Born - Haber cycle :

The direct determination of the lattice energy of an ionic crystal has been ~~clarified~~ carried out for only a few compounds. In many cases it is not possible to measure the lattice energy directly. Born and Haber ~~delivered~~ devised a cyclic process to find the lattice energy.

Born - Haber cycle can be explained taking the formation of sodium chloride from elementary solid sodium and elementary gaseous chlorine. Let us make the following asumptions.

Sodium metal is evaporated to sodium atom Na (g). The energy of sublimation is +S.

The diatomic chlorine gas is dissociated to chlorine atom Cl (g). The energy of dissociation for Cl_2 is + D.

The sodium atoms are ionised to form Na^+. The ionisation energy of sodium atom is + I.

The electrons obtained from sodium atoms are transferred to chlorine atoms to form negative chloride ions Cl^-. The electrons affinity of chlorine atom is − E.

The lattice energy of sodium chloride is $-U_0$.

The heat of formation 7of the crystals from its element is Q. All these changes can be represented by the Born-Haber cycle as follows.

$$\begin{tikzcd}
NaCl(s) & Na^+(g) \arrow[l, "-U_0"'] & + & Cl^-(g) \\
Na(g) + \frac{1}{2} Cl_2(g) \arrow[u, "-Q"] \arrow[r, "+S+\frac{1}{2}D"] & Na(g) \arrow[u, "+I"] & + & Cl(g) \arrow[u, "-E"]
\end{tikzcd}$$

The total energy of formation of the crystal from is elementary components is given by the equation.

$$-Q = S + \tfrac{1}{2} D + I - E - U_0$$

So,

$$U_0 = Q + S + \tfrac{1}{2} D + I - E$$

The values of Q are accurately known for many substances. Knowing the other thermochemical values, it is possible to calculate the lattice energy U_0.

pauling's scale of electronegativity :

On the basis of bond energies, pauling devised a scale for electronegativity. Bond energy of a compound A-B for pure covalency is geometric mean of the bond energies of A-A and B-B.

That is,

$$E_{A-B} = \left(E_{A-A} \times E_{B.B}\right)^{1/2}$$

But actual experimental values is found to be greater than this expected value. let the difference between the two be D.

i.e.,

$$D = E_{A.B} - \left(E_{A-A} \times E_{B-B}\right)^{1/2}$$

D is a measure of the polarity of the bond A-B. It depends on the difference in the electronegative character of A and B.

let X_A and X_B represent the electronegativity of A and B. Is the relationship between A and the electronegativity is,

$$X_A - X_B = 0.088\sqrt{\Delta}$$

The factor 0.088 converts Δ from KJ $mole^{-1}$ to eV (electron Volts) units.

pauling gave an arbitary value of electro negativity to hydrogen as $X_H = 2.1$. This is used as reference standard for calculating the electro negativities of other elements.

Mulliken Scale of electronegativity:

According to Mulliken, the electronegativity is related to its ionisation potential and its electron affinity. Ionisation potential measures an element's tendency to lose its valance electron while electron affinity measures its tendency to attract an extra electron. The elements having high values of ionisation potential and electron affinity will also have a high value of electronegativity. Thus,

$$X = \frac{IP + EA}{2}$$

where,

X = Electronegativity

IP = Ionisation potential in eV

EA = Electron affinity in eV.

Mulliken scale value of electronegativities are about 2.8 times larger than pauling's value. Hence to make both values approximately equal to Mulliken's value is divided by 2.8. Thus,

$$X = \frac{IP + EA}{2 \times 2.8}$$

$$X = \frac{IP + EA}{5.6}$$

The constant $1/5.6$ is called scale adjustment factor. This factor is used when IP and EA are expressed in eV. If they are expressed in K.cals, the following scale is used.

$$X = \frac{IP + EA}{2 \times 625}$$

HSAB Theory :

Hard and soft Acids and Bases :

In 1963 R, G. pearson classified the lewis acids and bases as hard and soft acids.

Soft and Hard bases :

Soft lewis bases are those in which the donor atoms are easily polarised and have low electronegativity. Hard lewis bases are those in which the donar atoms have low polarisablities and high electro-negativities.

It will be seen that within a group of the periodic table softness of the lewis bases increases with the increase in the size of the donor atom. Thus, among the halide ions, softness increases in the order $F^- < Cl^- < Br^- < I^-$. Thus F^- is the hardest and I^- is the softest lewis base.

Hard bases :

E.g, H_2O, OH^-, F^-, CH_3COO^-

Borderline (intermediate bases)

E.g,

$C_6H_5NH_2$, C_6H_5N, Br^-

Soft bases :

Eg : R_2S, RSH, RS^-, I^-, SCN^-

Soft and Hard Acids :

A hard acid like a hard base, is difficult to polarise. A cationic hard acid, such as Al^{3+}, generally has

a small size.
a high positive charge and.
a noble gas electronic configuration.

Hard Acids :

Eg : H^+, Li^+, Na^+, K^+, Be^{2+}, Ca^{2+}

Boderline (intermediate) Acids :

Eg : Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}.

Soft Acids :

Eg: Cu^+, Ag^{2+}, Au^-, Tl^+, Hg^+.

HSAB principle and stability of the compound A : B

The typical lewis acids - base reaction can be generated as

$$\underset{\substack{\text{lewis acid} \\ \text{(acceptor)}}}{A} + \underset{\substack{\text{lewis base} \\ \text{(donar)}}}{B} \longrightarrow \underset{\substack{\text{Adduct or} \\ \text{complex}}}{A:B}$$

A concept knows as principle of soft and Hard Acids and Bases (abbreviated to HSAB principle) is very helpful in making a prediction of the stability of the complex A : B. This principle was proposed by Ralph G. pearson (1963)

According to this principle the complex A : B is most stable when A and B are either both soft or both hard. The complex is least stable when one of the reactants (namely A and B) is very hard and the other one is very short.

This principle also means that if there is choice of reaction between an acids and two bases, or between a base and two acids, a hard acids will prefer to combine with a soft base and thus a more stable product will be obtained.