

HARD SOFT ACID BASE THEORY (HSAB THEORY) OF RALPH PEARSON

Chemistry

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KEYWORDS

Acid base was explained for a long time using the Lewis theory. It explained the donation of a proton or receiving of a pair of electrons. This sharing of electrons was more an electrostatic phenomenon. However, the extent of stability of the reaction was not known. The dilute acid was used for titration purposes in acid base titration. The classification of substances as hard acid and soft acid was possible with the help of the theory of hard and soft principle given by Ralph Pearson in the year 1960. The Hard Soft Acid Base (HSAB theory) is an initialism for 'hard and soft (Lewis) acids and bases. It is known as Pearson acid base concept. It is widely used in Chemistry for explaining stability of compound, reaction mechanisms and pathways. It is useful in relative ordering of ligands and transition metal ions in terms of their hardness and softness. HSAB theory is also useful in predicting the products of metathesis reactions. In the year 2005, it was shown that even the sensitivity and performance of explosive materials can be explained on the basis of HSAB theory. Person worked with Fred Bosolo in writing extensively on In organic chemical reactions. Theory: The HSAB theory states that soft acids react faster and form stronger bonds with soft bases, where as hard acids react faster and form stronger bonds with hard bases, all other factors being equal. The classification in the original work was mostly based on equilibrium constants for reaction of two Lewis bases competing for a Lewis acid. Theory is used in contexts where a qualitative, rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions. Ralph Pearson introduced HSAB principle in the early 1960's as an attempt to unify inorganic and organic reaction chemistry.

HSAB assigns the terms 'hard' or 'soft' and 'acid' or 'base' to chemical species. 'Hard' applies to species that are small and they have high charge states (the charge criterion applies mainly to acids, to a lesser extent to bases) and they are weakly polarizable. The Figure No.1 shows hard-soft trends for bases and Figure No. 2 shows the hard-soft trends for acids.

Hard-soft trends for bases

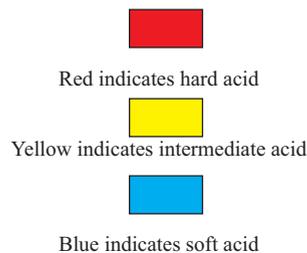
O and F are hard base- indicated by red colour			
N, S and Cl are intermediate -indicated by Yellow colour			
P,As,Se,Br,Sb,Te and I are soft Bases indicated by blue colour			
C	N	O	F
P	S	Cl	
As	Se	Br	
Sb	Te	I	

FIGURE NO.1 Showing Hard-Soft Trends for Bases

'Soft' applies to species that are big and they have low charge states and they are strongly polarizable. Hard acids and hard

bases tend to have the following characteristics: Small atomic/ionic radius, High oxidation state, Low polarizability, High electronegativity (bases), Hard bases have highest-occupied molecular orbitals (HOMO) of low energy, and hard acids have lowest-occupied molecular orbitals (LUMO) of high energy.

Examples of hard acids are H^+ , light alkali ions (Li through K all have small ionic radius), Ti^{4+} , Cr^{3+} , Cr^{6+} , BF_3 . Examples of hard bases are: OH^- , F^- , Cl^- , NH_3 , CH_3COO^- , CO_3^{2-} . The affinity of hard acids and hard bases for each other is mainly ionic in nature. Hard-soft trends for acids.



H																
Li	Be											Al	Si			
Na	Mg	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As		
K	Ca	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb		
Rb	Sr	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi		
Cs	Ba															

FIGURE NO. 2 Showing Hard-Soft Trends for Acids

Examples of soft acids are: CH_3Hg^+ , Pt^{2+} , Pd^{2+} , Ag^+ , Au^+ , Hg_2^{2+} , Hg_2^{2+} , Cd^{2+} , BH_3 . Examples of soft bases are: H^- , R_3P , SCN^- , I^- . The affinity of soft acids and bases for each other is mainly covalent in nature. The electrostatic forces of attraction shows a definite orientation towards the charge. The charge density is relatively high due to the covalent bonding. This could be indicated by the study of the dipole moment of the substances under consideration. There are border line acids such as trimethylborane, sulfur dioxide and ferrous Fe^{3+} , cobalt Co^{2+} . Chemical hardness: Examples of soft acids are: CH_3Hg^+ , Pt^{2+} , Pd^{2+} , Ag^+ , Au^+ , Hg_2^{2+} , Hg_2^{2+} , Cd^{2+} , BH_3 .

Examples of soft bases are: H^- , R_3P , SCN^- , I^- .

The affinity of soft acids and bases for each other is mainly covalent in nature.

Table No. 1 Showing hard and soft acids

Acids	
Hard	Soft
Hydronium H_3O^+ CH_3Hg^+ , Hg_2^{2+}	Mercury
Alkali metals Li^+ , Na^+ , K^+	Platinum Pt^{2+}
Titanium Ti^{4+}	Palladium Pd^{2+}
Chromium Cr^{3+} , Cr^{6+}	Silver Ag^+
Boron trifluoride BF_3	Borane BH_3
Cabocation R_3C^+	P-Chloranil
Lanthanides Ln^{3+}	bulk Metals M^0
Gold Au^+	

The chemical reactions of the carbon with the hard acids forms important organic reactions in chemistry such as Alkylation, Friedel Craft reaction, Carbocation etc. These are mostly addition reactions. The soft acids have become the catalyst in some of the chemical reactions. It is hard and difficult for the soft acids to react with any chemical under the standard temperature and pressure conditions.

TABLE NO. 2 Showing Hard And Soft Bases

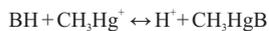
Bases		
Hard		Soft
Hydroxide	OH ⁻	Hydride H ⁻
Alkoxide	RO ⁻	Thiolate RS ⁻
Halogens	F ⁻ , Cl ⁻	Halogens I ⁻
Ammonia	NH ₃	Phosphine PR ₃
Carboxylate	CH ₃ COO ⁻	Thiocyanate SCN ⁻
Carbonate	CO ₃ ²⁻	Carbon monoxide CO
Hydrazine	N ₂ H ₄	Benzene C ₆ H ₆

There are borderline acids and borderline bases that help in the transformation of the chemicals. The identified borderline acids are trimethylborane, sulfur dioxide, and ferrous Fe²⁺, Cobalt Co²⁺, Caesium Cs⁺ and Lead Pb²⁺ cations. Borderline bases are:

aniline, pyridine, nitrogen N₂ and the azide, chloride, bromide, nitrate and sulfate anions. In the Table No. 1 listing of the hard and soft acids are presented.

In the Table No.2 listing of hard and soft bases are presented. Acids and bases interact and most of the stable interactions are hard-hard (ionogenic character) and soft-soft (co-valent character).

An attempt to quantify the 'softness' of a base consists in determining the equilibrium constant for the following equilibrium:



Where CH₃Hg⁺ (methylmercury ion) is a very soft acid and H⁺ (proton) is a hard acid, which compete for B (the base to be classified). Some examples illustrating the effectiveness of the theory:

Bulk metals are soft acids and are poisoned by soft bases such as phosphines and sulfides. Hard solvents such as hydrogen fluoride, water and the protic solvents tend to solvate strong solute bases such as the fluorine anion and the oxygen anions. On the other hand, dipolar aprotic solvents such as dimethyl sulfoxide and acetone are soft solvents with a preference for solvating large anions and soft bases. In coordination chemistry soft-soft and hard-hard interactions exist between ligands and metal centers.

Chemical Hardness: In 1983 Pearson together with Robert Parr extended the qualitative HSAB theory with a quantitative definition of the chemical hardness that is indicated by (η) as being proportional to the second derivative of the total energy of a chemical system with respect to changes in the number of electrons at a fixed nuclear environment. It is a closed system. The total enthalpy is zero. The chemical hardness as indicated as eta is shown as follows:

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

The factor of one-half is arbitrary and often dropped as Pearson has noted.

An operational definition for the chemical hardness is obtained by applying a three-point finite difference approximation to the second derivative.

$\eta = \frac{1}{2} (I - A)$ where I = ionization potential, A = electron affinity. This expression implies that the chemical hardness is proportional to the

band gap of a chemical system, when a gap exists. The first derivative of the energy with respect to the number of electrons is equal to the chemical potential, μ , of the system.

$$\mu = \left(\frac{\partial E}{\partial N} \right)_Z$$

Hardness is a measure for resistance to deformation or change. Likewise a value of zero denotes maximum softness, where softness is defined as the reciprocal of hardness. In a compilation of hardness values only that of the hydride anion deviates. Another discrepancy noted in the original 1983 article are the apparent higher hardness of Tl³⁺ compared to Tl⁺. Chemical hardness in electron volt is shown in Table No.3

Table No. 3 showing chemical hardness data (Chemical hardness in electron volt)

Acids	electronvolt	Bases	electron volt
Hydrogen H ⁺	∞	Fluoride F ⁻	7
Alluminium Al ³⁺	45.8	Ammonia NH ₃	6.8
Lithium Li	35.1	Hydride H ⁻	6.8
Scandium Sc ³⁺	24.6	Carbon monoxide	CO 6.0
Sodium Na	+21.1	Hydroxyl OH ⁻	5.6
Lanthanum La ³⁺	15.4	Cyanide CN ⁻	5.3
Zinc Zn ²⁺	10.8	Phosphane PH ₃	5.0
Carbondioxide CO ₂	10.8	Nitrite NO ₂ ⁻	4.5
Sulfur dioxide SO ₂	5.6	Hydrosulfide SH ⁻	4.1
Iodine I ₂	3.4	Methane CH ₄	4.0

Modifications: If the interaction between acid and base in solution results in an equilibrium mixture the strength of the interaction can be quantified in terms of an equilibrium constant. An alternative quantitative measure is the standard heat (enthalpy) of formation of the adduct in a non-coordinating solvent. Drago and Wayland proposed a two-parameter equation which predicts the formation of a very large number of adducts quite accurate.

$$-\Delta H^0(A-B) = E_A E_B + C_A C_B$$

Value of the E and C parameters can be found in Drago *et al.* Hancock and Martell found that an E and C equation analogous to that of Drago gave an excellent quantitative prediction of formation constants for complexes of 34 metal ions plus the proton with a wide range of unidentate Lewis acids in aqueous solution, and also offered insights into factors governing HSAB behavior in solution. Another quantitative system has been proposed, in which Lewis acid strength is based on gas-phase affinity for fluoride. When the substance is highly electronegative such as halogens (for example, fluorine) the reaction takes place fast and the fluoride formation occurs. The reason being that the electron affinity in the first order reaction is more. It is also possible to predict the energy changes possible in terms of the kilo calories. However, the accuracy with which the calculations could be made for the system is rather doubtful.

The hard and soft acid and base has helped the chemist in identifying the substance for the specific chemical reaction. However, the energy consumed for the chemical transformation is rather difficult to predict exactly. The transformation is more fast and almost complete with the result the enthalpy also becomes an important criteria for understanding the acid-base interactions.

It is highly useful when one considers the isomerism in some substances. The type of transformation taking place could be guided by the energy changes and the identification of the substance that is likely to transform. In fact, the cis transformation is identified easily than the trans transformation. There are criticism in the recent period that the HSAB theory cannot be applied to all the transformations.

The resistance to deformation of change is clearly identified in the case of crystals. The heat of reaction is an indicator of the deformation also. The chemical substance sometimes shows a slow reaction undergoing transformation gradually that makes the hypothesizing difficult. This happens in the nuclear environment where in the heat of reaction is mostly ionic and the total heat transfer takes place from one layer to the other. The Phase transformation is also equally effective resulting in total destruction of the material undergoing transformation.

The hypothesis that the acidic medium facilitates transformation is generally true but the acidic medium interacts with the chemical transformation resulting in more faster reaction.

REFERENCES

1. Jolly, W. L. (1984). Modern Inorganic Chemistry. New York: McGraw-Hill. ISBN 0-07-032760-2.
2. Koch, E.C. Acid-Base Interactions in Energetic Materials: I. The Hard and Soft Acids and Bases (HSAB) Principle-Insights to Reactivity and Sensitivity of Energetic Materials, Prop., Expl., Pyrotech. 30 2005, 5