The Effect of Global and Local Chemical Reactivity Descriptors in the Determination of Properties of Transition Metal Clusters

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ABSTRACT: Recently, research on material properties has got lots of attention because of their promising technological applications. In this paper, the author's focus is on the global and local chemical reactivity descriptors of some transition metal clusters. In addition, the author also include findings of chemical properties with reactivity descriptors. Furthermore, according to Thomas–Fermi approximation and from the exact formulation of Density Functional Theory by Hohenberg and Kohn's theorem, the author introduce electronegativity and the theory of hardness and softness for further investigation of chemical properties of the clusters. As a part of investigations, the author also introduce the Fukui functions with an emphasis for the determinations of chemical reactivity descriptors. All the results are obtained by theoretical investigation of electronegativity (χ), Chemical potential (μ), chemical hardness (η), and polarizability (α) of the given transition metal clusters (Cr and Mn). From the results, the author observed that the ionization potential of the clusters increases with decreasing cluster size as the clusters become more stable and tend towards chemical inertness. In conclusion, determination of the reactivity descriptors of the transition metal clusters show results that are in line with previous experimental and theoretical findings.

Keywords: Clusters ; Fukui functions; Reactivity descriptors

INTRODUCTION

The aim of the present work is to establish relations between the global and/or local chemical reactivity descriptors and basic properties of transition metal clusters. The theoretical and experimental study of the reactivity descriptors (polarizability, electronegativity, chemical hardness, chemical softness, chemical potential, and electron affinity, etc.) of materials at the cluster level is attracting the attention of researchers. The aforementioned chemical descriptors are important for understanding the size dependence of optical, electronic, and magnetic properties of small particles. The reactivity descriptors like dipole polarizability(Vivas-Reyes, R. and Aria, A.,2008; Patrick C., 2008), however, represent a suitable molecular property that can take on the role of the dielectric constant and can be measured without touching the cluster. On the one hand, the dipole polarizability comprises information on the bonding character in the cluster. Once we know the bonding character of the cluster, we can easily

determine the thermodynamic, electric, magnetic, optical and transport properties of the materials.

Nowadays, the main focus of researchers in the study of the physics of clusters of transition metals is identifying the similarities and differences between the magnetic, thermodynamic, electric, and transport properties of clusters and those of the corresponding bulk materials and this study is a part of that. One of the attractive properties of transition metal clusters comes from the fact that their properties are not only size dependent but also that size variation is non-monotonic.Moreover, this sizedependence on the properties of the transition metal clusters has many technological applications and gave big hope for futuretechnologial advancements. One can consider transition metal Cluster X_n, with *n* atoms of element *X*, which have properties between those of bulk systems and the constituent atoms (Vivas-Reyes, R. and Aria, A., 2008) .

The intrinsic properties of distinct isolated chemical species (atoms, ions, and molecules) are significant inputs for the determination of the properties of combined systems (molecules,

molecular ions), although they are in no simple sense completely sufficient. Futhermore the Classius-Mosotti relation yields information about the dielectric constant (Patrick C., 2008; Jose L. et al, 2013) of the solid-like macroscopic particle formed in the cluster. In the presence of an electric field, the neutral clusters are deflected in linear order. For instance, polarizability as one of the chemical reactivity descriptors can be one of the most important pieces of information about the nature of bonding and the geometrical structure of the neutral clusters.

Therefore electric dipolepolarizability plays a major role in both qualitative and quantitative considerations of chemical reaction paths and molecular interactions. One can consider that the role of polarizability may be used to explain the softness and hardness of base, acid, frontier orbitals, and analysis of the perturbation molecular orbital for a qualitative description. In addition, as a quantitative description, the induction energies of clusters, molecules, and atoms may be assumed to be directly proportional to the polarizabilities(Patrick C., 2008; Jose L. et al, 2013; Pratim K. et al, 2006). This implies that the polarizability of materials plays a major role in the understanding of dispersion interactions, substituent effects, and local solvation effects. Therefore, the study of global and local chemical reactivity descriptors has paramount importance in understanding the physical and chemical properties of materials based on their size. In this paper, the author will consider clusters of transition metals (Cr and Mn)and focus on the dependence of chemical reactivity descriptors on the size of the clusters and the role of chemical reactivity descriptors in the determination of physical and chemical properties of the transition metal clusters. the author will review the main physical concepts and theories underlying commonly used descriptors of chemical reactions, such as chemical hardness (softness), polarizability, chemical potential and electronegativity etc. The Fukui function can be considered the corner stone for the reactivity descriptors in the electron density theory in a similar manner as the chemical potential $\mu = \left(\frac{\partial E}{\partial N}\right)_{V(r)}$provided a ground for theoretical interpretation of the electronegativity concept. Therefore, the importance of the Fukui functions and their role in determining the region of a

molecule where it is more favorable to add or subtract an electron during a chemical reaction will be addressed.

Methods

Theoretically, global or local descriptors of chemical reactivity may be derived from the basic concepts of density functional theory. However, their explicit form depends on how the energy is defined as a function of the number of electrons. Based on the basic principle of density functional theory, it is possible to define global and local reactivity parameters that yield information about the general and specific chemical properties of a molecule. The energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), has molecular electrical transport properties. Hence, the HOMO-LUMO gap can be used to determine the global chemical reactivity descriptors of clusters like hardness, chemical potential, softness, polarizability, electronegativity, and electrophilicity index (Chattaraj P.K.et al, 2003). The global reactivity descriptors such as Chemical potential (μ), electronegativity (χ), chemical hardness (η) ,polarizability (α) and proportionality constant (K)(Chattaraj P.K.et al, 2003)are defined as:-

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{V(r)} = -\frac{1}{2}(IP + EA), \qquad (1)$$

$$\chi = -\mu, \qquad (2)$$

$$\eta = \left(\frac{\partial \mu}{\partial N}\right)_{V(r)} = \left(\frac{\partial^2 E}{\partial N^2}\right)_{V(r)} = (IP - EA) = \epsilon_{LUMO} - \epsilon_{HOMO},$$

$$(3)$$

$$\eta = \frac{1}{2}(K/\alpha)^{1/3}.$$

Where $E, N \ and \ V(r)$arethe electronic energy of the system, the number of electrons in the system, and the external potential energy of the system, respectively. While IP is the ionization energy and EA stands for the electron affinity. Ionization potential energy(IP),can be defined as the amount of energy needed to remove an electron from agiven cluster.The vertical electronic affinity of a system is calculated as $EA = E(N) - E(N + 1)$. From this expression $E(N)$ and $E(N + 1)$ are the total ground-state

energies in the neutral N and singly charged $(N + 1)$ configurations, respectively while ionization energy can be calculated through $IP = E(N - 1) - E(N)$. However, the chemical potential of the given system measures the escaping possibility of an electron and its magnitude is the negative of the Mulliken electronegativity of molecules (Jose L., 2008) while chemical hardness (η) is mathematically related to the polarizability of the molecules(Pratim K., and Paul W., 2005; Cristina C.et al,2018). In addition to μ, χ, andη, the global electrophilicity index w was investigated by Parr and it can be evaluated using the chemical potential µ and chemical hardness η(Xiaoshan, X. et al, 2011).

The outermost shell(s-shell) electrons are delocalized and they tend to significantly increase the polarizability(Alonso J.A. , 2000; Moro R. et al ,2003; Ayers, P. W. 2007). Hence the transition metal clusters are beyond their classical limit due to electronic spill out so their cluster polarizabilities are closely related to the effective radius of the cluster. Hence, electric dipole polarizability is highly sensitive to the structural geometry and delocalization of valence electrons of clusters, and it can provide valuable information on the electronic and transport properties and geometrical features of the clusters. Therefore, transition metal clusters can be considered uniform conduct spheres and have a radius of R, the polarizability of the clusters can be defined rigorously in terms of just the volume (V) of the sphere. All in all, from different theories we know that the mathematical expression of the polarizability of a classical metal sphere is:

$$\alpha = KR^3 \ or \ \alpha = \frac{3V}{4\pi}, \qquad (4)$$

where R is the Jellium cluster radius and it is defined as $R = N^{1/3}R_b$, R_b is the bulk Wigner-Seitz radius. Based on cluster radius electric dipole polarizability $\alpha = (R + a)^3$ here a is of the order of 1Å and is the spill-out distance to indicate the distance beyond the classical radius where external electric fields are screened (Lhermite J. et al, 2000). In transition metal clusters, the 4s electrons are more delocalized than the 3d electrons so they are spilling out more than the 3d electrons. Hence, the 4s electrons are primarily responsible for the

boosted polarizability [5] and shell structure effects. Therefore, from the aforementioned explanations, one can suggest that the electronic spill-out effect enhances polarizability.

According to (Xiaoshan, X. et al, 2011), the global electrophilic power of a molecule can be termed the electrophilicity index (ω). This new chemical reactivity index ascertains the stabilization in energy when the system acquires an additional electronic charge from the surrounding environment. This electrophilicity index (ω) is defined as follows(Xiaoshan, X. et al, 2011) :

$$\omega = \frac{\mu^2}{2\eta}, \qquad (5)$$

In eq.5, the electrophilicity index ω measures the susceptibility of chemical species to accept electrons. Thus, the smaller value of the electrophilicity index indicates that the value of nucleophiles is good while higher values of the electrophilicity index indicate the presence of good electrophiles(Xiaoshan, X. et al, 2011). In addition to the global chemical reactivity descriptors, it is also possible to define local chemical reactivity descriptors which can be applied to investigate the reactivity of different sites within a cluster. Based on this, the hard and soft Acid and Base principle (HSAB) has been useful to predict the reactivity of chemical systems (Debdutta C. and Pratim K., 2021; Ayers, P. W.,2007; Liu, S. B. ,2009; Ayers, P. W. and Parr, R. G., 2000; Parr, R. G. and Yang, W. , 1984); Ranajit S. et al, 2016; Ayers, P. W. ,2005). Thus, in addition to the Density Functional Theory concepts, in combination with the HSAB principle, it has been possible to identify many useful and important chemical reactivity concepts such as the Fukui Function ($f(r)$) [6]. The Fukui function is defined as(Debdutta C. and Pratim K., 2021):

$$f_k(r) = \left[\frac{\partial \rho(r)}{\partial N}\right]_{v(r)} = \left[\frac{\delta\mu}{\delta v(r)}\right]_N. \qquad (6)$$

From this mathematical relation, Fukui functions (f_k)at the site k of a molecule can be defined as the first-order differentiation of density of the electron $\rho(r)$of a system with respect to the number of electrons N at a fixed external potential $v(r)$(Domingo, L.R. and Saez, J.A., 2009). The more compact form of Fukui functions in a given

cluster with N electrons has been proposed by (Ranajit S. et al, 2016)as:

$f_k^+ = \beta_{k(}N+1) - \beta_k(N)$for the nucleophilic attack,

$f_k^- = \beta_k(N) - \beta_k(N-1)$for the electrophilic attack,   (7)

$f_k^0 = \frac{1}{2}[\beta_k(N+1) + \beta_k(N-1)]$ for the radical attack.

Where $\beta_k(N)$: The population of the electron of the atom at site k in the neutral molecule

$\beta_{k(}N+1)$: The population of the electron of the atom at the site k in the anionic molecule

$\beta_k(N-1)$: The population of the electron of the atom at site k in the cationic molecule

To identify the most electrophilic site, we can consider the product of the global electrophilic index ω and the electrophilic Fukui index f_k^+. Hence, the site is designated by (ω_k) and its quantitative value can be identified by the determination of the local electrophilic index (ω_k)(Toledo, O.R. and Contreras, R., 2014) and it is defined as:

$$\omega_k = \omega f_k^+. \qquad (8)$$

In the same way, the nucleophilic site can be located by the local nucleophilic index, N_k (Reed, A.E. and Weinhold, F., 1983) and it is a product of the global nucleophilic index N and the nucleophilic Fukui indexf_k^- :

$$N_k = \omega f_k^-. \qquad (9)$$

According to (Domingo et al.,2000) the local electrophile ω_k and local nucleophilic index N_K are well-grounded descriptors for the estimation of the most favorable nucleophilic-electrophilic interaction for the formation of a chemical bond between two atoms(Yan, W.G. and Parr, R.G., 2000). However, this chemical bond occurs between the nucleophilic site (characterized by the highest $N_K$value) of the nucleophilic cluster and the electrophilic site (characterized by the greater ω_k value) of the electrophilic cluster. By using the compact Fukui Functions $f_k^{\mp}$ and the global softness S it can be possible to evaluate the

local softness S_k(Yan, W.G. and Parr, R.G., 2000)as:

$$S_k = \left[\frac{\partial \rho}{\partial \mu}\right]_{v(r)} = \left[\frac{\partial \rho}{\partial N}\right]\left[\frac{\partial N}{\partial \mu}\right] = Sf_k \qquad (10)$$

The dense local softness's of $f_k^{\mp}$ can be determined from the expressions:

$$S_k^+ = Sf_k^+; \qquad S_K^- = Sf_k^-; \qquad S_k^0 = Sf_k^0, \qquad (11)$$

here $+, -,$ and $\mathbf{0}$ indicate a nucleophilic, electrophilic, and radical attack, respectively. Based on the rule of Gazquez-Mendez (Targema M. et al, 2013), two chemical species interact through atoms having equal or neighboring softness.

RESULTS AND DISCUSSION

In this paper, the author discuss the chemical reactivity descriptors and their effect on the basic properties of the considered materials. The author determined the chemical reactivity descriptors(ionization potential, chemical hardness and softness, electronegativity and polarizability) using the energy gap betweenthe highest occupied molecular orbital and the lowest unoccupied molecular orbital to identify the chemical and physical properties of the given clustes.

Ionization potential energy can be termed a fundamental descriptor of the chemical reactivity of atoms and clusters. Hence, high ionization potential energy leads to high stability, and chemical inertness, andsmall ionization potentialenergyindicates high reactivity of the atoms and molecules. Therefore, from **Figs.1** and **2,** It may be asserted that smaller sizes of transition metal clusters correspond to higher stability, i.e. more inert. Chemical hardness and softness are essential properties to measure the stability and reactivityof the transition metal clusters.From **fig 2&3,** it may be asserted that for smaller cluster size the chemical hardness is almost the same for the two clusters(Cr &Mn) but when the size of the clusters are increasing, the chemical hardness of the two are a bit different. In this case, our results suggest that the chemical hardness of the clusters (Azeez Y. H. & Ahmed H. S.H., 2021; Oyeneyin O. et al., 2022; Baicheng Z. etal.,2022; Ehouman A.et al., 2021) fundamentally explains the resistance towards the polarization of the electron

cloud of atoms, ions, or clusters under a small perturbation of the chemical reaction.

From this, it may be suggested that high ionization potential energy shows high stability and chemical inertness, whereas small ionization potential energy mplies high reactivity of atoms, molecules, and clusters. It is in line with the results in the literature (Azeez Y. H. & Ahmed H. S.H., 2021; Oyeneyin O. et al., 2022; Baicheng Z. etal.,2022; Ehouman A.et al., 2021).

Electric dipole polarizability is used to determine the strength of molecular interactions (bond strength) and optical properties of a system (Luca G. et al, 2002). Clusters with a low HOMO-LUMO gap, i.e., the low value of chemical hardness, are more polarizable and possess high chemical reactivity, low kinetic stability, and high electro-optic response and the cluster will be soft (Luca G. et al, 2002). In this case, we can see the effect of the medium on the electric dipole polarizability of the materials. The higher value of the medium (dielectric constant) leads to the higher value of polarizability of the system and the softness of the materials. As clearly shown by **fig.4**,when the cluster size is decreasing the polarizibility is increasing and the cluster possess high chemical reactivity and low stability and vice versa.

Electrophilicity is a descriptor of reactivity that allows a quantitative classification of the global electrophilic nature of a cluster within a relative scale (Lesar, A. and Milosev, I.,2009). According to the definition, this index measures the propensity of a chemical species to accept electrons. A good, more reactive, the nucleophile is characterized by a lower value of μ, ω, and conversely a good electrophile is characterized by a high value of μ, ω.From **Fig.5** and **6,** we infer that the nucleophile is characteristic of the smaller cluster size of transition metals, whereas the electrophile is that of a higher cluster size of the transition metals. This new reactivity index measures the stabilization in energy when the system acquires an additional electronic charge from the environment (Lee, C., Yang, W. and Paar, R. G.,1988).

The band gap (chemical hardness)can be used to characterize the chemical reactivity descriptors and kinetic stability ofthe clusters that we considered .In general, a cluster with a small orbital gap i.e, characteristic of high transition metal size (**Figs.3** and **4),** is more polarizable andis directly related to high chemical reactivity,whereasthe low kinetic stability of the cluster indicates that the cluster is soft. **Figs.3** and **4**suggest that for higher cluster sizes the chemical reactivity is also high. For these systems, the HOMO is considered an electron donor while the LUMO acts as the electron acceptor.

In this work, the author considered on the the orbitals between the HOMO and LUMO to dermine the chemical reactivity descriptors of the given clusters. Theforethe highest value of the HOMO and LUMO gap (it coincides with the enegy gap) implies that the highest stability. According to **fig2.**for small cluster sizes, the chemical hardness of the clusters becoming high(high value of the energy gap) and stability is increasing.Mimimum polarizibilty principle which states that the natural direction of evolution of any system is towards a state of minimum polarizability. Based on this, as indicated in **fig4,** for the smaller cluster sizes the energy gap is high(high chemical hardness), the mimimum polarizibility and the more stable system. These implies that for smaller claster sizes, the stablility is increasing and the more magnetizible the cluster. All in all the determination of the reactivity descriptors of the transition metal clusters show results that are in line with previous experimental and theoretical findings (Habte D. , Qinfang Z., &Baolin W. 2018) .
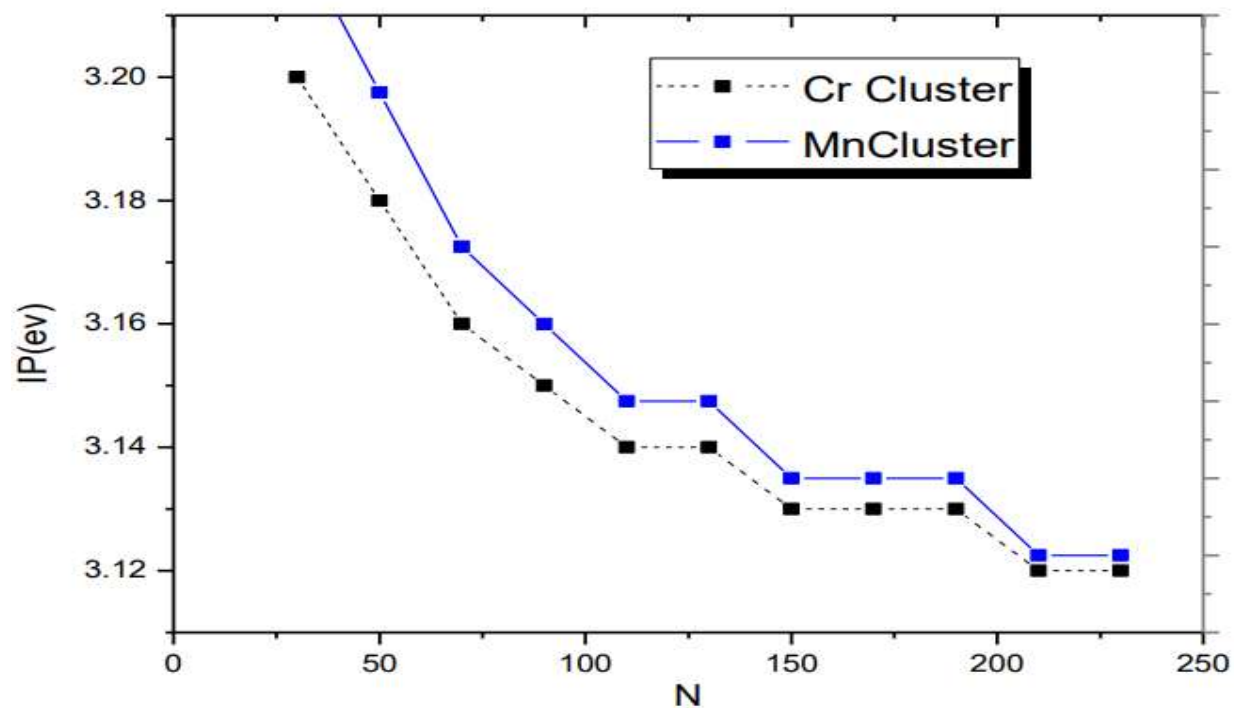
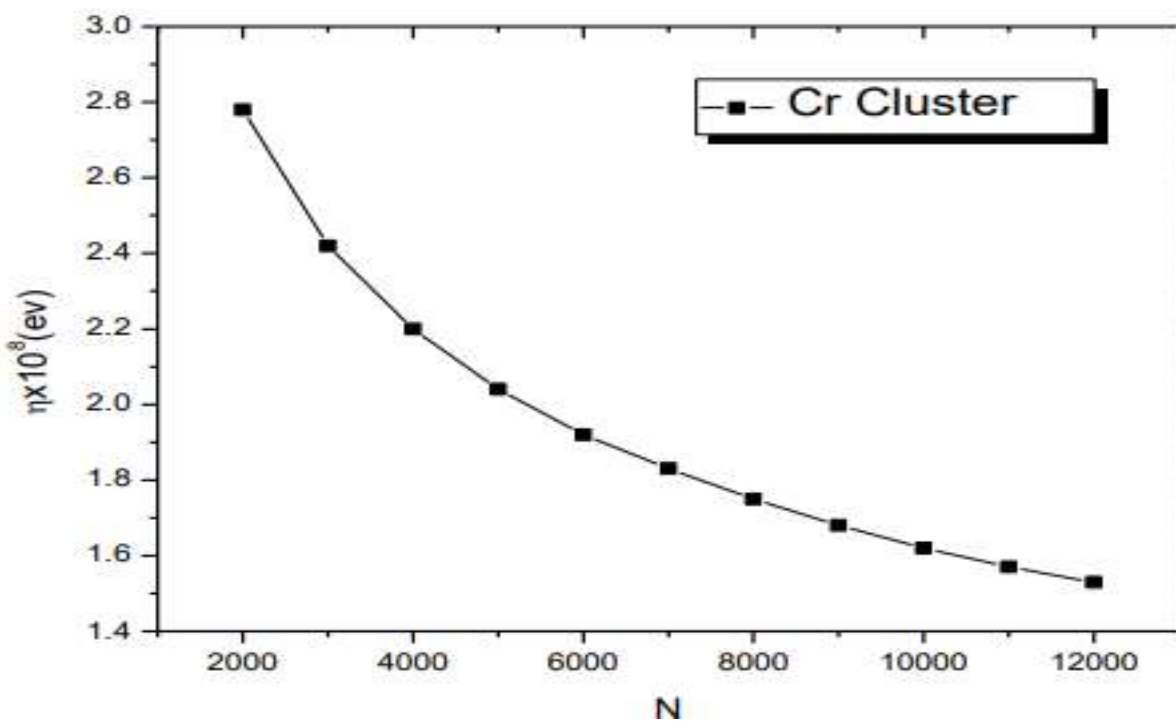**Figure1. The relationship between ionization potential (IP) and cluster size (N).**

Figure 2. The dependence of the chemical hardness of the cluster on the size of the cluster.
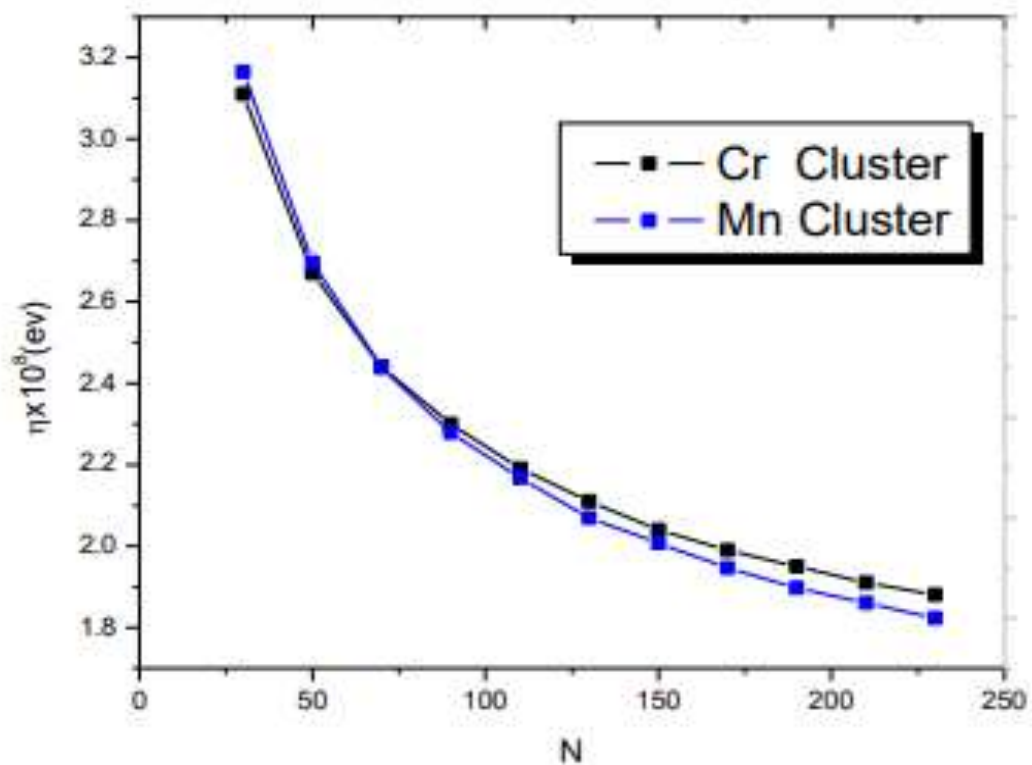
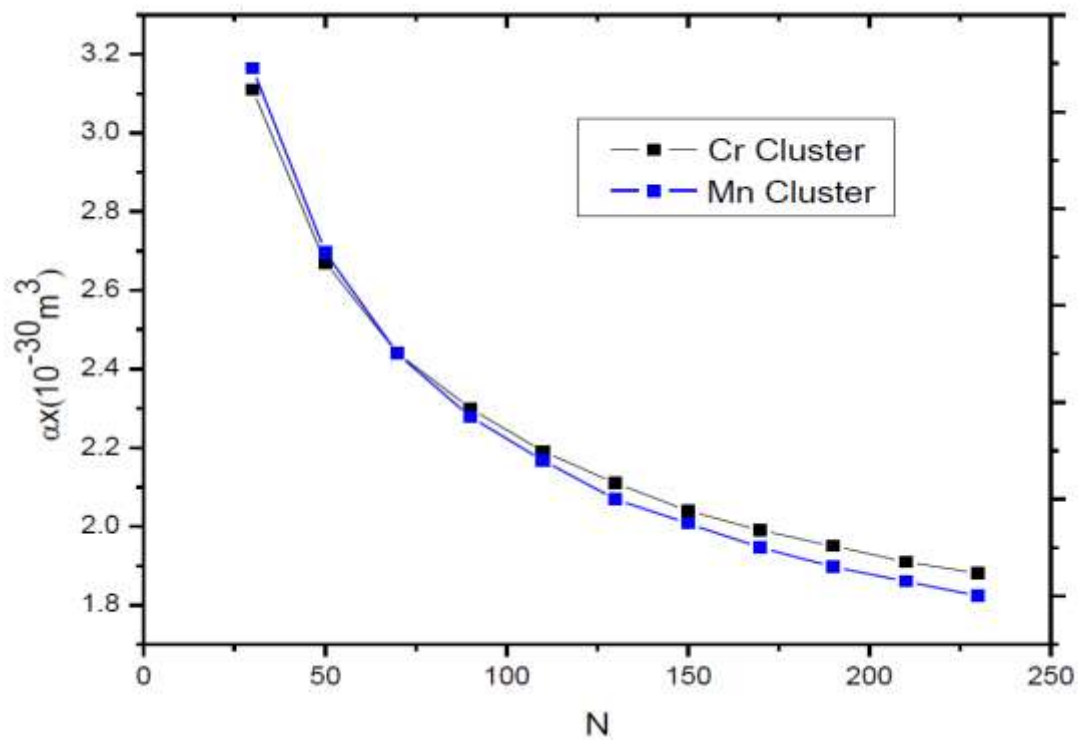**Figure 3. The dependence of chemical hardness on the cluster size (N).**

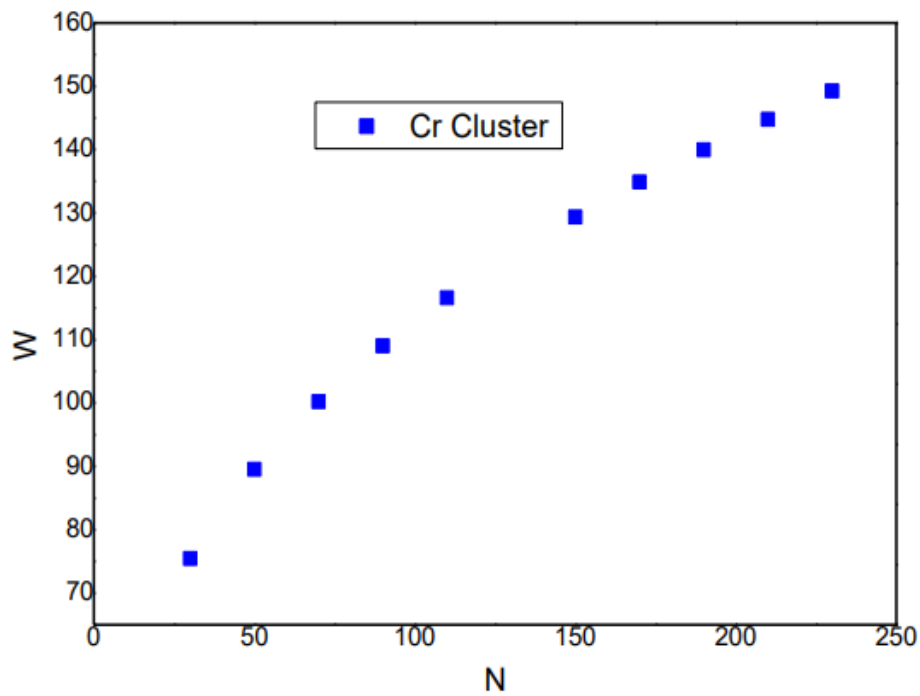**Figure 4. The dependence of polarizability on the cluster size (N).**

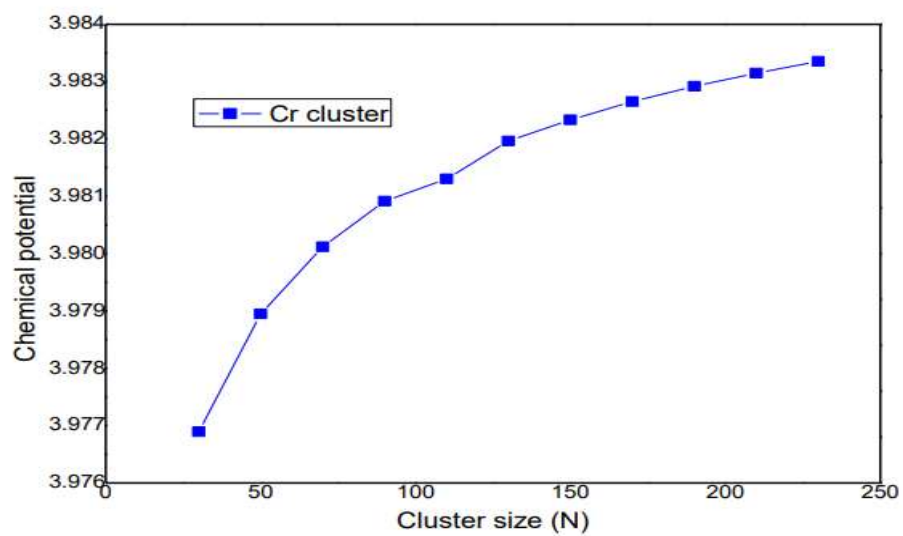Figure 5. The dependence of electrophilicity on the cluster size (N).

Figure 6. The dependence of chemical potential on the cluster size (N).

CONCLUSION

In this article, the author considered different reactivity descriptors (chemical potential, global hardness, softness, electrophilicity index, and nucleophilicity) of transition metal (Mn and Cr) clusters.

The chemical hardness (softness) value of the transition metal cluster is lesser (greater) among all clusters. Thus, such a cluster is found to be more reactive than all considered clusters. These properties of the cluster lead to a higher electronegativity value than allclustersso; it is the best electron acceptor.

Based on the analysis above, it is observed that for the low value of chemical hardness is characteristic of high cluster size of transition metal, the clusters are more polarizable and possess high chemical reactivity and kinetic stability. Furthermore, it is found that ionization potential increases with a decrease in cluster size as the clusters become more stable and chemically inert. In addition, it is found that a good and more reactive nucleophile is characterized by a lower value of chemical potential and electrophilicity index. This indicat that the smaller cluster size (a lower value of chemical potential) leads to more reactive nucleophile.

ACKNOWLEDGMENT

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