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Redox and Lewis acid–base activities through an electronegativity–hardness landscape diagram

Ranjita Das · Jean-Louis Vignerese ·
Pratim Kumar Chattaraj

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Abstract Chemistry is the science of bond making and bond breaking which requires redistribution of electron density among the reactant partners. Accordingly acid–base and redox reactions form cardinal components in all branches of chemistry, e.g., inorganic, organic, physical or biochemistry. That is the reason it forms an integral part of the undergraduate curriculum all throughout the globe. In an electronegativity (χ)–hardness (η) landscape diagram the diagonal $\chi=\eta$ line separates reducing agents from oxidizing agents as well as Lewis acids from Lewis bases. While electronegativity is related to the degree of electron transfer between two reactants, hardness is related to the resistance to that process. Accordingly the electronegativities of oxidizing agents/Lewis acids are generally greater than the corresponding hardness values and the reverse is true for reducing agents/Lewis bases. Electrophiles and nucleophiles are also expected to follow similar trends.

Keywords Conceptual density functional theory · Electrophiles · Nucleophiles · Oxidizing agent · Reducing agent · Reactivity descriptors

Introduction

As chemistry is the subject of bond-making and bond-breaking the central idea in chemical reaction is that of the transfer of electrons between chemical species either in a direct or an indirect manner. The basic chemical reactions

are redox reactions, Lewis acid–base reactions, complexation reactions, precipitation reactions etc. In this article we will emphasize on the redox activity and Lewis acid–base activity of the chemical species. The chemical species can be divided into oxidizing or reducing agents and Lewis acid or base according to their electron accepting power as well as their electron donating tendency. The general tendency of an oxidizing agent/Lewis acid is to accept electron(s) in a chemical response, whereas the reducing agent/Lewis base is prone to donate one or more electron(s).

The main idea of this article is to familiarize the reader with the redox and Lewis acid–base activities of different chemical species on the basis of two quantities viz., electronegativity (χ) [1, 2] and hardness (η) [3, 4], which have been shown to be density functional theory [5–7] based reactivity descriptors. In several previous studies [8–13] attempts are made to use reactivity descriptors as the coordinates in structure-stability diagrams and stability-reactivity landscapes. In view of the fact that it is essential for all chemical reactions to have a change in the electron density, an ideal parameter is required which should portray that.

Electronegativity can be defined as the propensity for change in electron density whereas hardness is a measure of the resistance to this change. Hence electronegativity (χ) and hardness (η) should be obvious potential choices to be used as the coordinates of a reactivity landscape. Moreover, it is shown by Parr and Pearson [3] that the amount of electron transfer and the associated stabilization (decrease in energy) not only depends on the difference in electronegativity values of the reacting partners but also on their hardness sum. A larger value of the former and a smaller value of the latter provide a better choice. Even the former dictates the direction of the electron flow. Here we will show that in the electronegativity–hardness landscape we can find a rough guide to the activity domains of both oxidizing versus reducing and Lewis acid versus base reactivity. Previously Pearson confirmed that the relative strength of Lewis

R. Das · P. K. Chattaraj (✉)
Department of Chemistry and Center for Theoretical Studies,
Indian Institute of Technology Kharagpur, Kharagpur 721302, India
e-mail: pkc@chem.iitkgp.emet.in

J.-L. Vignerese
Nancy-Université, UMR 7566 G2R, BP 23,
54501 Vandoeuvre cédex, France

acids/bases can be well justified through their absolute hardness values and absolute electronegativity values [14]. The hard acids exhibit higher values of η than that of the soft acids. The activity of some well known electrophiles and nucleophiles is also verified in electronegativity-hardness landscape.

Reducing and oxidizing agents

The oxidation-reduction concept is widely used in chemistry in analyzing a variety of chemical reactions as a part of high school as well as undergraduate chemistry curriculum [15–21]. Fundamentally, redox reactions are a group of reactions that are concerned with the transfer of electrons between species. The term comes from the two concepts of reduction and oxidation.

Reduction: Oxidant + $e^- \rightarrow$ Product

Oxidation: Reductant \rightarrow Product + e^-

In a very general approach a reducing agent loses electrons and an oxidizing agent gains electrons in a redox reaction. Oxidizing agents are typically chemical substances containing elements in relatively high oxidation states (e.g., H_2O_2 , MnO_4^- , CrO_3 , $Cr_2O_7^{2-}$, OsO_4), or highly electronegative elements (O_2 , F_2 , Cl_2 , Br_2) that can accept extra electrons. In contrast to this, chemical substances consisting of elements with low electronegativity which can easily lose an electron make good reducing agents. The simplest example of oxidation-reduction includes the formation of cations and anions from the elements. The readers are already familiar with the fact that the chemical potential is related to the degree of electron transfer and accordingly it qualitatively measures the tendency for a redox reaction to occur. The chemical potential denotes the escaping tendency of electron from a system. During a chemical change electron flows from a system with higher chemical potential to a system with lower chemical potential until the equilibrium is reached. Hence in a redox reaction the chemical potential can decide the direction of electron flow vis-à-vis recognizes the reducing agent and oxidizing agent. In the past, several scientific studies were carried out which enriched the redox chemistry. In the year 1970 M.P. Goodstein [22] gave an interpretation of the oxidation number system based on the electronegativity principle. Using this principle redox reactions are divided into three different groups [22] based on the change in the oxidation state, viz., pseudo redox reaction, very weak oxidation and strong oxidation. The approximate degree of electronegativity variation between the atoms experienced during oxidation state change differentiates the groups. The typical pseudo oxidation reactions are organic elimination reactions, photoexcitations, radiolyses, and the solution of halogens in water. In case of stronger oxidations, the electronegativity difference between atoms undergoing oxidation state change is an important factor in causing them to undergo the changes in oxidation state. For example, the electrochemical reactions and inorganic reactions

where transfer of electrons takes place belong to this type of reaction. Among the organic reactions bromine oxidation of alcohols is also a good example of strong oxidation reaction. On the other hand very weak oxidations are those in which the electronegativity difference among the atoms undergoing a change in oxidation state is a very trivial factor in causing the reactions to occur. In general, homolytic halogenation and hydrogenation reactions belong to very weak oxidation type reactions.

Lewis acid and base

Another most important class of chemical reactions is the acid–base reaction. In the year 1923 G. N. Lewis proposed a general theory to characterize a substance as acid/base according to its inherent electronic structure. In reactions between Lewis acids and bases, an adduct is formed when the highest occupied molecular orbital (HOMO) of a molecule, with available lone electron pair(s) donates the same to the electron-deficient molecule's lowest unoccupied molecular orbital (LUMO) through a co-ordinate covalent bond; in such a reaction, the HOMO-interacting molecule acts as a base, and the LUMO-interacting molecule acts as an acid. The Lewis acids are electron pair acceptors. The electron deficient compounds such as metal cations, electron deficient π systems can act as Lewis acids. Common Lewis bases, classified as electron-pair donors, include anions, species containing lone pairs of electrons or electrons, and electron rich π systems. Frequently the terms Lewis acid and base are defined within the framework of a precise chemical reaction. For example, CO acts as a Lewis base (σ -donor) but in the presence of some transition metals with low electronegativity (such as V, Fe, and Ni) CO acts as a Lewis acid, since the π -back-bonding overshadows the σ -bonding. Apart from the strength of a Lewis acid/base it may be classified as hard or soft as was suggested by Pearson [14, 23]. According to Pearson [14] the hard and soft acid and base are defined as:

“Soft base	donor atom is of high polarizability, low electronegativity, easily oxidized and associated with empty, low-lying orbitals.
Hard base	donor atom is of low polarizability, high electronegativity, hard to reduce and associated with empty orbitals of high energy and hence inaccessible.
Soft acid	the acceptor atom is of low positive charge, large size, and has several easily excited outer electrons. Polarizable.
Hard acid	the acceptor atom is of high positive charge, small size, and does not have easily excited outer electrons. Not polarizable.”

As is mentioned above, in reactions between Lewis acids and bases, an adduct is formed through a co-ordinate covalent bond,

and this is the fundamental difference between Lewis acid and base reactions and redox reactions [24]. The redox reactions focus more on physical electron transfer processes, rather than bond making/bond breaking processes, even if there is some ambiguity regarding the difference between these two processes.

Electronegativity and hardness

Popular qualitative chemical concepts like electronegativity (χ) and hardness (η) are provided with quantitative definitions within a conceptual DFT framework [2–7]. The DFT based global reactivity descriptors, i.e., electronegativity (χ) and hardness (η), are competent to provide an improved perception of chemical bonding and reactivity of molecular systems.

The concept of electronegativity was first proposed by Pauling [1]. Electronegativity was defined as the ability of an atom (or a functional group) in a molecule to attract bonded electrons (or electron density) toward itself. Afterward Mulliken [25] proposed that the arithmetic mean of the first ionization energy and the electron affinity should be used to evaluate the propensity of an atom to attract electrons.

Parr et al. [2] defined the absolute electronegativity as the negative of the chemical potential defined as the first order derivative of the energy, E , of a system with respect to the number of electrons N .

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(r)} \quad (1)$$

In the above equations μ and $v(r)$ represent the chemical and external potentials respectively. Hence if the energy of any chemical system is plotted as a function of the number of electrons, then chemical potential (negative of electronegativity) is the instantaneous slope ($\partial E/\partial N$) of the curve.

Using a finite difference approximation, Eq. (1) can be written as

$$\mu = -\chi \cong -\frac{I + A}{2} \quad (2)$$

where I and A are the ionization potential and electron affinity of the system respectively. The DFT based absolute electronegativity within the finite difference approximation is thus equal to the Mulliken electronegativity [25].

This definition of the electronegativity (χ) is independent of any arbitrary relative scale and therefore, unlike Pauling's prescription of χ is invariant with the chemical environment. So the drift of electrons during a chemical process occurs from a less electronegative center to a more electronegative center accompanied by a gradual lowering of energy of the system till the system reaches an energy minimum and there results an electronegativity equalization.

The other most important parameter is the absolute hardness (η). Parr and Pearson [4] proposed hardness as the curvature or rate of change of the slope of the E vs. N plot in a DFT framework as

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (3)$$

From the method of finite differences, the definition of hardness becomes,

$$\eta \cong \frac{I - A}{2} \quad (4)$$

We note from Eq. 1 and 3 that hardness is related to electronegativity or chemical potential through the following characteristics

$$\eta = \frac{1}{2} \left(\frac{\partial \mu}{\partial N} \right)_{v(r)} = -\frac{1}{2} \left(\frac{\partial \chi}{\partial N} \right)_{v(r)} \quad (5)$$

The terms chemical hardness and absolute hardness are often used as synonyms. The common meaning of “hardness” is resistance to deformation or change. Equation 5 demonstrates that chemical hardness is resistance of the chemical potential (μ) to alter with the number of electrons.

This notion of hardness and softness helps to rationalize a great deal of inorganic and organic chemistry.

The ionization potential, I , of an atom or a molecule is defined as the amount of energy required to remove an electron from that atom or molecule in the gas phase. More generally, the n th ionization potential is the energy required to strip off the n th electron after the first $(n-1)$ electrons are detached. The electron affinity, A , of an atom or molecule is defined as the amount of energy released when an electron is added to a neutral atom or a molecule to form a negative ion (for general definitions see Eqs. 6 and 7).

The ionization potential, I , and electron affinity, A , are computed using the energies of the N -electron system with energy $E(N)$. They may be expressed as follow:

$$I = E(N-1) - E(N), \quad (6)$$

$$A = E(N) - E(N+1) \quad (7)$$

The ionization potential (I) and the electron affinity (A) are also calculated with the help of Koopmans' theorem [26] in terms of the appropriate frontier orbital energies:

$$I = -\varepsilon_{HOMO} ; A = -\varepsilon_{LUMO}, \quad (8)$$

where ε_{HOMO} and ε_{LUMO} are the energies of the highest occupied and lowest unoccupied molecular orbitals, respectively.

Needless to mention that it is less accurate than that given by Eqs. 6 and 7.

For a stable system or a favorable path of a physico – chemical process hardness frequently gets maximized. A maximum hardness principle (MHP) [27–30] is shown to be valid under the conditions of constant chemical and external potentials. Further Pearson also discussed the validity of a principle of maximum physical hardness [31] (PMPH). The PMPH deals with the resistance of a solid to change its shape. Chemical periodicity [32] and aromaticity [33] can also be explained through the use of MHP.

Computation

In this article the redox activity of some familiar reducing and oxidizing agents (Table 1) are revisited within an electronegativity-hardness landscape. The redox behavior of some atoms and their cations, dications, anions and dianions are analyzed. Some well known acids and bases (Table 2) are checked for their Lewis acid–base activity within the electronegativity-hardness landscape. The optimization of reducing agents and oxidizing agents; the Lewis acids and bases as well as the electrophiles and nucleophiles (Table 3) are performed at the B3LYP/6-311++G(d, p) level by using the Gaussian 09 program [34]. The atoms and their ions are optimized at the B3LYP/6-311+G(d) level by using the Gaussian 09 program [34]. The ionization potential and electron affinity are calculated using the Eqs. 6 and 7 respectively.

Results and discussion

Redox activity

The reducing agents generally possess low electronegativity values. The electron transfer is hindered by hardness. This fact is portrayed in Fig. 1. The reducing agents exhibit lower electronegativity value compared to that of the oxidizing agents and mostly appear at the lower part (below the diagonal line) of the electronegativity(χ)-hardness(η) landscape. In contrast to this, the oxidizing agents with a tendency to take an electron exhibit a higher electronegativity, compared to that

Table 2 List of selected Lewis acids and bases

Lewis acids	Lewis bases
BH ₃ , BF ₃ , BCl ₃ , BBr ₃ , AlH ₃ , AlCl ₃ , Al(CH ₃) ₃ , B(CH ₃) ₃ , Be(CH ₃) ₂ , SO ₃ ,	N ₂ , N ₂ H ₄ , CO, H ₂ O, NH ₃ , CH ₃ NH ₂ , (CH ₃) ₂ O, CH ₃ OH, C ₆ H ₆

of reducing agents. Hence they are in the upper part of the χ - η landscape. This difference in electronegativity makes it possible to draw a line, with the points having $\chi=\eta$ values, to place the reducing agents and the oxidizing agents in two separate domains. The reducing and oxidizing agents are in fact separated by a line with points having the same ($I+A$) and ($I-A$) values. Hence the systems having negligible A values (almost $A=0$) will appear on this line. The systems with negative A (electron affinity) value will appear below the $A=0$ line, i.e., upon addition of an electron the corresponding anion becomes energetically less stable than the neutral species. On the other hand the systems with a positive A value will appear above the $A=0$ line. Hence for these systems, upon addition of electron the resulting anions are energetically more stable than the neutral systems. It appears that A can roughly dictate the electron accepting/donating tendency of a system. Since η is always positive due to the convexity of the E vs N curve [5] and I is generally greater than A and hence positive (to give $\eta>0$ as well as the fact that the ejection of electrons overcoming nuclear attraction requires energy), a comparison of χ and η depends solely on the sign of A . Cations would like to attract electrons so that it gets stabilized due to additional coulomb attraction ($A>0$) the reverse happens in the case of anions. Moreover the magnitude of A of a cation is roughly equal to I of the corresponding neutral atom. The reducing agents (mostly have negative A value) appear below the $\chi=\eta$ line ($(\chi/\eta)<1$ zone) with some exceptions, whereas the oxidizing agents (mostly have positive A value) emerge above the line ($(\chi/\eta)>1$ zone). In this figure H₂O₂ which can act as both oxidizing agent and reducing agent appears in the $\chi<\eta$ zone ($(\chi/\eta)<1$ zone). The anionic systems like SO₄²⁻, CrO₄²⁻, ClO₃²⁻, due to the presence of negative charge show less electronegativity, and appear close to the $\chi=\eta$ line. In both CrO₂Cl₂ and CrO₄²⁻ the Cr center is in +6 oxidation state, but due to the presence of negative charge CrO₄²⁻ (less electronegative) is a weaker oxidizing agent than neutral CrO₂Cl₂. It is observed that the stronger oxidizing agent, CrO₂Cl₂ appears above the K₂CrO₄ in the χ - η landscape.

Atoms and ions

In general it is known that the atoms with large atomic radius have a propensity to be a better reductant. The atom with large atomic radius will have a low ionization potential and low

Table 1 List of selected oxidizing and reducing agents

Oxidizing agents	Reducing agents
O ₂ , F ₂ , Cl ₂ , Br ₂ , I ₂ , HNO ₃ , H ₂ O ₂ , KMnO ₄ , LiClO ₃ , H ₂ SO ₄ , CrO ₂ Cl ₂ , K ₂ CrO ₄ , NaClO ₃	C ₂ H ₂ O ₄ , HCOOH, C ₆ H ₈ O ₆ , Hydrazine, Dithiothreitol, Diisobutylaluminium hydride, Phosphorous acid, 2-Mercaptoethanol, diborane, CH ₃ MgBr, n-BuLi

Table 3 List of selected electrophiles and nucleophiles

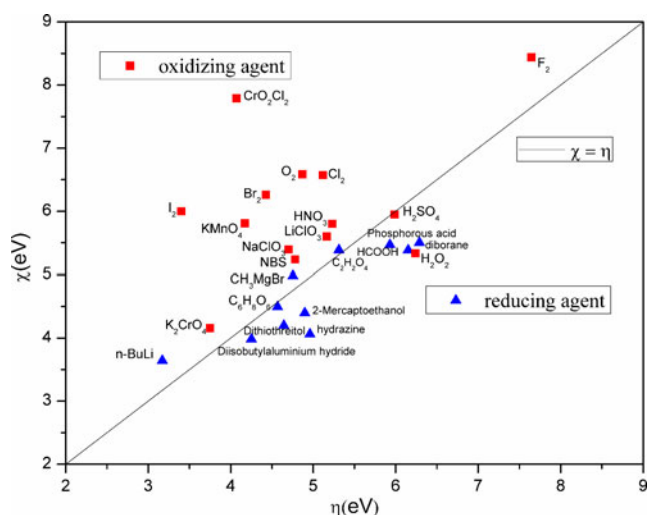
Electrophiles	Moderate electrophiles	Nucleophiles
1,1-dicyanoethylene; acrolein; acrylonitrile; maleic anhydride; methyl acrylate; methyl propiolate; methyl vinyl ketone; nitroethylene; tetracyanoethylene	1 acetoxyl 1,3 butadiene; 1,3 butadiene; 2 methyl 1,3 butadiene; 1,3 pentadiene (E); 4 methyl 1,3 pentadiene; cyclopentadiene	1-methoxy-1 3-butadiene; ethylene; furan; acetylene; 2 methyl furan; methyl vinyl ether; pyrrole; dimethyl vinyl amine

electronegativity, hence they can lose electron easily in a redox reaction than the atoms with higher electronegativity. Now on going from Li to Ne in the periodic table, the atomic radius gradually decreases, due to the change in effective nuclear charge and consequent orbital energy change, making the loss of an electron difficult in redox reactions. Hence the atoms with low I value and less electronegativity (χ) will act as reducing agents, while the atoms with high value of I and χ are expected to act as oxidizing agents. In Fig. 2 it can be seen that the atoms likely to act as reducing agents (like Li, Be, B, C) appear either in $\chi < \eta$ zone ($(\chi/\eta) < 1$ zone) or just on the $\chi = \eta$ line, in contrast to this the atoms with high electronegativity value are in the oxidizing zone, i.e., $\chi > \eta$ zone ($(\chi/\eta) > 1$ zone), which is expected. The Ne atom exhibits a high η value, which implies that Ne atom is stable and unwilling to take part in reaction. Now the cations and dications due to high electronegativity values appear as oxidizing agents (positioned above the separating line). It is observed that the cations/dications of more electronegative atoms are better oxidants than the cations of less electronegative atoms as the former appear in the higher zone than the latter in the corresponding $\chi - \eta$ landscape (Fig. 2). The Li^+ ion and Be^{2+} ion due to the closed shell structure have very high value of ionization potential. They also exhibit very high hardness values and suggest that they are reluctant to take part in any further reaction. In contrast to this the anions and dianions due to the presence of negative charge are liable to give away the electron in a redox reaction and act as reducing

agents. These anions and dianions are found in the $\chi < \eta$ zone (reducing zone) of the landscape. It is observed that the anions and dianions of more electronegative atoms (N, O, F) exhibit higher hardness compared to the rest implying the stability of the former. Hence it can be said that the anions and dianions of less electronegative atoms are expected to act as stronger reducing agents.

Lewis acid–base activity

Here some well known neutral strong Lewis acids and bases are studied. The Lewis acids are characterized by their electron deficient nature. Hence the Lewis acids are expected to have a tendency to accept electrons and to exhibit high electronegativity values. The Lewis bases are the electron rich species with a well localized HOMO. Hence the Lewis bases are expected to donate electrons easily to a Lewis acid in a Lewis acid–base reaction. In Lewis acid and base reactions, the highest occupied molecular orbital (HOMO) of a base molecule, overlaps with the lowest unoccupied molecular orbital (LUMO) of the acid molecule. The Lewis bases are the atomic or molecular species with a comparatively low electronegativity. Figure 3 shows that the Lewis bases (negative A value in most cases) with a low electronegativity appear in the $\chi < \eta$ zone ($(\chi/\eta) < 1$ zone) of the $\chi - \eta$ landscape (with some exceptions), just like the reducing agents. Whereas, most of the Lewis acids just like the oxidizing agents appear in the $\chi > \eta$ zone ($(\chi/\eta) > 1$ zone) of the $\chi - \eta$ landscape. Now some facts can be explained through this diagram. The acid strength order of boron trihalides are $\text{BF}_3 < \text{BCl}_3 < \text{BBR}_3$, is well justified by the $\chi - \eta$ landscape diagram. We can see that due to lower electronegativity value compared to high value of hardness BF_3 appears in the $\chi < \eta$ zone, implying a weak Lewis acid activity whereas BCl_3 is positioned just on the $\chi = \eta$ line due to comparable electronegativity and hardness values and finally BBR_3 (more electron deficient), due to higher electronegativity value compared to the corresponding hardness parameter appears in the $\chi > \eta$ zone ($(\chi/\eta) > 1$ zone) of the $\chi - \eta$ landscape, suggesting it to be a strong Lewis acid. In a previous study Pearson [14] mentioned that CO and N_2 exhibit very high hardness values, which is consistent with the low reactivity of these molecules. Pearson also points out that in presence of some transition metals with low electronegativity (such as V, Fe, and Ni) CO act as a Lewis acid, since the π -back-bonding outweighs the σ -bonding.

**Fig. 1** χ vs η plot of selected oxidizing and reducing agents

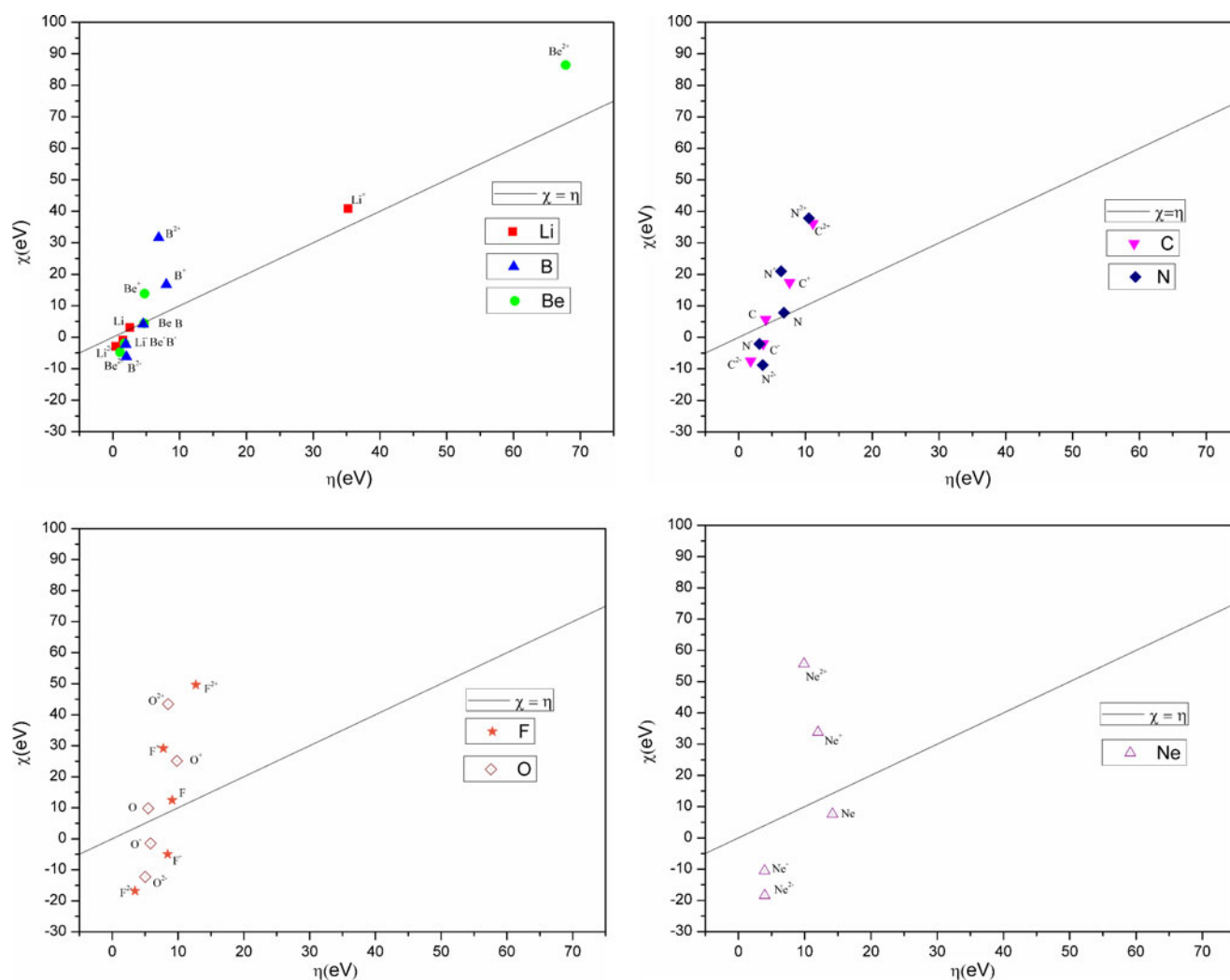


Fig. 2 χ vs η plot of selected atoms and their cations, dications, anions and dianions

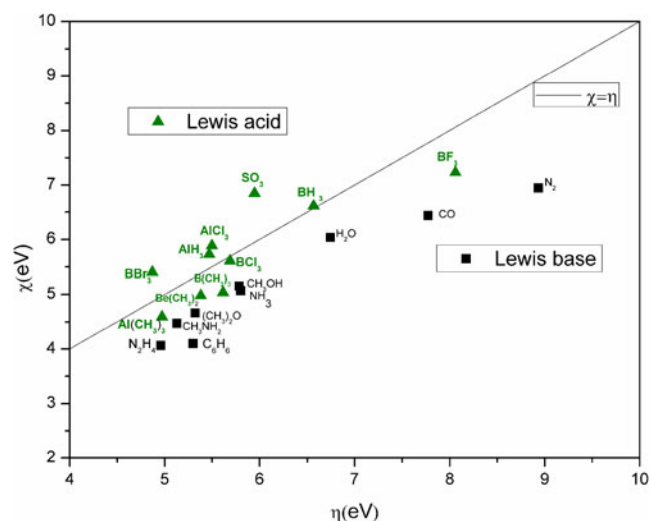


Fig. 3 χ vs η plot of selected Lewis acids and bases

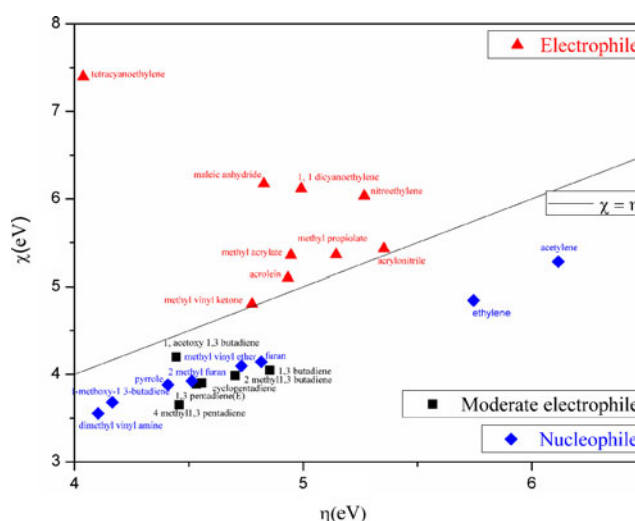


Fig. 4 χ vs η plot of some selected electrophiles and nucleophiles

Electrophiles and nucleophiles

In general, an electrophile is a reagent attracted to electrons that participates in a chemical reaction by accepting an electron pair. Mainly electrophiles are positively charged, have an atom that carries a partial positive charge, or have an atom that does not have an octet of electrons. Here we have studied some electrophiles and nucleophiles (Table 3). The nucleophiles are electron rich species that donate an electron pair to form bonds with the electrophiles (electron poor elements). Mostly molecules or ions with a free pair of electrons or π bond can act as nucleophiles. Figure 4 shows that the electrophiles appear in the $(\chi/\eta) > 1$ zone. On the other hand the nucleophiles appear in the $(\chi/\eta) < 1$ zone in most cases. There is another set of points, i.e., the black points, appear in the $(\chi/\eta) < 1$ zone. According to Domingo et al. [35] these systems are moderate electrophiles but the points appear in the same zone as that of the nucleophiles. During reactions with stronger electrophiles the moderate electrophiles do behave [35] like nucleophiles.

Conclusions

Conceptual density functional theory based reactivity descriptors, electronegativity and hardness are used to construct a landscape diagram. Redox and Lewis acid–base activities can be analyzed in terms of the $\chi = \eta$ line. The reducing agents are generally found in the $(\chi/\eta) < 1$ zone while most of the oxidizing agents appear in the $(\chi/\eta) > 1$ zone. The $\chi - \eta$ landscape can elucidate the redox activity of the atoms and their cations, dications, anions, and dianions. It can also be used to differentiate the Lewis acids from Lewis bases. The Lewis acids are shown to appear in the $(\chi/\eta) > 1$ zone whereas the Lewis bases appear in the $(\chi/\eta) < 1$ zone in most cases. Electrophiles and nucleophiles also lie in the $(\chi/\eta) > 1$ and the $(\chi/\eta) < 1$ zones respectively.

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