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Investigation of relationship with electron configuration of chemical hardness, absolute electronegativity and electrophilicity

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ABSTRACT

Chemical hardness (η) , absolute electronegativity (χ) , and electrophilicity (ω) have important applications in inorganic chemistry. These concepts are defined quantitatively as $\eta = (I - A)/2$, $\chi = (I + A)/2$, $\omega = \chi^2/2\eta$. Where I is the ionization energy and *A* is the electron affinity. In this study, graphical method was used to see the relation of electron configuration with chemical hardness, absolute electronegativity and electrophilicity. For this purpose, sequential ionization of atoms were considered. In this method, chemical hardness, absolute electronegativity, electrophilicity and effective nuclear charge (*Z**) were calculated for all ions formed with sequential ionization of an atom and chemical hardness, absolute electronegativity and electrophilicity with respect to effective nuclear charge were illustrated in the graphs. Besides, the same charged ions were considered in order to see more clearly relationship with electron configuration of these three features because charge is effective on chemical hardness, absolute electronegativity and electrophilicity. Likewise, chemical hardness, absolute electronegativity and electrophilicity values were calculated and graphs of these three features were plotted with respect to atomic number (*Z*). As to conclude, it was proven that chemical hardness, absolute electronegativity and electrophilicity increase in some specific electron configurations and this means that configuration effect is a more effective factor than radius and charge.

Keywords: Chemical Hardness; Absolute Electronegativity; Electrophilicity; Electron Configuration

INTRODUCTION

1Chemical hardness, absolute electronegativity and electrophilicity are the properties related to reactivity of chemical species. Chemical hardness can be described as the resistance towards the deformation or polarization of electron cloud of atoms, ions or molecules [1]. Hardness is an important quantity, as it serves as the input in HSAB [2-4] and MHP [5] studies of chemical reactivity and stability. Based on this concept, Lewis acids and bases [6,7] were classified as

hard and soft and HSAB Principle was put forward by Pearson. According to HSAB Prenciple [8,9], "Hard acids prefer to coordinate with hard bases and soft acids with soft bases." Low polarizability chemical species are defined with hard concept while high polarizability chemical species are defined with soft concept. The interaction between hard acids and hard bases is an electrostatic interaction and the interaction between soft acids and soft bases is a covalent interaction.

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Both electrostatic interaction and covalent interaction are strong interactions [10,11].

In density functional theory, some chemical properties are identified as response functions of the electronic energy (*E*) with respect to number of electrons [12,13]. Thus, mathematical definitions were obtained for chemical concepts such as electronegativity and chemical hardness. Absolute electronegativity and hardness are defined as first and second derivate of the energy *E* with respect to the number *N* of the electrons [14,15]. Pearson and Parr described [16,17] as chemical potential slope of the curve in Figure 1. According to this approach, chemical potential (μ) , chemical hardness (η) and absolute electronegativity (y) are given as follow;

$$
\mu = \left(\frac{\partial E}{\partial N}\right)_v \tag{1}
$$

$$
\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu} \tag{2}
$$

$$
\eta = \frac{1}{2} \left(\frac{\partial E^2}{\partial N^2} \right)_v \tag{3}
$$

Chemical hardness and electronegativity can be calculated using the ionization potential and electron affinity as;

$$
\eta = \left(\frac{I - A}{2}\right) \tag{4}
$$

$$
\chi = \left(\frac{I + A}{2}\right) \tag{5}
$$

where *I* and *A* are respectively ionization potential and electron affinity. N is number of elecron and reactions of ionization energy and electron affinity are shown below.

Fig. 1. Relationship with number of electron of total electronic energy for any atom.

Electronegativity has important application in chemistry. Pauling's definition [18] is most suitable for theoretical explanations although many definitions is recommended for electronegativity. According to Pauling definition, electronegativity is defined as "the power of an atom in a molecule to attract electrons toward itself." According to Mulliken definition [19], electronegativity is defined as average of ionization energy and electron affinity an atom, molecule and radical.

 According to Mulliken-Jaffe electronegativity definition, electronegativity of an atom depends on its charge [20]. It is expressed with this electronegativity definition that electronegativity increases as the charge increases. For this definition, electronegativity is given as follows;

$$
\chi = \alpha + \beta \delta \tag{6}
$$

where δ is atomic charge, α and β are parameters that depend on valence state ionization energy and electron affinity values of atoms. The relationship with atomic size of electronegativity has been given by Allred- Rochow electronegativity

definition. According to this definition, electronegativity is electrostatic force between nucleus of atom and valence electrons of atom [21]. Allred- Rochow electronegativity is given as follow;

$$
\chi_{AR} = \frac{Z^* e^2}{r^2} \tag{7}
$$

where r is covalent radius in picometer unit, *Z** is effective nuclear charge and *e* is charge of electron. It is seen from equation that if effective nuclear charge increases and radius decrease, electronegativity of atom increases. As a result of this, it can be said that electronegativity is associated with atomic size with Allred-Rochow electronegativity definition.

Electrophilicity of a system is the measure of its reactivity towards attracting electrons from a nucleophile so that they form a bond. a definition of an electrophilicity index (ω) is proposed by Parr as [22,23],

$$
\omega = \frac{-\mu^2}{2\eta} = \frac{\chi^2}{2\eta}
$$
 (8)

We know that stability increases in global electron configuration such as halffull and full electron configuration and atoms or ions have low reactivity in steady state. Relationship with atomic size and charge of chemical hardness, absolute electronegativity and electrophilicity has been given in existing literate. This study was made to demonstrate that electron configuration effect is more dominant effect than atomic size and charge effects on chemical hardness, absolute electronegativity and electrophilicity.

THEORETICAL METHOD

Chemical hardness and absolute electronegativity values were calculated from experimental ionization energy and electron affinity values for certain ions

using equation 4 and equation 5. Electrophilicity values were calculated using obtained chemical hardness and absolute electronegativity for same ions using equation 8. Relationship with electron configuration of chemical hardness, absolute electronegativity and electrophilicity was investigated with graphical method plotting graph with respect to atomic number and effective nuclear charge of obtained chemical hardness, absolute electronegativity and electrophilicity values.

Fig. 2. Z^* - η graph for Argon.

Fig. 3. Z^* - η graph for Phosphorus.

Fig. 4. Z^* - η graph for Calcium.

Table 3. Data Z^{*} and η for Calcium

Ion	\mathbf{Z}^{\ast}	
$Ca+$	3.20	2.87
$Ca2+$	8.75	19.51
Ca^{3+}	9.10	8.09
$Ca4+$	9.45	8.65
Ca^{5+}	9.80	12.18
Ca^{6+}	10.15	9.45
$Ca7+$	10.50	9.77
Ca^{8+}	10.85	20.65
$Ca9+$	11.20	11.36

Table 4. Z and η values for $+1$ charged ions

Ion	Z	η	Ion	$\tilde{}$ Z	η
$He+$		14.91	\overline{Na}^+		21.07
$Li+$		35.12	$Mg+$	12	3.69
$Be+$		4.44	AI^+	13	6.42
B^+		8.42	$Si+$	14	4.09
$\overline{\mathbf{C}}^*$		6.56	$\overline{\mathbf{P}^+}$	15	4.61
$\overline{\mathbf{N}^+}$		7.53	S^+	16	6.48
\mathbf{O}^*		10.74	$\mathbf{C}\mathbf{I}^+$	17	5.41
$\overline{\mathbf{F}^+}$		8.77	$\overline{\mathbf{Ar}}^+$	18	5.93
Ne^+	10	9.69			

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Fig. 5. Z - η graph for +1 charged ions.

Ion	Z	n	Ion	\mathbf{z}	m
$Li2+$	3	23.40	Al^{2+}	13	4.80
Be^{2+}	4	67.80	$Si2+$	14	8.57
B^{2+}		6.38	\mathbf{p}^{2+}	15	5.22
\mathbf{C}^{2+}		11.75	S^{2+}	16	5.75
N^{2+}		8.92	$Cl^{\overline{2+}}$	17	7.90
$\overline{\mathbf{O}^{2+}}$	8	9.90	Ar^{2+}	18	6.55
\mathbf{F}^{2+}	9	13.86	$\overline{\mathbf{K}^{2+}}$	19	7.04
Ne^{2+}	10	11.24	Ca^{2+}	20	19.51
Na^{2+}	11	12.17	Sc^{2+}	21	5.98
Mg^{2+}	12	32.55	Ti^{2+}	22	6.95

Table 5. Z and η values for $+2$ charged ions

Fig. 6. Z- η graph for $+2$ charged ions.

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Table 6. Z and η values for $+3$ charged ions

Fig. 7. Z- η graph for $+3$ charged ions.

RESULTS AND DISCUSSION

As is known, the reactivity of chemical species relates with their chemical hardness, absolute electronegativity and electrophilicity. This condition has been demonstrated with Hard and Soft Acid and Base (HSAB) Theory. Chemical properties such as chemical hardness, absolute electronegativity and electrophilicity depend on size and charge of chemical species. This study showed that electron configuration effect is influence more dominant than atomic charge and size on chemical hardness, absolute electronegativity and electrophilicity of chemical species. Chemical hardness,

absolute electronegativity and electrophilicity values are higher than expected values according to size and charge in particular configurations.

Fig. 8. χ -Z* graph for phosphorus.

Fig. 9. χ -Z^{*} graph for sulfur.

Table 7. Data Z^* and η for Phosphorus

Ion	\mathbf{Z}^*	
\mathbf{P}^+	5.15	15.10
$\overline{\mathbf{P}^{2+}}$	5.50	24.95
$\overline{\mathbf{p}^{3+}}$	5.85	40.77
$\overline{\mathbf{p}^{4+}}$	6.20	58.19
$\overline{\mathbf{p}^{5+}}$	10.85	142.72
$\overline{\mathbf{p}^{6+}}$	11.20	241.82
$\overline{\mathbf{p}^{7+}}$	11.55	286.31
$\overline{\mathbf{p}^{8+}}$	11.90	340.56
$\overline{\mathbf{P}^{9+}}$	12.25	398.11

Fig. 10. γ -Z^{*} graph for Silicon.

Namely, electron configuration effect is more dominant than effect of atomic size and charge.

It was seen from graphs related with chemical hardness that chemical hardness increases in half-full and full electron configuration such as ns^1 , ns^2 , np^3 , np^6 . But, chemical hardness has the highest value in noble gas configuration. In such configurations, charge and atomic radius effects should not be considered while comparisons related with chemical hardness is made. For instance, it can be thought that Al^{4+} is harder than Al^{3+} when a comparison in terms of charge and size is made. Graphs related with chemical hardness showed that Al³⁺is harder than $Al⁴⁺$. The reason for this situation is that electron configuration of Al^{3+} ends with $2p^6$ or Al^{3+} has noble gas configuration. In figure 3, P^{8+} and P^{9+} can be shown as instance in order to see that the hardness increases in half-full configuration. When effect to hardness of charge is considered,
it is expected that P^{9+} is harder than P^{8+} .
But, results showed that P^{8+} is harder than P^{9+} because electron configuration of P^{8+} ends with $2p^3$.

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Table 10. Z and χ values for +1 charged ions

Fig. 11. $Z - \chi$ graph for +1 charged ions.

Ion	Z	χ	Ion	Ζ	χ
$Li2+$	3	99.03	Al^{2+}	13	23.63
Be^{2+}	4	86.05	$Si2+$	14	24.91
B^{2+}	5	31.54	\mathbf{P}^{2+}	15	24.95
\mathbf{C}^{2+}	6	36.13	S^{2+}	16	29.08
N^{2+}	7	38.52	$CI2+$	17	31.70
$\overline{\mathbf{O}^{2+}}$	8	45.02	Ar^{2+}	18	34.18
$\overline{\mathbf{F}^{2+}}$	9	48.83	\mathbf{K}^{2+}	19	38.67
Ne^{2+}	10	52.20	Ca^{2+}	20	31.38
Na^{2+}	11	59.46	$\overline{\text{Sc}^{2+}}$	21	18.77
Mg^{2+}	12	47.58	Ti^{2+}	22	20.53

Table 11. Z and χ values for +2 charged ions

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Fig. 12. Z - χ graph for +2 charged ions.

Table 12. Z and χ values for +3 charged ions

Ion	Z	χ	Ion	Z	χ
$Be3+$	4	185.80	$Si3+$	14	39.31
B^{3+}	5	148.64	\mathbf{p}^{3+}	15	40.77
\overline{C}^{3+}	6	56.18	$\overline{S^{3+}}$	16	41.06
N^{3+}	7	62.45	Cl^{3+}	17	46.53
$\overline{\mathbf{O}^{3+}}$	8	66.17	$Ar^{\overline{3+}}$	18	50.27
F^{3+}	9	74.92	K^{3+}	19	53.31
$Ne^{\overline{3+}}$	10	80.27	Ca^{3+}	20	59.00
Na^{3+}	11	85.27	Sc^{3+}	21	49.11
Mg^{3+}	12	94.68	$Ti3+$	22	35.37
AI^{3+}	13	74.22	$\overline{\mathbf{V}^{3+}}$	23	38.00

Fig. 13. Z - χ graph for +3 charged ions.

According to HSAB Theory, complexes which form with hard acid-hard base and soft acid-soft base reactions are more stable. Therefore, the hardness of the central atom in the complex in terms of complexes stability is an important parameter. In the present study, because electron configuration effect is more dominant effect than charge and radius effects, electron configuration of center atom should be considered for the formation of a stable complex. For instance, a ligand which has hard electron donor atoms forms more stable complexes with hard central atoms. Likewise, a ligand which has soft electron donor atoms forms more stable complexes with soft central atoms. So, accordance in terms of chemical hardness of ligand and central atom is very important with regard to complex stability. The selection of central atom is considerable in complexes and should be cared to electron configuration of central atom.

 It was seen from graphics related with absolute electronegativity that absolute electronegativity increases in electron configuration such as ns^1 and np^5 . An atom or ion which has one of these electron configuration reaches to full electron configuration. For this reason, electron affinity is high in these configurations. Because electron affinity is high, absolute

Table 13. Data Z^* and ω for Sulfur

Ion	Z	ω
S^+	5.80	21.87
$\overline{S^{2+}}$	6.15	73.51
$\overline{S^{3+}}$	6.50	135.27
$\overline{S^{4+}}$	6.85	141.79
$\overline{S^{5+}}$	7.20	420.32
$\overline{S^{6+}}$	11.85	176.46
$\overline{\mathbf{S}^{7+}}$	12.20	1961.21
$\overline{S^{8+}}$	12.55	2458.91
$\overline{\mathbf{S}^{9+}}$	12.90	2509.89

electronegativity increases in these configurations. For example, it can be thought that Mg^{2+} is more electronegative than Na^{2+} . But, figure 12 related with absolute electronegativity showed that Na^{2+} is more electronegative than Mg^{2+} because electron configuration of $Na²$ ends with $2p^5$.

Fig. 14 , Z - ω graph for Sulfur.

Ion	Z÷	ω
${\bf P}^+$	5.15	24.69
$\overline{\mathbf{P}^{2+}}$	5.50	59.55
$\overline{\mathbf{P}^{3+}}$	5.85	78.45
$\overline{P^{4+}}$	6.20	248.16
$\overline{\mathbf{p}^{5+}}$	10.85	131.08
$\overline{\mathbf{p}^{6+}}$	11.20	1366.89
$\overline{\mathbf{P}^{7+}}$	11.55	1774.61
P^{8+}	11.90	1861.16
$\overline{\mathbf{P}^{9+}}$	12.25	3003.17

Table 15. Data Z^* and ω for Phosphorus

Fig. 16. Z- ω graph for Phosphorus.

As shown in electrophilicity equation of Parr, electrophilicity increases when absolute electronegativity increases and chemical hardness decreases. It was seen from graphics related with electrophilicity (from figure 13 to figure 19) that electrophilicity increases such as $ns¹$ and np⁵ similarly to absolute electronegativity. Consequently, it can be said that electron configuration effect is the most important effect on chemical hardness, absolute electronegativity and electrophilicity.

CONCLUSION

In this study, effect on absolute electronegativity, chemical hardness and electrophilicity of electron configuration was examined using graphical method. It is seen from obtained results that electron configuration of any atom or atomic ion has important effect in terms of chemical hardness, electronegativity and electrophilicity of atom or ion. The hardness of the central atom in the complex in terms of complexes stability is an important parameter. Therefore, this study will provide benefit in the selection of central metal ion in synthesis of complexes.

Table 16. Z and ω values for $+1$ charged ions

Ion	Z	ω	lon	Z	ω
$He+$	2	52.29	$Na+$	11	16.30
Li^+	3	23.37	Mg^+	12	17.40
$Be+$	4	21.32	AI^+	13	11.99
B^+	5	16.59	$Si+$	14	18.31
\mathbf{C}^+	6	24.20	P^+	15	24.69
N^+	7	32.31	S^+	16	21.87
\mathbf{O}^+	8	27.62	\mathbf{CI}^+	17	31.18
F^+	9	39.10	Ar^+	18	39.64
Ne^+	10	50.38			

Fig. 17. Z- ω graph for +1 charged ions.

Fig. 18. Z- ω graph for +2 charged ions.

Table 17. Z and ω values for +2 charged ions

Ion	Ζ	ω	Ion	ັ Z	ω
$Li2+$	3	209.50	Al^{2+}	13	58.08
Be^{2+}	4	54.60	$Si2+$	14	36.21
B^{2+}	5	77.86	\mathbf{P}^{2+}	15	59.55
$\overline{\mathbf{C}^{2+}}$	6	55.55	\mathbf{S}^{2+}	16	73.51
N^{2+}	7	83.15	$CI2+$	17	63.61
$\overline{\Omega^{2+}}$	8	102.29	Ar^{2+}	18	89.13
\mathbf{F}^{2+}	9	85.99	$K^{\overline{2+}}$	19	106.13
Ne^{2+}	10	121.19	Ca^{2+}	20	25.24
Na^{2+}	11	145.18	$\overline{\text{Sc}^{2+}}$	21	29.48
Mg^{2+}	12	34.78	Ti^{2+}	22	30.30

Table 17. Z and ω values for +3 charged ions

Fig. 19. Z- ω graph for +3 charged ions.

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