

The Use of Electronegativity and Hardness Towards Understanding Pearson's Hard-Soft Acid-Base Principle

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The advent of Density Functional Theory [DFT] realises the two new concepts namely electronegativity χ and hardness η . These two parameters have been very useful in understanding the insight of atoms, molecules, ions in isolated system, which are further extended to study the chemical reactions, namely double displacement reactions. These reactions were categorised on the basis of Pearson's HSAB principle which indicates that hard-hard and soft-soft interactions are preferable to hard-soft interaction. The present work is devoted to some reactions and their feasibility on the basis of change in hardness ($\Delta\eta$) and change in electronegativity ($\Delta\chi$).

INTRODUCTION

The intrinsic properties of isolated chemical species (atoms, ions, molecules) are significant input for the determination of the properties of combined systems. Though, they are in a no simple sense, completely sufficient.

One atomic parameter has been of great use in chemistry, namely, the electronegativity (χ_s) obtained approximately from experimental ionization potential (I) and electron affinity (A)

$$\chi_s = 1/2 (I_s + A_s) \quad (1)$$

This has been, theoretically, reached to the exactness through Density Functional theory (DFT),¹ in the form

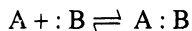
$$\chi = (\partial E / \partial N)_v = -\mu \quad (2)$$

Where E is the electronic energy, N is the number of electron transferred and 'v' is the nuclear potential. In fact the advent of DFT realises the two new concepts^{2,3} namely electronegativity (χ) and hardness (η). The parameter absolute hardness (η) which takes the form,

$$\eta = 1/2 (\partial^2 E / \partial N^2)_v = 1/2 (\partial \chi / \partial N)_v \quad (3)$$

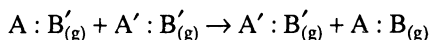
has been very useful in chemistry. The reasons for its usefulness lies in a way that earlier Pearson⁴ adopted the generalized acid-base view of chemistry introduced by Lewis

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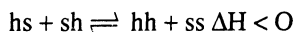


Where A is electron acceptor and B is electron donor, which could not be quantified.

Pearson^{4,5} used the actual experimental data to exchange reaction such as,



If other bond-determining factors are constant, the reaction will be exothermic. If A' is softer than A and B' is softer than B. This may be re-stated as,



So, the density functional theory confirms and amplifies the reasons for HSAB^{5,6} principle. Soft acid and bases form covalent bonds stabilized by mutual polarization including hyper-conjugation. Hard acids and bases form ionic bonds.

Recently, Datta and Singh⁷ used the concepts of chemical hardness and dissociative (heterolytic) Pauling's bond-energy equation to study the exothermicity and endothermicity of the exchange reactions (neutral molecules and molecular species) on the basis of γ -parameter, given as

$$D(A^+B^-) - 1/2[D(A^+A^-) + D(B^+B^-)] = 2|\Delta\gamma|^2$$

for hard-hard and soft-soft interaction. These workers have successfully made the universal scale of γ -parameters for most of atomic and molecular ionic species. Most of the reactions (*ca.* 255) of double-displacement nature have been explained and are given in Tables 1 and 2.

TABLE-1
EXPERIMENTAL IONIZATION POTENTIAL AND ELECTRON AFFINITIES OF THE
VARIOUS ATOMS AND RADICALS USED IN THE PRESENT STUDY^a

Atom/radicals	i.p.	e.a.	n
H	13.60	0.75	6.43
Li	5.39	0.62	2.39
F	17.42	3.40	7.01
Na	5.14	0.55	2.30
Cl	13.01	3.62	4.70
K	4.34	0.50	1.92
Cu	7.73	1.23	3.25
Br	11.84	3.36	4.24
Rb	4.18	0.49	1.85
I	10.45	3.06	3.70
Cs	3.85	0.47	1.71
SiH ₃	8.14	1.41	3.37
NO ₂	9.78	2.38	3.70

a. Taken from reference 10.

TABLE-2
EXCHANGE REACTIONS OF THE TYPE AB + CD → AD + BC (Ref. No. 7)

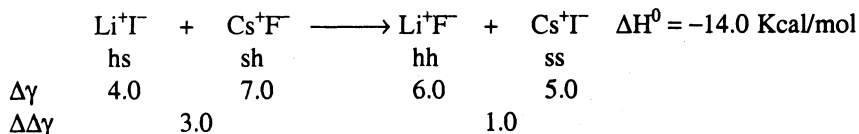
Reaction	ΔH^0 (k cal mol ⁻¹) ^a	$\Delta\Delta\gamma$ /LHS	$\Delta\Delta\gamma$ /RHS
1. LiI + CsF → LiF + CsI 4.0 7.0 6.0 5.0	-14.0	3.0	1.0
2. CuCl + IF → CuF + ICl 5.5 5.0 6.5 4.5	15.7	0.5	2.0
3. SiH ₃ + CH ₃ F → SiH ₃ + CH ₃ Cl 3.5 6.5 4.5 3.0	-20.0	3.0	1.5
4. CH ₃ F + HNO ₂ → CH ₃ NO ₂ + HF 6.5 5.5 10.0 2.0	19.3	1.0	8.0
5. CsF + HI → CsI + HF 7.0 0.0 5.0 2.0	-24.6	7.0	3.0

a. Taken From Reference 7.

In the present work, the author has taken same reactions as given by Datta and Singh⁷, and studied them and characterize the hard-hard, soft-soft interactions on the basis of absolute hardness.

RESULT AND DISCUSSION

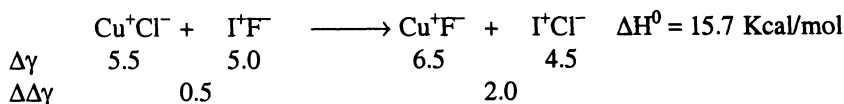
The preliminary reaction studied earlier, is as follows



so

$$\Delta\Delta\gamma_{\text{L.H.S.}} > \Delta\Delta\gamma_{\text{R.H.S.}}$$

hence the reaction will go in forward direction. Another reaction



since $\Delta\Delta\gamma_{\text{L.H.S.}} < \Delta\Delta\gamma_{\text{R.H.S.}}$, hence the reaction will go in the backward direction.

There are certain exceptions where $\Delta\gamma$ -scale does not match the experimental findings. The reasons are obvious, being, polarization, steric repulsions are not taken into account.

If the hardness parameter is taken as the fundamental tool for the molecular reactions, most of the ambiguities are removed. The results of the present study are given in Table 3. It can be seen from the table, that all the reactions explain their feasibility on the basis of change in hardness on reactant side and the product side.

Recently Sekhon⁸ used the electronegativity equalisation concept to study HSAB principle through protonated and double-displacement reactions. Some of

his results are listed in Table 4. He used Bratch method to calculate. Values for molecules, as

$$\chi_{eq} = \frac{N + q}{\Sigma(v/\chi)} \quad (4)$$

Where $N = \Sigma v =$ the number of atoms in the species formula q is the charge of the species and χ is the Pauling electronegativity as determined by Allred and Rochow.⁹ We have applied our concept of change in hardness to these reactions and it is interesting to note that it testifies the HSAB principle successfully¹⁰.

TABLE-3
EXCHANGE REACTIONS OF THE TYPE $AB + CD \rightarrow AD + BC^b$

Reactions	ΔH^{0a} (k cal mol) ^a	L.H.S ($\Delta\eta$)	R.H.S. ($\Delta\eta$)
CsCl + KI \rightarrow CsI + KCl	0.99	0.865	0.869
CuF + ICl \rightarrow CuCl + IF	-15.70	0.381	0.411
CsBr + KCl \rightarrow CsCl + KBr	6.00	0.902	0.812
C ₂ H ₅ F + CsI \rightarrow C ₂ H ₅ I + CsF	14.30	0.705	0.635
CsF + RbH \rightarrow CsH + RbF	0.00	0.723	0.723
LiF + HBr \rightarrow LiBr + HF	-14.40	0.413	0.449
*CH ₃ F + HNO ₂ \rightarrow CH ₃ NO ₂ + HF	-7.60	0.270	0.198
*SiH ₃ H + HI \rightarrow SiH ₃ I + HH	-14.50	0.143	0.119

(a) Taken from reference 7. (b) The present work.

*Reactions are not occurring according to the theory.

TABLE-4
 X_{eq} AND ΔX_{eq} . VALUES FOR EXCHANGE REACTIONS OF THE TYPE
 $AB + CD \rightarrow AD + BC$

Reaction	ΔH^0 (K Cal/mol) ^a	$\Delta\chi_{eq}$ (RHS) ($\Delta\eta_{eq}$ (RHS) ^b)	$\Delta\chi$ (LHS) ($\Delta\eta_{eq}$ (LHS))
LiF + HI \rightarrow LiI + HF 1.5727 2.4082 1.4323 2.8390	-10.6	1.4070 (7.3500)	0.8355 (0.7300)
LiCl + NaF \rightarrow LiF + NaCl 1.4960 1.5145 1.5727 1.4370	-9.5	0.1357 (2.4000)	0.0185 (2.2200)
CsF + HCl \rightarrow CsCl + HF 1.3183 2.5940 1.2640 2.8390	-16.7	1.5750 (7.0300)	1.2757 (2.4100)
HI + NaF \rightarrow HF + NaI 2.4082 1.5145 2.8390 1.3782	-23.4	1.4610 (7.4400)	0.8937 (0.8200)
LiI + CsF \rightarrow LiF + CsI 1.4323 1.3183 1.5287 1.2182	-14.0	0.3045 (3.9900)	0.1140 (2.6300)

(a) Taken from reference 7. (b) Values in parantheses are from the present work.

Conclusion

The usefulness of the absolute electronegativity and absolute hardness are the essential parameters to understand HSAB principle specifically the insight of electronic structure of atom, molecules and their ionic species. Since these form the basis for any reaction and assigning the feasibility of the reactions. It has got vast application in organic reactions and synthesis. Further, the clear picture will emerge when in each atomic species, the charges are calculated and then collectively used for the χ and η values.

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REFERENCES

1. R.G. Parr and W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York (1989).
2. R.G. Parr, R.A. Donnelly, M. Levy and W.E. Palke, *J. Chem. Phys.*, **68**, 3801 (1976).
3. R.G. Parr and R.G. Pearson, *J. Am. Chem. Soc.*, **107**, 6811 (1983).
4. R.G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
5. R.G. Pearson, *Proc. Natl. Acad. Sci.*, **83**, 8440 (1986).
6. G. Klopman, *J. Am. Chem. Soc.*, **90**, 223 (1968).
7. D. Datta and S.N. Singh, *J. Chem. Soc. Dalton Trans.*, 1541 (1991).
8. B.S. Sekhon, *Proc. Natl. Acad. Sci. (India)*, **66(A)**, 111 (1996).
9. A. Allred and F.G. Rochow, *J. Inorg. Nucl. Chem.*, **5**, 264 (1958).
10. R.G. Pearson, *Inorg. Chem.*, **27**, 734 (1988).

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