\) (with a concomitant high negative value of \(\Delta G_{0,\text{ox}}^0/F\)) and the highest negative reduction potential \(E^0_0\) (the highest negative slope of \(\Delta G_{0,\text{ox}}^0/F\), as shown in Figures S1 and S2). (2) The lower proclivity of Ag and Au, and noble metals Pd and Pt to be used as superconductor materials are correlated to the high value and positive slope of \(\Delta G_{0,\text{ox}}^0/F\), indicating a striking tendency to reduction (Figure S2). (3) The topological similitude in the electrochemical behavior of Cu, Tl, and Hg (Figures S3 and S4), in particular, Hg\(^{2+}\) with Hg\(^2+\).\(^2\) On the other hand, there is a parabolic trend of the energy \(E\) on the formal charge \(Q\). In this case, the Gibbs free energy of oxidation \(\Delta G_{0,\text{ox}}^0\) for the isoelectronic series \(4s^2/3d^5\) is shown in Figure S5 of the Supporting Information.\(^3\) Importantly, the isoelectronic series only indicates the same number of electrons in the element or ion not the electronic configuration. Thus, the virtual isoelectronic configurations \(ns\) can take the electronic configuration \(ns^2\) or the electronic configuration \((n-1)d^5\) and in the 6th period the electronic configurations \(6s^2\) or \(4f^2\).

The same happens in the virtual isoelectronic configuration \(4f^66s^2\) that can take the electronic configuration \(4f^66s^2\) or the electronic configuration \(4f^55d^2\). The criterion for selecting a specific electronic configuration is its lower energy in relation to the other configurations. In this context, the orbital energies of the one-electron configurations \(ns^2\) and \((n-1)d^5\) taken from Mann et al.\(^4\) and reported in Table S2 are used as reference for the selection of the electronic configuration of the ion or element in an isoelectronic series. Besides, we consider that the energy of the orbital \(4f\) is similar to the orbital \(5d\) with \(4f < 5d < 6s\) in the transition elements, as explained by Huheey et al.\(^3a\) and Mann et al.\(^7\) Thus, the selection of the electronic configuration affects the value of the effective nuclear charge \(Z^*\), and jumps are possible. Nevertheless, \(E_{\text{elec}}\) in general, has continuity in the isoelectronic series because the trend of radius counterbalances the jumps of \(Z^*\), as observed below. In the case of the isoelectronic configuration \(nd^{10}\), for example, in \(3d^{10}\), the sequence of Ga\(^{3+}\), Zn\(^{2+}\), and Cu\(^+\) (all with configurations \(3d^{10}\)) follows Ni\(^{2+}\), but this element has a configuration \([\text{Ar}] 3d^9\) (in reality, \([\text{Ar}] 3d^{10}4s^1\)).\(^4\) The other elements of group 10, Pd and Pt, also have the same characteristic with a tendency to have the \(d^{10}\) electronic configuration (Pd: \([\text{Kr}] 4d^{10}5s^2\) and Pt: \([\text{Xe}] 5d^{10}6s^2\)).\(^5\) In this case, we have evaluated the configuration \(nd^{n}(n+1)s^2\) for \(Z^*\) corroborated for Ni, Pd, and Pt. The confirmation of this assignment was corroborated by the trend of the other cations in the electric force \(F_{\text{elec}}\), as observed below. In order to systematize the notation in an isoelectronic series, the representative configuration is written first and the next possible electronic configurations are written separated by a slash, for example, \(ns^2/(n-1)d^7/4f^4\), where the representative configuration is \(ns^2\). Besides, the Gibbs free energy of oxidation \(\Delta G_{0,\text{ox}}\) is not affected by the selection of the electronic configuration because it considers the experimental oxidation state and not the electronic configuration. In this context, the reduction potential \(E_0^0\) can be defined as the derive of the standard reduction potential \(\Delta G_{0,\text{ox}}^0\) or at least an average of the increment or decrement of \(\Delta G_{0,\text{ox}}^0\) per electron

\[
E_0^0 = \frac{\Delta G_{0,\text{ox}}^0}{(n - 0)F} = \frac{\Delta G_{0,\text{ox}}^0}{(n - 0)eN_A}
\]  

(4)

where \(N_A\) is Avogadro’s constant. Thus, it is expected that the reduction potential \(E_0^0\) has a lower curved trend than \(\Delta G_{0,\text{ox}}^0\) as shown in Figure S5 of the Supporting Information. Even, a departure from the linear behavior indicates a more asymmetric behavior of the parabolic behavior of \(\Delta G_{0,\text{ox}}^0\). Besides, as observed in Figure S6, there is almost a linear trend of decrease of \(E_0^0\) from the anions to the element until the monovalent cation. This linear trend indicates that the average of the reduction potential per interchanged electron decreases until the monovalent cation. The following linear trend of increase of \(E_0^0\) with an increase of oxidation of the isoelectronic series indicates an increase of the positive reduction potential per electron interchanged. On the other hand, the absolute electronegativity of an element \(\chi\) may be defined as the variation of the energy \(E\) with the change of the formal charge \(Q\) on an atom or ion, that is, the electronic chemical potential \(\mu\) or Lagrange multiplier with the constraint of \(N\) electrons at constant external one-potential \(V\).\(^3a\)\(^5\)\(^6\)

\[
\chi = -\frac{\delta E}{\delta Q} = \left( \frac{\delta E}{eN} \right)_V = -\mu
\]

(5)

where \(\delta\) indicates the functional derivative\(^c\) and \(\delta E\) indicates a positive increase of the energy with the increase of \(eN\) electrons, and we must consider the discreteness of the number of electrons \(N\) in an isolated molecule but not in solution.\(^3a\)\(^5\)\(^6\)

If we relate the energy \(E\) to the standard Gibbs free energy of oxidation \(\Delta G_{0,\text{ox}}^0\) and eqs 4 and 5, we observe that the reduction potential \(E_0^0\) is linked to the concept of electronegativity \(\chi\) and has an approximately linear behavior with respect to \(Z^*\) in an isoelectronic series, as shown in Figure S6, for the isoelectronic configuration \(4s^2/3d^7\). Thus, \(E_0^0\) is the normalization of the value of \(\Delta G_{0,\text{ox}}^0\) per electron and can be considered as a macroscopic electronegativity. Besides, the separation of the linear trend indicates the perturbation of the atomic structural factors in the electronegativity, the lowest value of \(E_0^0\) in the monocation indicates a lower electronegativity, and the increase of \(E_0^0\) in the higher oxidation states indicates a higher electronegativity, as shown in Figure S6.

We have also defined a reduction potential that starts from the cation and ends at the element \((Z^0)\) for the cations and that starts from the element and ends at the anion, named \(E^{0,0}\). The relation of the values for cations and anions for this reduction potential \(E^{0,0}\) is more related to the ranking of electronegativity: higher for the elements which are prone to be converted to anions and lower for the elements which tend to form cations, as shown in Figure S9, for the isoelectronic configuration \(3p^6\): (1) a more positive value of \(E^{0,0}\) specifies an increment of the macroscopic electronegativity, that is, an increase of the macroscopic power to attract the electrons = more easiness of being reduced. (2) A more negative value of \(E^{0,0}\) indicates less macroscopic electronegativity, that is, more capacity to release the electrons = more easiness of being oxidized. On the other hand, a negative value \(\Delta G_{0,\text{ox}}^0\) for a cation indicates that it is stable, and a positive value for a cation indicates that it is unstable. Then, \(\Delta G_{0,\text{ox}}^0\) determines the macroscopic stability of the cations, and \(E^{0,0}\) determines the macroscopic power to attract or release the electrons. We must note that the values for \(E^{0,0}\) are equal to \(E^{0,0}\) for cations and opposite in sign to \(E^{0,0}\) for anions. Thus, there is an abrupt change of the Gibbs free energy of the reaction associated with \(E^{0,0}\), named \(\Delta G^{0,0}\), as shown in Figure S10, as compared with \(\Delta G_{0,\text{ox}}^0\) of Figure S11, for example. Accordingly, we have used the trend of \(\Delta G_{0,\text{ox}}^0\) because it gives a more continuous trend of the values in the isoelectronic configuration \(4s^2/(n - 1)d^7/4f^4\) and \(np^5\). Indeed, the Frost diagrams of the first 80 elements of the periodic table, without
counting the noble gases, give better continuity of $\Delta G_{g=0}^{Ox}/F$ than that of $\Delta G_{g=0}^{Ox}/F$ with the exception of N, As, Se, Sb, Au, Bi, and Po.

In general, the expectation is that an increment of the absolute electronegativity increases the reduction potential $E_0^\text{f}$ (=$E^{0,0}$ in the case of cations, see above). For example, the Pauling electronegativity values of sodium and silver are $\chi_{P,Na} = 0.93$ and $\chi_{P,Ag} = 1.93$, respectively, and the corresponding values of the standard reduction potential in aqueous acidic solution at pH = 0 are $E_0^\text{f}(Na^+/Na^0) = −2.71$ V and $E_0^\text{f}(Ag^+/Ag^0) = 0.80$ V. However, this rule does not apply in other cases, for example, the absolute electronegativity of Li is higher than that of Na, but the reduction potential $E_0^\text{f}$ is lower: $\chi_{P,Li} = 0.98$ and $E_0^\text{f}(Li^+/Li^0) = −3.04$ V. These discrepancies could be explained based on the atomic structure. In this case, the more negative standard reduction potential $E_0^\text{f}$, which indicates a lower macroscopic power to attract electrons, can also be explained by the elevated higher hydration of Li$^+$, which has a lower radius (128 pm) than Na$^+$ (160 pm), and then the attraction potential becomes higher. There are cases where this rule is not valid, which can be observed when the radii in Figure S12 and their standard reduction potential $E_0^\text{f}$ in Figure S13 are compared: in the case of the isoelectronic configuration 1s$^2$, the radii of C$^{4+}$ (CO$_2$) and B$^{3+}$ are lower than those in Be$^{2+}$ and Li$^+$, as shown in Figure S12. However, B$^{3+}$ and C$^{4+}$ have a higher standard reduction potential $E_0^\text{f}$ than Be$^{2+}$ and Li$^+$, as shown in Figure S13. Then, we consider that the reduction potential $E_0^\text{f}$ of a particular element not only on the hydration radius but also on the physicochemical factors such as the orbital overlap, the nephelaelectric effect, the width of the band gap, the low value of energy of the highest occupied molecular orbitals, the ligand field stabilization energy, the penetration of the orbitals, and the lattice energy. These factors are explained in an article that has been submitted for publication in order to propose a new more applicable scale of electronegativity.

In principle, the electronegativity can be defined for elements or ions. Besides, the electronegativity for the elements according to Alfred and Rochow (in Pauling units) $\chi_{P,AR}$ is directly proportional to the electric force $F_{elec}$. Then, we can make the relationship of the electronegativity to the charge of the nucleus and the radius of the element through the evaluation of $F_{elec}$

$$\chi_{P,AR} = 35904\pi\epsilon_0 e^2 F_{elec} + 0.744$$ (6)

where

$$F_{elec} = \frac{e^2}{4\pi\epsilon_0} \frac{Z^*}{R_{cav}^2}$$ (7)

$Z^*$ is the effective nuclear charge given by the rules of Slater with the supposition that the additional electron of the other atom also participates in the screening of the nuclear charge. $R_{cav}$ is the radius of the covalent bond of the elements. The values of $Z^*$ for all the elements, cations, and anions of the isoelectronic series and lanthanides are given in Figure S14A–C of the Supporting Information. On the other hand, the definition of the Mulliken electronegativity in the scale of Pauling $\chi_{P,M}$ is

$$\chi_{P,M} = 0.336 \left( \frac{E_{Iv} + AE_e}{2} - 0.615 \right)$$ (8)

where $E_{Iv}$ is the ionization energy of the electron in the valence orbital and $AE_e$ is the electronic affinity of the valence shell. $E_{Iv}$ indicates how much the electron is attracted to the nucleus and $AE_e$ indicates how much the electron is held by the atom. Thus, if we match eqs 6 and 8, we can conclude that the evaluation of $F_{elec}$ corresponds to the effect of both $E_{Iv}$ and $AE_e$ that is, the attraction and holding of the valence electrons, respectively. Indeed, it is also possible through $F_{elec}$ to consider the electronegativity of cations and anions because the Slater rules also consider the nuclear effective charge $Z^*$ for cations and anions. Thus, the electronegativity of O$^{4+}$ is $\chi_{P,AR,Os} = 37$ in the scale of Pauling when we transform the corresponding values of $F_{elec}$ (5p$^6$, Figure S15A) in $\chi_{P,AR}$ (3s$^2$, Figure S16A) through eq 6. We consider that the electronegativity values obtained by the approximation of Alfred and Rochow are overestimated because a linear relationship between the electric force $F_{elec}$ and electronegativity is considered. Sanderson has explained that when an ion is bound to another ion, the electrons flow from the more electronegative ion to the less electronegative ion until their electronegativities are equalized. Indeed, the parabolic trend of the cations was shifted to a lower value of $\Delta G_{g=0}^{Ox}$.

In this work, we use the periodicity of the standard reaction Gibbs free energy of oxidation $\Delta G_{g=0}^{Ox}$ in the isoelectronic series of the orbitals $nl$ (e.g., $nd^{10}/nd^3(n+1)s^2$). Thus, the isoelectronic configurations allow to have a continuity in the values of $\Delta G_{g=0}^{Ox}$ (as shown in Figure S5) and $F_{elec}$ (as shown in Figure S15A–C) between the periods of the periodic table. This continuity in the periodicity is broken in other physical properties such as radius or electronegativity and even $Z^*$ (Figure S14A–C) as a function of the nuclear charge $Z$. Thus, in the configuration 3p$^6$, the values of $\Delta G_{g=0}^{Ox}$ for the anion S$^{2−}$, the noble gas Ar, the alkaline earth cation Ca$^{2+}$, and the transition metal cation Mn$^{2+}$ are related. Similarly, for the electric force $F_{elec}$ the anion Au$^{−}$ is related to the cation At$^{5+}$ in the isoelectronic configuration 5d$^{10}6s^2$. Thus, we analyze the relationship between anions, elements, and cations. Besides, we have found that the kind of isoelectronic orbital $nl$ determines the relationship between $\Delta G_{g=0}^{Ox}$ and $F_{elec}$ and two fittings are necessary: the fitting of the trend of the minima of the curve of

| orbital | cation | Z | $Z^*$ | $\Delta G_{g=0}^{Ox}/F_{elec}$ | $E_0/V$ | $F_{elec}/\mu N$ | $R/\text{pm}$ |
|--------|--------|---|------|-----------------------------|--------|-----------------|----------|
| 2s$^2$ | B$^+$  | 5 | 2.11 | −1.53                       | −1.53  | 110             | 67       |
| 4d$^2$ | Sc$^{2+}$ | 21 | 6.71 | −2.47                       | −2.47  | 87              | 134      |
| 5d$^2$ | Y$^{3+}$ | 39 | 16.01| −3.06                       | −3.06  | 203             | 135      |
| 6s$^2$ | La$^{3+}$ | 57 | 19.66| −3.50                       | −3.50  | 81              | 160      |
| 4f$^2$ | Ce$^{3+}$ | 58 | 20.66| −5.80                       | −2.90  | 291             | 128      |
| 4f$^4$ | Pr$^{3+}$ | 69 | 28.5 | −3.34                       | −3.34  | 300             | 148      |
| 4f$^6$6s$^2$ | Lu$^{3+}$ | 71 | 8.67 | −1.110                      | −1.11  | 151             | 115      |


$\Delta G_{0,ox}^{\circ}$ and the fitting from the minimum of the curve of $\Delta G_{0,ox}^{\circ}$ for a specific isoelectronic orbital nl. In order to split the cations with higher incertitude in the electronic configuration because they have not been found experimentally and cations which have been found experimentally, whose electronic configuration can be determined experimentally, we have named the first cations as possible new cations and the second ones as noncommon cations. These cations can have a filled or unfilled electronic configuration. Besides, the methodology used to evaluate the parameters of this work is given after the Conclusions section.

## Results and Discussion

### Relation of $\Delta G_{0,ox}^{\circ}$ with Z.

Through the periodicity of the isoelectronic series of the nf orbitals for the electronic configurations $n^{2}/(n-1)d^{2}/4f^{2}$, np$^{3}$, nd$^{2}/n^{2}(n+1)s^{2}$, nd$^{4}(n+1)s^{2}$, $4f^{4}$, and $4f^{4}6s^{2}/4f^{6}d^{2}$ (see above), we have found the physicochemical properties of possible new cations (Table 1) and of noncommon cations (Table 2) not reported in the literature. In the case of the values of $\Delta G_{0,ox}^{\circ}$, we have used the periodicity of the values of columns and rows for $\Delta G_{0,ox}^{\circ}$ and $E_{G}^0$ of the isoelectronic series and the trend of the respective Frost diagram for an element.

Concerning all the isoelectronic configurations, we have found a parabolic functionality for $\Delta G_{0,ox}^{\circ}$ at pH = 0 of the isoelectronic nf orbitals versus Z for a certain range of Z, as shown in Figure 1. This parabolic behavior has also been found for the ionization of the electronic affinity curve. For the isoelectronic $n^{2}/(n-1)d^{2}/4f^{2}$ orbitals, a parabolic trend of $\Delta G_{0,ox}^{\circ}$ for their minima with the increment of Z is observed, as shown in Figure 1. Indeed, there are two parabolas for the minima of the electronic configuration $n^{2}/(n-1)d^{2}/4f^{2}$, which are joined in the extremes by Ti$^{2+}$ ($Z = 22, 3d^{2}$) as seen in Figure 1. Importantly, the value of Ti$^{2+}$ ($\Delta G_{0,ox}^{\circ}/F = -3.26 \text{ V}$) was found by the trend of the Frost and reduction potential $E_{G}^0$ diagrams for the isoelectronic configuration 4s$^2$/3d$^2$ and also for the different oxidation states of Ti at pH = 0 at standard conditions, as shown in Figures 2 and 3, respectively. This value indicates the higher stability of this ion. On the other hand, the proximity of the empty np$^{2}$ orbital to the occupied ns$^2$ orbitals for n = 2, 3 produces a low increase of the stability for their minima with an increase of Z: B$^{+}$ (Z = 5, 2s$^2$, $\Delta G_{0,ox}^{\circ}/F = -1.526 \text{ V}$) and Si$^{+1}$ (Z = 14, 3s$^2$, $\Delta G_{0,ox}^{\circ}/F = -1.62 \text{ V}$). Then, after Si$^{+}$, there is a higher increase of stability for Ti$^{3+}$ (Ti$^{3+}$, Z = 22, 4d$^2$, $\Delta G_{0,ox}^{\circ}/F = -3.26 \text{ V}$). This cation has unfilled s and d orbitals. Thus, the lower value of $\Delta G_{0,ox}^{\circ}$ for Ti$^{3+}$ with a higher curvature in the first parabola indicates that the stability of the cation at the minima in 2s$^2$ and 3s$^2$ and 4d$^2$ increases with an increase of Z when there is a change of a proximal p0 orbital to unfilled s and d orbitals. It is also observed that the curvature of the second parabola of the minima of the configurations nd$^2$ or 4f$^2$ in n = 4, 5, 6, is lower with higher Z than that of the first parabola, and then, the increment of stability is also lower. On the other hand, for the filled isoelectronic np$^2$ orbitals, the minima of the parabolas of $\Delta G_{0,ox}^{\circ}$ with the increment of Z has an exponential decay: Be$^{2+}$ (Z = 4, 1s$^2$) > Al$^{3+}$ (Z = 13, 2p$^3$) > Sc$^{3+}$ (Z = 27, 3p$^3$) > Y$^{3+}$ (Z = 39, 4p$^3$) > La$^{3+}$ (Z = 57, 5p$^3$), as shown in Figure 1. We have included the cation Be$^{2+}$ because the sequence of 4p$^6$, 3p$^6$, 2p$^6$ orbitals followed the 1s$^2$ orbital which is the ns$^2$ orbital more similar to the np$^2$ orbitals than to the other ns$^2$ orbitals. As observed, the trend of the np$^2$ isoelectronic configurations reaches Be$^{2+}$. Also, the exponential decay indicates an increment of the stability of the cations of the minima of the filled isoelectronic np$^2$ orbitals with an increment of the period because of an increment of the radius, which allows more stability of cations (less attraction of electrons), as it is expected.

On the other hand, in the particular case of S$^{2-}$, although the oxide was supplanted by a hydride in H$_{2}$S in the isoelectronic configuration 3p$^6$, the trend was also present, as observed in Figure 2. Thus, there is a trend of the anion S$^{2-}$ with the other anions, such as Si$^{2-}$, P$^{3-}$, and Cl$^{-}$, which form hydrides. Indeed, the parabolic trend of the cations was shifted to a lower value of $\Delta G_{0,ox}^{\circ}$. Nevertheless, we have used the anion S$^{2-}$ and the other anions with a negative oxidation state in the derivation of the equations of the parabolic trend. Besides, it is also observed in Figure 2 that the value of the Gibbs free energy of oxidation $\Delta G_{0,ox}^{\circ}$ of Ar obtained in the gas phase has a sequential trend with anions and cations because of the physical state of Ar in the gas phase. This value of $\Delta G_{0,ox}^{\circ}$ for Ar was obtained by the trend of the thermochemical data, and, as explained, it is more congruent with the isoelectronic trend of 3p$^6$ than that of $\Delta G_{0,ox}^{\circ} = 0$ for an element.

On the other hand, for the isoelectronic nd$^{10}$/nd$^9$/n$^{2}(n+1)s^{2}$ orbitals, the trend of the minimum of $\Delta G_{0,ox}^{\circ}$ with the increment of Z was a slightly concave parabola with a positive slope, as shown in Figure 3: Ga$^{3+}$ (Z = 31, 3d$^{10}$) > In$^{3+}$ (Z = 49, 4d$^{10}$) > Au$^{+}$ (Z = 79, 5d$^{10}$). This indicates an increase in the tendency to be reduced from the cations. If we compare the value of $\Delta G_{0,ox}^{\circ}$ of Figures 1 and 3, we observe that the values of the configuration nd$^{10}$/nd$^9$/n$^{2}(n+1)s^{2}$ are more positive, indicating that these ions are more prone to be reduced with the increment

![Graph](image_url)
of Z. We consider that the \( n^d(n + 1)s^2 \) orbitals tend to get the \( n^d(n + 1)s^2 \) configuration, resulting in their instability. Thus, the proximity of the partial empty \((n + 1)\) orbitals allows an increase of the possibility of reduction of these cations with the increment of the period. An example of this trend is the reduction of Ag" (4d\(^{10}\)) and Au" (5d\(^{10}\)). The relativistic expansion and contraction of orbitals \( d \) and \( s \), respectively, produce a superior band gap between the \( d \) and \( s \) orbitals for Ag" than for Au", as reported by Mann.\(^{3,4,12}\) For this reason, Au" (5d\(^{10}\)) is more easily reduced than Ag" (4d\(^{10}\)). The decrement of the \( s^2 \) than in \( 6s^2 \) (comparing the energy of \( 5s^2 \) in Cd to the energy of \( 6s^2 \) in Hg).\(^3\) For example, in the case of Sn\(^{2+} \) (4d\(^{10}\)) and Pb\(^{2+} \) (5d\(^{10}\)6s\(^2\)), the lower band gap is between the \( s \) and \( p \) orbitals in Sn\(^{2+} \) than in Pb\(^{2+} \), as shown in Figure 11 of ref 13. Therefore, the lower band gap in Sn\(^{2+} \) increases the possibility of the reduction of Sn\(^{2+} \) in comparison to that of Pb\(^{2+} \). The increase of electronegativity (possibility of reduction) with a decrease of the band gap is due to the inverse variation of the hardness \( \eta \) (half of the band gap) to the electronegativity.\(^{5,6}\)

\[
\left( \frac{\partial \eta}{\partial E} \right)_{E_HOMO} = -\left( \frac{\partial \eta}{\partial E} \right)_{E_LUMO}
\]

(9)

In the case of noble gases, we have interpolated the values of \( \Delta G_{0,OX} \) and the predicted values are \((/kJ mol^{-1}\) K\(^{-1}\)) as follows: 132 (He), 0.238 (Ne), −218 (Ar), −193 (Kr), −145 (Xe), −77 (Rn). The trend is shown in Figures 1 and 4. The negative values of \( \Delta G_{0,OX} \) indicate that they are stable for oxidation. On the other hand, the trend of the filled isoelectronic mp\(^n\) orbitals for elements and anions, labeled with \( X^0 \), \( X^- \), and \( X^{2-} \) as shown in Figure 4, is an increment of the value of \( \Delta G_{0,OX} \) with the period \( n \). This increment of \( \Delta G_{0,OX} \) with a concomitant increase of the stability of elements and anions to rest in states of reduction, probably happens because they can release less electrons with the increment of the radius. This trend is opposite to the stability of the cations for the minima of configuration np\(^n\), which increases with the increment of the period \( n \), as seen above (lower value of \( \Delta G_{0,OX} \)). On the other hand, higher stability is observed for Pt in the isoelectronic configuration 5d\(^{6s^2}\), more exactly [Xe] 4f\(^{14}\)5d\(^{6s^2}\) (as shown in Figure 4), that is, Pt is more prone to remain reduced = not to be oxidized = more stable to the oxidation. The opposite happens with Pd (4d\(^{10}\)5s\(^2\)), more exactly [Kr] 4f\(^{14}\)5d\(^{6s^2}\) (as also shown in Figure 4). A middle value is found in Ni (3d\(^{10}\) more exactly [Ar] 3d\(^{8}\)4s\(^{2}\)4p\(^{6}\)), as shown in Figure 4. The more stability of Pt (5d\(^{6s^2}\)) is produced by the difficulty of accepting electrons in the 6s orbital as a consequence of the relativistic contraction of the orbital 6s and expansion of the orbital 5d.\(^{3,4,13,14}\) We consider that the proximity of the partially filled \( d \) and \( s \) orbitals avoids the
acceptation of the electrons in the d orbital of the configuration [Xe] 5d^{9.20} 6s^{0.79} of Pt. Similarly, the orbital configuration [Kr] 4d^{9.60} 5s^{0.43} in Pd is less prone to be reduced because of a lesser contraction of the orbital 5s^2 with a subsequent higher band gap. Also, the higher stability of the orbital d in the electronic configuration [Ar] 3d^{9.46} 4s^{0.53} of Ni, due to its lower energy than the orbital s in comparison to Pd and Pt, counterbalances the higher band gap between these orbitals, and then ΔG_{0,ox} is intermediate between Pd and Pt. Besides, it is also observed in Figure 4 that the stability remains constant with ΔG_{0,ox} = 0 (no tendency to be oxidized and no tendency to be reduced) in the case of elements X^0 of configuration ns^2/(n−1)d^2/4f^2, nd^{10}/nd^2(n+1)s^2, nd^{10}(n+1)s^2, 4f^4, and 4f^66s^2/4f^{14}6d^2, with no tendency to be reduced in the noble gases. In the case of the anions of the configuration ns^2 (with the trend given by the line X^−), the higher value of ΔG_{0,ox} indicates that these anions are more stable than the anions of the other isoelectronic configurations.

Relation of $E^{0}_n$ and $E^{0}_n$ with Z. The evaluation of the trends of periodicity for $E^{0}_n$ with Z was based on the isoelectronic orbitals nl: ns^2/(n−1)d^2/4f^2, np^6, nd^{10}/nd^2(n+1)s^2, nd^{10}(n+1)s^2, 4f^4, and 4f^66s^2/4f^{14}6d^2 as it was made in ΔG_{0,ox}. Figure 5 shows the values of $E^{0}_n$ for these orbitals: (a) the dashed line indicates the trend of the minima for the np^6 orbital, which corresponds to the point of change from a decrease of $E^{0}_n$ with an increase of the oxidation state to an increase of $E^{0}_n$ (abrupt change of the slope). It is also remarkable that the values of the minima are almost constant. As also observed, the filled isoelectronic configuration np^6 includes the isoelectronic configuration 1s^2 (see Li^+ in Figure 5), and then, all the minima lay in the same dashed curve. This is also observed in the previous section for ΔG_{0,ox} versus Z where the minimum of 1s^2 is in Be^3+, as shown in Figure 1, but in this case, Li^+ is the minimum of the isoelectronic 1s^2 orbital for E^{0}_n versus Z. (b) The dotted—dotted—dashed line indicates the values of ΔG_{0,ox} = 0 for the configuration ns^2, which corresponds to the elements Be, Mg, Ca, Sr, and Ba (X^0). (c) The dotted line indicates the values of the anions of the alkali metals (X^−). All these values allowed to have a continuity in the trend of the ns^2/(n−1)d^2/4f^2 electronic configuration and then to predict the values of the cations B^+, Al^3+, Sc^3+, Y^3+, and La^3+. We also used the periodicity of ΔG_{0,ox} and the trend of the configurations ns^2/(n−1)d^2/4f^2 for n = 4, 5, 6.

The reduction scale $E^{0}_n$, as explained above, is more related to the concept of electronegativity. Besides, a more positive value of $E^{0}_n$ increases the power to form the anion and a more negative value increases the power to be oxidized, and a value of zero indicates no tendency to be reduced or to be oxidized. Thus, it is observed in Figure 6 that the noble gases (gray squares) have a higher reduction potential $E^{0}_n$, especially Ne, and La^+ (new cation) has the highest tendency to be oxidized (to La^3+), with a lower value of $E^{0}_n$. We consider that it would be interesting to react Ne and La^+, seeking the possibility to form a compound, in which the configuration goes from the configuration 3p^6 to the 4s^1. Besides, it is also observed that the cations X^+ (red dashed line below the X^− line) of the configuration np^6 and anions X^− of the configuration ns^2, which correspond to the same elements of Li, Na, K, Rb, and Cs, have similar negative values of $E^{0}_n$. A little less negative the anions, as seen in Figure 6. Thus, the cations X^+ of the isoelectronic configuration ns^2/(n−1)d^2/4f^2 have a less macroscopic electronegativity than the anions X^−.

We applied the same methodology of first using the trend of the reduction potential $E^{0}_n$ and then to find the relation of electronegativity by the reduction potential for the configurations nd^{10}/nd^2(n+1)s^2, nd^{10}(n+1)s^2, 4f^4, and 4f^66s^2/4f^{14}5d^2. Figures S17 and S18 are plotted in the Supporting Information. Figure S18 shows that the reduction potential $E^{0}_n$ of the elements Ni, Pd, and Pt is sequentially more negative (less electronegativity, less power to attract electrons), indicating that Pt is more susceptible to form hydrides. Besides, as observed in Figure 4 and explained above, the sequence of stability, that is, an increase in the negative value of ΔG_{0,ox} is Pt < Ni < Pd. On the other hand, Er and Au^+ have a more positive $E^{0}_n$, as shown in Figure S18, with an added possibility to be reduced. In the case of gold, it is known that it tends to rest as an element.

Relation of ΔG_{0,ox} with $F_{sluc}$. One of the objectives of this work is to find a relation between the parameters of the atomic structure of the atom (effective nuclear charge $Z^*$, radius, and type of orbital). For this reason, we have evaluated $F_{sluc}$, following eq 7. We have found, as expected, an exponential variation of $F_{sluc}$ with Z in almost all the orbitals, as shown in Figure S15 of the Supporting Information. The next step was to relate ΔG_{0,ox} with $F_{sluc}$. The last one is, in general, proportional to the electronegativity, as seen above through eq 6. We have found that this relationship was dependent on the isoelectronic nl orbitals. With this constraint, we have evaluated ΔG_{0,ox} in two forms. First, we have evaluated the relationship of the minima of
\( \Delta G_{0,\text{ox}}^{0}(Z') = \Delta G_{0,\text{ox}}^{0}(F_{\text{elec}}[Z_{\text{min}},n]) + \Delta G_{0,\text{ox}}^{0}(F_{\text{elec},n}, Z_{\text{min}}) \) (10)

\( \Delta G_{0,\text{ox}}^{0}(Z'^{n}) = \Delta G_{0,\text{ox}}^{0}(Z_{\text{min}},n) + \Delta G_{0,\text{ox}}^{0}(F_{\text{elec},n}, Z_{\text{min}}) \) (11)

\( \Delta G_{0,\text{ox}}^{0}(Z') = \Delta G_{0}^{0} + \Delta G_{1}^{0} \) (12)

where \( \Delta G_{0,\text{ox}}^{0}(F_{\text{elec}}[Z_{\text{min}},n]) = \Delta G_{1}^{0} \) is dependent on the electric force \( F_{\text{elec}} \) of the cations at the minimum of \( \Delta G_{0,\text{ox}}^{0}(Z') \) for each isoelectronic orbital \( n \); \( \Delta G_{0,\text{ox}}^{0}(F_{\text{elec},n}, Z_{\text{min}}) = \Delta G_{2}^{0} \) is the parabolic dependence of \( \Delta G_{0,\text{ox}}^{0} \) on the electric force \( F_{\text{elec}} \) of an isoelectronic orbital \( n \) with the vertex in \( Z_{\text{min}} \); and \( \Delta G_{1}^{0} \) is the tabulated \( \Delta G_{0,\text{ox}}^{0} \) for \( Z_{\text{min}} \). It must be emphasized that the first term on the right of eqs 10 and 11 gives the value of \( \Delta G_{0,\text{ox}}^{0} \) for \( Z_{\text{min}} \) and the second term gives the change of \( \Delta G_{0,\text{ox}}^{0} \) on \( F_{\text{elec}} \) with respect to \( Z_{\text{min}} \).

In order to obtain the first term of the right side of eq 10, we have interpolated the values of \( \Delta G_{1}^{0} \) with \( F_{\text{elec}} \) for \( Z_{\text{min}} \) of the isoelectronic orbitals; however, the isoelectronic configuration for \( n s^{2} / (n - 1)d^{2}/4f^{2} \) does not allow establishing a trend, as shown in Figure 7a, as a consequence of the changes of configuration among the periods. In the isoelectronic series \( n s^{2} / (n - 1)d^{2}/4f^{2} \), there is an increment of \( \Delta G_{1}^{0} \) with a decrement of \( F_{\text{elec}} \) in \( B^{+}, Si^{2+}, \) and \( Ti^{2+} \) (a decrement of stability of the oxidation state), which is shown in the pink square of Figure 7a. We consider that the volume of the empty \( np^{6} \) and unfilled \( (n - 1)d \) orbitals increases the value of \( \Delta G_{1}^{0} \) in \( B^{+}, Si^{2+} \), and \( Ti^{2+} \) with a concomitant decrease of \( F_{\text{elec}} \) respectively. In other words, the possibility of reduction is increased because the new charge can be dispersed in the empty \( np^{6} \) and unfilled \( (n - 1)d \) orbitals. On the contrary, the cations \( Be^{2+} \), \( Zr^{2+} \), and \( Pr^{3+} \) have a lower value \( \Delta G_{1}^{0} \) with a higher \( F_{\text{elec}} \) as shown in the blue square of Figure 7a (an increase of the stability of the oxidation state). This behavior is opposite to the relation of \( F_{\text{elec}} \) to electronegativity: an increment of \( F_{\text{elec}} \) increases the capacity of reduction of the cation. In the case of \( Zr^{2+} \) and \( Pr^{3+} \) with configurations \([Kr]\) 4d\(^{2}\) and \([Xe]\) 4f\(^{3}\), respectively, the less proclivity of dispersion of the new charge on the energetic degenerate orbitals \( d \) and \( f \) produces the high stability of these ions. We consider that the similar behavior of \( Be^{2+} \) is due to its electronic configuration of the noble gas of \( Be^{2+},[He]\), that gives more stability to the cation. On the other hand, with respect to the configuration \( np^{6} \): (1) if a cation with an isoelectronic configuration \( np^{6} \) belongs to the 2nd and 3rd periods of the periodic table, an exponential decay of \( \Delta G_{1}^{0} \) with \( F_{\text{elec}} \) is found from \( Be^{2+} \) to \( Al^{3+} \), as shown in Figure 7b, as expected from the relation of \( F_{\text{elec}} \) versus electronegativity. (2) If a cation with an isoelectronic configuration \( np^{6} \) belongs to the 3rd and 4th periods, an exponential decay versus \( F_{\text{elec}} \) is predicted from \( Al^{3+} \) to \( Sc^{3+} \) or a sigmoidal growth versus \( F_{\text{elec}} \) from \( La^{3+} \) to \( Al^{3+} \), including \( Sc^{3+} \). This indicates a zone of transition by the appearance of the orbital 4d and hysteresis in the value of \( \Delta G_{1}^{0} \) versus \( F_{\text{elec}} \) as shown in Figure 7b. (3) If a cation with an isoelectronic configuration \( np^{6} \) belongs to the 4th, 5th, and 6th periods of the periodic table, with the \((n - 1)d \) and 4f orbitals, the change of \( \Delta G_{1}^{0} \) is sigmoidal with \( F_{\text{elec}} \) with a remarkable similarity of \( \Delta G_{1}^{0} \) between \( Y^{3+} \) and \( La^{3+} \) and almost a vertical change from these cations to \( Sc^{3+} \), as shown in Figure 7b. (4) A regular behavior of the minima of the filled electronic configuration \( np^{6} \) is observed: an increase of the possibility of reduction with an increase of the electric force, different from the behavior of the configuration \( n s^{2} / (n - 1)d^{2}/4f^{2} \).

In the case of \( nd^{10}/nd^{9}(n + 1)s^{2} \) orbitals, the dependence of \( \Delta G_{1}^{0} \) for the minima of the parabolas versus \( F_{\text{elec}} \) is almost linear, with a negative slope, as shown in Figure S19 of Supporting Information, Section S-5, indicating that the reduction of the cations is diminished (better stability) with a higher \( F_{\text{elec}} \) (higher macroscopic power of attraction of electrons and higher macroscopic electronegativity). This trend is opposite to the trend related to \( Z \) for \( nd^{10}/nd^{9}(n + 1)s^{2} \). This decrease of \( \Delta G_{1}^{0} \) in the orbital \( nd^{10}/nd^{9}(n + 1)s^{2} \) with the increase of \( F_{\text{elec}} \) contradicts the asseveration that when \( F_{\text{elec}} \) augments, its electronegativity increases, and its stability goes up. We consider that the relativistic effects in \( In^{3+} \) and \( Au^{3+} \) produce an increase of their values of \( \Delta G_{1}^{0} \) (an increment of the reduction power, an increment of the macroscopic electronegativity, and an increment of the instability as cations), although these cations have a less value of \( F_{\text{elec}} \) than \( Ga^{3+} \). On the other hand, the values of \( \Delta G_{1}^{0} \) for the cations of the minima of the \( nd^{10}/nd^{9}(n + 1)s^{2} \) configuration (\( Ga^{+}, Sn^{2+}, Ti^{2+} \)) are similar [when we compare them to the scale of the \( nd^{10}/nd^{9}(n + 1)s^{2} \) configuration], as shown in Figure S20 of the Supporting Information. This happens although the electric force \( F_{\text{elec}} \) varies. This is indicative that the proximity of filled \( d^{10} \) and \( p^{6} \) empty orbitals produces stability to oxidation and reduction of these cations because their \( \Delta G_{1}^{0} \) values are almost 0 (a little more stable to be reduced because of \( \Delta G_{1}^{0} < 0 \)). Indeed, \( Ga^{+} \) is more prone to be oxidized, as shown in Figure S19. As a note, the higher electric force \( F_{\text{elec}} \) in the cation of \( Sn \) is due to its higher oxidation state \( (2+) \) than those of \( Ga (1+) \) and \( Ti (1+) \).

In order to obtain the second term of the right side of eq 11, \( \Delta G_{2}^{0} \) we have normalized the nuclear charge \( Z \) to \((Z - Z_{\text{min}})\) for each isoelectronic \( nl \) orbital. In principle, we have found an exponential growth trend of \( F_{\text{elec}} \) versus \((Z - Z_{\text{min}})\) and a

Figure 7. Interpolation of the data of \( \Delta G_{1}^{0} \) with \( F_{\text{elec}} \) for the cations of the isoelectronic orbitals (a) \( ns^{2} / (n - 1)d^{2}/4f^{2} \) and (b) \( np^{6} \).
parabolic trend of $\Delta G_{2}$ versus $(Z - Z_{\text{min}})$, for example, for $n^{10}/n^{d}(n + 1)s^2$, as shown in Figures S15B, 1, and 8. The other nl isoelectronic orbitals are shown in Supporting Information, Section S-7 in Figures S21–S25. We have also fitted the cations, elements, and anions, and this gives a parabolic behavior in $\Delta G_{2}$. The anions in an acidic aqueous environment $pH = 0$ are more stabilized, and then the value of $\Delta G_{2}$ becomes more negative, as shown in Figure 2 for the isoelectronic configuration $n^{p6}$. In particular, we observe a lower value of $F_{\text{elec}}$ for the exponential growth curve fitting, as shown in Figure 8a. The decrement of $F_{\text{elec}}$ in the configuration $5d^{10}/5d^{6}s^{2}$ can be associated with the expansion of the radius of d orbitals because of relativistic effects, as shown in eq 7. It is also possible that this expansion of the radius is due to the delocalization of the charge in the next 6s orbital because of the tendency to fulfill the configuration $5d^{6}s^{2}$. Also, the electric force $F_{\text{elec}}$ of the $n^{d}/n^{d}(n + 1)s^2$ isoelectronic series decreases from $n = 3$ to $n = 5$ in relation to $Z - Z_{\text{min}}$ as shown in Figure 8a. In the case of $n = 3$ and $5$, this is due to the high oxidation state of $Z_{\text{min}}$ in $n = 3$ (Ga$^{3+}$) than that of $n = 5$ (Au$^{3+}$). Besides, a lower value of $\Delta G_{2}$ versus $Z - Z_{\text{min}}$ than the overall trend is observed, as it happens in relation to the electric force $F_{\text{elec}}$ for the configuration $5d^{10}/5d^{6}s^{2}$ in Figure 8b, for example, in Bi$^{5+}$ ($Z = 83, Z - Z_{\text{min}} = 3$, $\Delta G_{2}^{\text{fl}}/F = 98$ V, $5d^{10}$). This indicates that the cations in the configuration $5d^{10}/5d^{6}s^{2}$ are, with respect to their minimum of $\Delta G_{2}^{2}$, more stable with the addition of electrons in order to occupy the 6s orbital (lesser possibility of reduction) than the other periods ($n = 3d^{10}/3d^{4}4s^{2}, 4d^{10}/4d^{4}5s^{2}$) because the relativistic contraction of the orbital 6s and expansion of the orbital 5d decrease the capability of reduction. Probably, the high dispersion of the new charge in orbitals s and d does not allow this reduction. As a consequence, the minima of the configuration $3d^{10}/3d^{4}4s^{2}$ (Z$i$rn $\text{Ga}^{3+}$) and configuration $4d^{10}/4d^{4}5s^{2}$ (Z$i$rn $\text{In}^{3+}$) have a different oxidation state than the configuration $5d^{10}/5d^{6}s^{2}$ ($Z_{\text{min}}$ at Au$^{3+}$). This indicates additional stability at a low oxidation state in gold for the configuration $3d^{10}$. There is also an abrupt increment of $\Delta G_{2}^{2}$ in platinum Pt from its minimum ($Z = 78, Z - Z_{\text{min}} = -1, \Delta G_{2}^{2}/F = 3.7$ V, $5d^{6}6s^{2}$), as shown in Figure 8b, that is, an abrupt decrement of possibility to remain oxidized in comparison to the isoelectronic configurations $3d^{10}/3d^{4}4s^{2}$ and $4d^{10}/4d^{4}5s^{2}$, as explained above.

On the basis of the relationships of $F_{\text{elec}}$ versus $(Z - Z_{\text{min}})$ and $\Delta G_{2}^{2}$ versus $(Z - Z_{\text{min}})$, we have found the relationship of $\Delta G_{2}^{2}$ versus $F_{\text{elec}}$. Thus, the parabolic average behavior of $\Delta G_{2}^{2}$ versus Z in the isoelectronic configurations $n^{s^{2}}/(n - 1)d^{2}/4f^{2}$ and $n^{p6}$ in Figures 21b and 22b, respectively, is contracted in their relationship of $\Delta G_{2}^{2}$ versus $F_{\text{elec}}$ in Figure 9. This contraction is influenced by the atomic structure represented by $F_{\text{elec}}$. We also found a higher value of $\Delta G_{2}^{2}$ of the anions at lower $F_{\text{elec}}$ that is, the further possibility to remain reduced, probably due to the overlapping of the orbitals with a lower ionic interaction. We must also emphasize that the general trends of the isoelectronic $n^{s^{2}}/(n - 1)d^{2}/4f^{2}$ and $n^{p6}$ orbitals hide the particular behavior of a specific nl configuration, as also shown in Figure 9.

Figure 10 shows all the average values of $\Delta G_{2}^{2}$. We can say that Figure 7 gives the reference value at the minimum of $\Delta G_{2}^{2}(\Delta G_{2}^{2})$, which results from the increment of the effective nuclear charge and the variation of radius represented by $F_{\text{elec}}$ taking into account the behavior of the overall nl orbitals (in the different periods). On the other hand, Figures 8 and 9 give the change in the value of $\Delta G_{2}^{2}$ with the electric force $F_{\text{elec}}$ (\(\Delta G_{2}^{2}\)), in an nl isoelectronic configuration. Thus, we have found that there is an increment of $\Delta G_{2}^{2}$ when $F_{\text{elec}}$ is almost 0 in the following sequence: $n^{s^{2}}/(n - 1)d^{2}/4f^{p6} > 4f^{4} > 4f^{4} + nd^{10}/n^{d}(n + 1)s^{2} > 4f^{4}6s^{2}/4f^{4}5d^{2} \approx nd^{10}(n + 1)s^{2}$, as shown in Figure 10 (this trend is the average of $\Delta G_{2}^{2}$). This behavior is due to the fact that the $n^{s^{2}}/(n - 1)d^{2}/4f^{p6}, 4f^{4}6s^{2}/4f^{4}5d^{2}$ and $nd^{10}(n + 1)s^{2}$ orbitals at $F_{\text{elec}}$ near 0 are more prone to be reduced by the filling of the empty $n^{p6}$ or $nd^{10}$ or nonempty 4d and 4f, $n^{s^{2}}, 4f^{4}6s^{2}$, $nd^{10}$, and $nd^{10}(n + 1)s^{2}np^{6}$ orbitals, respectively. On the other hand, with the increment of $F_{\text{elec}}$, $\Delta G_{2}^{2}$ goes through a minimum

![Figure 8](https://example.com/figure8.png)

**Figure 8.** Behavior of (a) $F_{\text{elec}}$ and (b) $\Delta G_{2}^{2}$ vs $Z - Z_{\text{min}}$ for the isoelectronic $n^{d^{10}}/n^{d}(n + 1)s^{2}$ orbitals.

![Figure 9](https://example.com/figure9.png)

**Figure 9.** Behavior of $\Delta G_{2}^{2}$ vs $F_{\text{elec}}$ for the isoelectronic electronic configurations (a) $n^{s^{2}}/(n - 1)d^{2}/4f^{2}$ and (b) $n^{p6}$ orbitals. The continuous line is the average.

![Figure 10](https://example.com/figure10.png)

**Figure 10.** Behavior of $\Delta G_{2}^{2}$ vs $F_{\text{elec}}$ for the isoelectronic nl orbitals.
in all of these orbitals, as shown in Figure 10. After the minimum, there is an increment of \( \Delta G_{fi}^0 \) in the sequence \( 4f^6 6s^2 / 4f^{15}d^4 > nd^{10}(n + 1)s^2 > np^6 \approx nd^{10}/nd^{10}(n + 1)s^2 > ns^2/\sqrt{(n - 1)d^2 / 4f^6} > 4f^4 \) (in reference to their minimum of \( \Delta G_{fi}^0 \)). This sequence indicates the highest possibility of the cations of the isoelectronic configuration \( 4f^6 6s^2 / 4f^{15}d^4 \) to be reduced in the average and the lowest possibility of the cations of the isoelectronic configuration \( 4f^4 \) in the average to be reduced after their minima of \( \Delta G_{fi}^0 \) versus \( F_{dec} \).

Thus, we can evaluate \( \Delta G_{fi}^0(Z') \) by using Figures 7 and 10 (eq 10) for \( ns^2/\sqrt{(n - 1)d^2 / 4f^6} \) and \( np^6 \). The other method also uses Figure 10, but the tabulated values for the minima of the isoelectronic nl orbitals are employed.

**Frost Diagram of the Possible New Cations.** The analysis of the stability of the possible new cations can be evaluated through the Frost diagrams of \( \Delta G_{fi}^0/Z(n) \) versus the electric charge \( Q \), as shown in Figure 11. It is seen that the cations that comproportionate (they are more stable) are as follows: \( \text{Ce}^{2+} > \text{Tm}^3 \approx \text{La}^4 \approx \text{Y}^3 > \text{Sc}^2 > \text{B}^+ \) and the ion that disproportionates is \( \text{Lu}^+ \) (less stable). Thus, the more stable cation is \( \text{Ce}^{2+} \).

We must also take into account that internal and external factors can influence the stability of the ions and the macroscopic electronegativity, such as the orbital shielding, the polarizability of the electronic cloud, the hydration of the ions, the similarity of the band gap, the relativistic effects with contraction of the s orbital and the expansion of the d orbital, the more penetration of the s orbitals, which increases the electronegativity, the orbital overlapping, the electronegativity alternation of the elements, the formation of multiple bonds, the bond length, the silicon rule, \( \pi \) backbonding, the lattice energy with the Madelung constant, the Racah’s constant, the spin of the orbital, the accuracy of the metal bond energy, and so forth. Thus, the above factors form a pool for future technological and scientific research.

**CONCLUSIONS**

Commonly, it is said that qualitatively the first elements of the transition series in a period can be easily oxidized, which decreases in the half of the period in the d\(^{10}\) configuration, and the reactivity is lower in elements with almost a filled configuration d\(^{10}\). Concerning the oxidation states, a common trend is that the low ones tend to be reducing and the higher ones to be oxidizing, such as happens to Mn, Co, and Ni in Figure S3. Thus, Frost diagrams are used for the analysis of the reduction potential of the different oxidation states for the same element.

It is also explained in the literature that high oxidation states are more common in the half of a period of the transition elements near to the electronic configuration \( (n - 1)d^{10}ns^2 \) (e.g., V, Cr, Mn in the 4th period). Following our methodology, we have found quantitative curves of chemical behavior given by the stability \( \Delta G_{fi}^0(Z') \) and the possibility of reduction \( E^{0,0} \) for the isoelectronic series, with the last concept related to the electronegativity. Thus, we analyze the stability of ions with Frost diagrams of \( \Delta G_{fi}^0/Z(n) \) versus the oxidation states of isoelectronic series with respect to Z. The parabolic trends indicate, for example, a higher stability to the oxidation of the anions and elements in the isoelectronic configuration \( ns^2/\sqrt{(n - 1)d^2 / 4f^6} \) than in the configuration \( np^6 \). In particular, the configuration \( ns^2/\sqrt{(n - 1)d^2 / 4f^6} \) has a higher tendency to reduce in lower and higher oxidation states than the configuration \( 4p^6 \) considering the minima of their isoelectronic parabola. Thus, we have analyzed the effect of structural factors such as the radius, the effective nuclear charge, and the kind of orbitals joined in all in the electronic force \( F_{elec} \) to predict the stability and reduction potential of the elements based on the Frost diagrams. Besides, the periodicity of \( \Delta G_{fi}^0/Z(n) \) and \( E^{0,0} \) versus Z for the isoelectronic nl orbitals can also help to predict the respective values of possible new cations and noncommon cations and noble gases. We have determined that the dependence of \( \Delta G_{fi}^0/Z(n) \) versus Z (or \( F_{elec} \)) indicates that the form of the orbital, its penetration, the proximity of other unfilled orbitals of low energy, and radial probability density influence the value of the reduction potential. Then, we have found that the cations tend to be or to go into the configuration of noble gas \( ns^2np^6 \) or an \( nd^{10}(n + 1)s^2 \) configuration, which are wells of stability in periods 4–6, as indicated by the first ionization energy. We have also found that averaging the change of \( \Delta G_{fi}^0/Z(n) \) per electron, that is, the analysis of the reduction potentials \( E^{0,0} \) versus Z, is more related to the concept of electronegativity, and a nonlinear trend indicates a variation of the effect of structural factors on the electronegativity, as explained in the paragraph related to eq 4.

**METHODOLOGY**

In the evaluation of \( F_{elec} \) versus \( \Delta G_{fi}^0/Z(n) \) for cations and anions and elements, we have used the following:

(a). The radius of Shannon and Prewitt in octahedral coordination.\(^{34,35}\) When this was not possible, the tetrahedral coordination was employed, which has a lower ionic radius, and then \( F_{elec} \) increased. For the elements, we have used the values of their covalent radius given in the Cambridge Structural Database.\(^{19}\) In the case of anions, we have also obtained the anionic radii values from Pauling.\(^{20}\)

(b). Tables for evaluating the nuclear effective charge \( Z^* \). In order to have a more exact evaluation of the nuclear effective charge \( Z^* \) up to \( Z = 86 \), the diagrams of Clementi and Raymondi were employed, which are considered more rigorous than the Slater evaluation.\(^{3,21}\) They proposed their evaluations for cations and neutral atoms, but their results can also be applied to anions, as can be concluded when one evaluates the Slater formulae and the results of Clementi and Raymondi’s equations and diagrams in the first three periods of the periodic

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**Figure 11.** Frost diagram of the predicted cations in aqueous solution at pH = 0.
(c). Experimental values of the standard reduction potentials $E^\circ_0$ in acidic aqueous solutions (pH = 0) from the tables of Bratsch, Bard, Atkins, and Pourbaix.\textsuperscript{7,11,15,22} The values of the cations are mainly for the oxides, a middle strength field ligand, while we do not specify another thing. For the anions, we used the values of the hydrides. We can say that the periodicity of $\Delta G^\circ_{\text{ox}}$ gives the trend of stability of the ions, elements, and anions in an isoelectronic series. On the other hand, the periodicity of $E^\circ_1$ and $E^\circ_{\text{red}}$ gives a trend more related to the concept of macroscopic electronegativity, which is influenced in this case by the hydration of the ions or anions, the nephelauxetic effect, and overlap of the orbitals, for example.

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Notes

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Additional Note

“The correctness of the assignation of configuration $nd^l(n+1)s^2$ to Ni, Pd, and Pt was verified because their electric force $F_{\text{elec}}$ follows the trend of the other cations with configuration $nd^{10}$, as shown in Figure 8a. Indeed, the assignation of configuration $nd^{10}$ to these elements gives a value approximately twice that of electric force $F_{\text{elec}}$ which less follows the trend of the other cations.

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