STUDY MATERIAL

Dumkal College
Basantapur,Dumkal

Topic: Chemical Bonding-1:Born-Haber cycle and its applications

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11.5 ENERGETICS OF IONIC BOND FORMATION : BORN-HABER CYCLE

11.5.1 Born-Haber Cycle in Ionic Bond Formation

In predicting the possibility of an ionic bond formation in a particular compound, it is more important to consider the energetics of the process of formation rather than the concept of attaining the stable electronic configuration of the constituent ions in the compound under consideration. If the process is exothermic* (i.e. $\Delta H < 0$) the compound is stable, but if the process is endothermic (i.e. $\Delta H > 0$) the compound is unstable. The enthalpy change (i.e. ΔH) of the process can be computed from the Born-Haber cycle which is based on the basic principle (Hess's law) of thermochemistry. ΔH being a state function does not depend on the path through which the process is carried out but on the initial and final state.

ΔH of the process leading to an ionic crystal may be obtained experimentally by the direct combination of the constituent elements. It can also be computed by using the Born-Haber cycle which involves the following steps :

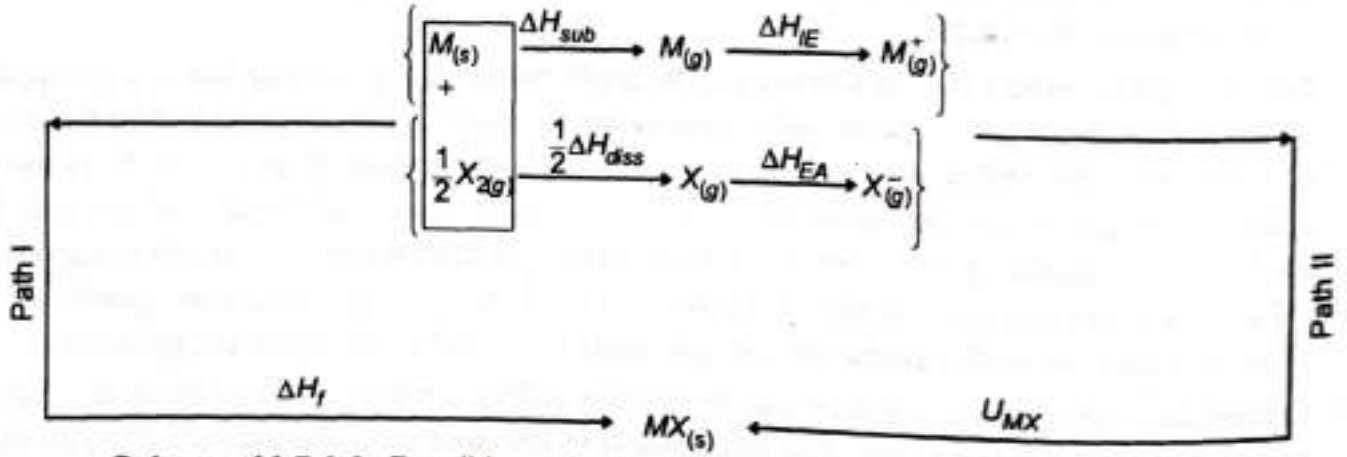
(i) Vaporisation of the involved reactant elements.

(ii) Formation of the required ions from the isolated gaseous atoms.

(iii) Combination of the gaseous ions to produce the solid product.

To illustrate the principle of Born-Haber cycle, let us consider the formation of the simple ionic compound M^+X^- (e.g. $NaCl$) in computing the standard molar enthalpy of formation (ΔH_f) which is defined as the change of enthalpy in the formation of one mole of the ionic compound M^+X^- from its constituent elements in their most stable physical states at 298 K and 1 atm. pressure.

Formation of M^+X^- can be considered to take place in two paths (assuming M and X_2 to exist in solid and gaseous state respectively at ordinary condition) as shown in the Scheme 11.5.1.1.



Scheme 11.5.1.1. Possible paths leading to the formation of M^+X^- crystal.

* More correctly, to predict the stability we should consider ΔG ($= \Delta H - T\Delta S$) rather ΔH alone. **But in the formation of an ionic lattice starting from a solid metallic crystal, ΔS is not very much significant.** Here, at an ordinary condition consideration of ΔH predicts almost the correct result.

Path II consists of the following steps :

(i) ***First* step :** It involves the sublimation of solid M into its vapour. It requires the *sublimation energy*, ΔH_{sub}.

(ii) ***Second step* :** It involves the ionisation of the isolated gaseous atoms of M. It requires the *ionisation energy* (i.e. first *IE*), ΔH_{IE}.

(iii) ***Third step* :** It involves the *bond dissociation* of the halogen gas X_2 (say Cl_2) to form gaseous atoms. As the process requires half mole of X_2 to form one mole of MX, the requirement of energy is $\frac{1}{2}\Delta H_{diss}$.

(iv) ***Fourth step* :** It involves the gaining of an electron by the isolated gaseous atom (X) to form X^-. It measures the **electron affinity**, ΔH_{EA}.

(v) ***Final step* :** It involves the combination of the oppositely charged isolated gaseous ions (in the gaseous phase, they may exist as ion pairs, but here we are ignoring this aspect for the sake of simplicity) to form a solid crystal in which the omnidirectional electrostatic force works throughout the crystal. It leads to the **release of lattice energy,** U_{MX}. Thus, we get the following relation with *appropriate signs of the energy terms* (according to the convention of thermodynamics).

$$\Delta H_f = \Delta H_{sub} + \Delta H_{IE} + \frac{1}{2}\Delta H_{diss} + \Delta H_{EA} + U_{MX} \qquad \ldots(11.5.1.1)$$

From the standard convention of thermodynamics, when the energy is released (i.e. exothermic) it is associated with a negative sign (–ve) while for the energy requiring (i.e. endothermic) process, the energy term is associated with a positive sign (+ve). In forming the lattice from the isolated gaseous ions, the energy measured by lattice energy (U_{MX}) is released. Generally the energy term (ΔH_{EA}) measuring the electron affinity is exothermic.

In the case of *NaCl*, by using the calculated value of lattice energy and other energy terms experimentally determined, let us calculate the enthalpy of formation (ΔH_f^{298}). ΔH_{sub} = 108.8 kJ mol^{-1}, ΔH_{IE} = 493.8 kJ mol^{-1}, $\frac{1}{2}$ (ΔH_{diss}) = 121.3 kJ mol^{-1}, ΔH_{EA} = –348.5 kJ mol^{-1}, U_{NaCl} = – 757.3 kJ mol^{-1}. By using these energy values in Eqn. 11.5.1.1 we get, ΔH_f = – 381.9 kJ mol^{-1}. This calculated value can be compared with the experimental one, – 411 kJ mol^{-1}. The calculation from the Born-Haber cycle shows that the formation of $Na^+Cl^-_{(s)}$ is exothermic and it occurs so in reality.

11.5.2 Drawbacks in the Concept of Born-Haber Cycle

The calculated values of lattice energy or electron affinity from the Born-Haber cycle are found to deviate significantly in many cases from the values reported from other reliable sources. It is due to the fact that in constructing the Born-Haber cycle, 100% ionic character is considered, but in reality, in many cases this approximation does not agree with the actual nature of bonding existing in the compounds. When the degree of covalency as predicted from the Fajans' rules becomes significant, the discrepancy between the prediction from the Born-Haber cycle and the finding from other sources becomes prominant.

11.5.3 Factors Favouring the Formation of Ionic Bonds

From the consideration of the Born-Haber cycle representing the formation of an ionic bond, it is evident that the sublimation energy (ΔH_{sub}) of $M_{(s)}$ and bond dissociation energy (ΔH_{diss}) of X_2 are always positive (i.e. endothermic) though these values are relatively smaller compared to the other terms involved. The ionisation energy of M_g is always positive. The electron affinity process leading to $X^-_{(g)}$ for the halogens is exothermic but for the chalcogens leading to $X^{2-}_{(g)}$, it is positive (because during the second electron capture, **$X^-_{(g)}$ is forced to accept the second electron in spite of the severe electron-electron repulsion).** However, in all the cases, the summation of sublimation energy of $M_{(s)}$, half of the bond dissociation energy of $X_{2(g)}$, ionisation energy of $M_{(g)}$ and electron affinity energy of $X_{(g)}$ is always positive. Thus to make the overall process exothermic, the lattice energy (exothermic) should be high. Therefore, in general we can conclude for the formation of ionic MX as :

$$|U_{MX}| > |(\Delta H_{sub} + \frac{1}{2}\Delta H_{diss} + \Delta H_{IE} + \Delta H_{EA})|$$

Thus to favour the formation of an ionic compound, the following factors are to be considered.

(i) ***Low sublimation energy of the metal and low bond dissociation energy of the nonmetal*** : The values of sublimation energy (ΔH_{sub}) and bond dissociation energy (ΔH_{diss}) are in general relatively smaller compared to the other energy terms involved. The bond dissociation energies for N_2 (941 kJ mol^{-1}) and O_2 (507 kJ mol^{-1}) are fairly high, but still compared to the other energy terms these are small. But, for the noble metals, the *high sublimation energy* may direct the process towards endothermicity.

(ii) ***Highly electropositive character of the metal*** : The ionisation energies of the metal under consideration should be small. This condition is well satisfied by the alkali and alkaline earth metals. The ionisation energies increase successively. Hence, a very high positive oxidation state is not favoured in the formation of an ionic bond. Let us take the case of $AlCl_3$.

$$Al_{(s)} + \frac{3}{2}Cl_{2(g)} \rightarrow AlCl_{3(s)}, \Delta H_{f(\text{expt})} = +\text{ve}$$

It requires the successive ionisation energies in the corresponding Born-Haber cycle as follows,

$Al_{(g)} \rightarrow Al^+_{(g)} + e$, $\Delta H_{IE(1)} = 577.4$ kJ mol^{-1}; $Al^+_{(g)} \rightarrow Al^{2+}_{(g)} + e$, $\Delta_{IE(2)} = 18330.0$ kJ mol^{-1}; $Al^{2+}_{(g)} \rightarrow Al^{3+}_{(g)} + e$, $\Delta_{IE(3)} = 2703.5$ kJ mol^{-1} i.e. $\Sigma\Delta H_{IE} = 5113.9$ kJ mol^{-1}.

Thus, in forming the $Al^{3+}_{(g)}$ ion, the process has become so endothermic that *the electron affinity and lattice energy cannot compensate the endothermicity of the process.* Hence, $AlCl_3$ is predominantly covalent. However, on hydration (exothermic process) of $AlCl_3$, the process becomes exothermic giving rise to $Al(H_2O)^{3+}_6$ *and* $3Cl^-_{aq}$. Here it is worth mentioning that the high positive charge bearing metal ions are highly polarising to introduce a good deal of covalent character in the compounds.

$$AlCl_3 \text{ (significantly covalent)} \xrightarrow{\text{Hydration}} \text{Hydrated } Al^{3+} \text{ and } Cl^- \text{ ions, (Exothermic process)}$$

(iii) ***High electron affinity of the nonmetal*** : The electron affinity (which leads to the release of energy) of the nonmetal under consideration should be high, so that it can help to direct the whole process in the exothermic direction. Formation of high negative charge bearing anions

such as N^{3-}, P^{3-}, etc. is so endothermic that they can never exist in the ionic compounds. In fact, such anions are highly polarisable to favour covalency rather than ionic valency.

(iv) ***High lattice energy*** : The lattice energy (exothermic process) should be high to favour the process. The lattice energy which is a Coulombic energy (extending throughout the cluster) depends on the product of the charges of the cation and anion involved, interionic separation, and the *Madelung constant A* (i.e. geometry of the crystal) of the crystal structure. It is related as follows:

$$U \propto (Z^+)(Z^-),\ U \propto 1/(r_+ + r_-),\ \text{and}\ U \propto A$$

All the above factors should run in favour to direct the overall process in the exothermic direction. From the standpoint of electron affinity, formation of O^{2-} is energetically unfavourable, **but many oxides are ionic because of the high lattice energy, a consequence of higher charge.** It is evident that the small ions such as F^-, O^{2-} are the better candidates for forming the ionic compounds. These involved factors will be discussed at a greater length in Sec. 11.7.5.

From the above discussion, it is evident that the conditions predicted for the formation of an ionic compound from the concept of energetics in the light of the involved Born-Haber cycel are in conformity with the predictions from the Fajans' rule. These aspects are compared below.

Nature of the ions	*Prediction from Fajans' Rule*	*Prediction from Born-Haber cycle*
(i) High charge on the cation	High polarising power disfavours ionic bonding	High ionisation energies make ΔH_f positive to disfavour ionic bonding
(ii) High charge on the anion	High polarisability disfavours ionic bonding	High endothermicity in creating the highly charged anions disfavours ΔH_f. Besides this, the large ionic radius lowers the lattice energy to disfavour ionic bonding

11.6 APPLICATIONS OF BORN-HABER CYCLE

(i) **Computation of lattice energy** : The lattice energy of a particular ionic compound can be determined by using Eqn. 11.5.1.1 from the knowledge of the other energy terms (with appropriate signs) involved. Except the electron affinity, other energy terms such as heat of formation (ΔH_f), ionisation energy (ΔH_{IE}), sublimation energy (ΔH_{sub}) can be experimentally determined. ΔH_{EA} can be taken from other sources (generally determined by using the Born-Haber cycle for other compounds containing the species under consideration). Here it is worth remembering that the method does not work good when the degree of covalency is significant. A comparison between the Born-Haber value and the calculated value by considering the electrostatic interaction is shown in Table 11.7.2.1.

Here it is worth mentioning that the Born-Haber value is an experimental quantity which takes care of both electrostatic interaction and crystal field stabilisation energy (CFSE), if any, but the theoretically calculated value only considers the electrostatic interaction. Hence the agreement is good only when CFSE is zero.

(ii) **Computation of electron affinity** : By using the Born-Lande equation (see Sec. 11.7.1), the lattice energy of a particular ionic compound can be theoretically calculated. By using the calculated value of lattice energy and other energy terms (with appropriate signs) which can be

experimentally determined, the electron affinity of the concerned element can be calculated from Eqn. 11.5.1.1. Here it is worth mentioning that it is very difficult to determine the elctron affinity by any other method. **But, for the compounds having a good degree of covalency, the procedure is not applicable.**

The application of the process can be illustrated in evaluating the electron affinity of chlorine from different alkali metal chlorides which are predominantly ionic. These are shown in Table 11.6.1.

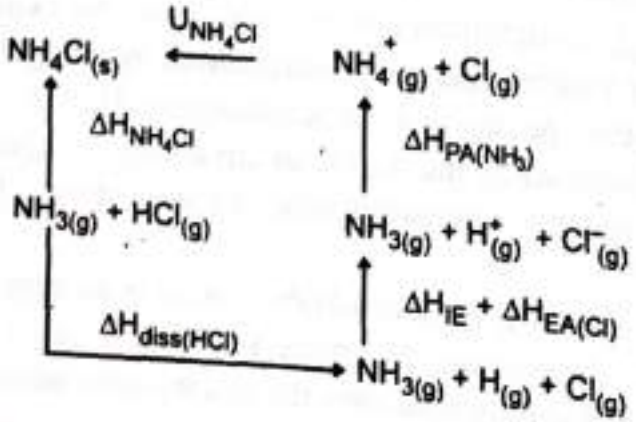
Table 11.6.1. Born-Haber data for alkali metal chlorides to evaluate the electron affinity of chlorine (in kJ mol^{-1})

Compound (MCl)	$-\Delta H_{f(MCl)}$	$\Delta H_{sub(M)}$	$\Delta H_{diss(Cl_2)}$	$\Delta H_{IE(M)}$	$-U_{MCl}$	$-\Delta H_{EA(Cl)}$
LiCl	405.9	163.2	242.7	518.9	841.2	368.2
NaCl	410.1	108.8	242.7	493.8	770.0	364.1
KCl	435.2	83.7	242.7	418.5	703.1	355.7
RbCl	439.4	79.5	242.7	401.7	678.0	364.0

From this table, it is evident that the almost constancy in the calculated values of $\Delta_{EA(Cl)}$ evidences the validity of the procedure. The direct determination of electron affinity of chlorine from the electron emission experiments gives the value 360 kJ mol^{-1} which is in good conformity with the calculated value.

In this way, the electron affinity of many other species can be calculated.

(iii) **Computation of proton affinity :** The Born-Haber cycle can be used to determine the proton affinity of a species. The proton affinity of a chemical species X is measured by the enthalpy change (ΔH_{PA}) in the process, $X_{(g)} + H^+_{(g)} \rightarrow HX^+_{(g)}$. From the definition, proton affinity = $-\Delta H_{PA}$ (cf. definition of electron affinity). Let us illustrate the process for NH_3. The lattice energy of the ammonium salt (say, NH_4Cl) is to be determined first by using the Born-Haber cycle. Then the following treatment is to be carried out :



where, U_{NH_4Cl} = lattice energy of NH_4Cl, $\Delta H_{PA(NH_3)}$ = **– proton affinity of NH_3**, ΔH_{IE} = ionisation energy of H, ΔH_{EA} = electron affinity of Cl, $\Delta H_{diss(HCl)}$ = bond dissociation energy of HCl, ΔH_{NH_4Cl} = heat of the reaction, $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(s)}$.

Thus,

$$\Delta H_{NH_4Cl} = \Delta H_{diss(HCl)} + \Delta H_{IE} + \Delta H_{EA(Cl)} + \Delta H_{PA(NH_3)} + U_{NH_4Cl}$$

and from the knowledge of the other energy terms, $\Delta H_{PA(NH_3)}$ can be computed.

Now let us consider the **proton affinity of H_2O** to be determined. NH_4ClO_4 and H_3OClO_4 have been found isomorphous and from the comparison of X-ray maximum intensity reflection of the two species, they are found to have almost the same crystal constants (i.e. axial ratios, interfacial angles, etc.). Hence it is assumed that they are having almost the same lattice energy i.e. $U_{NH_4ClO_4} = U_{H_3OClO_4}$.

From the consideration of two separate cycles as done for NH_4Cl, we have :

$$U_{NH_4ClO_4} = \Delta H_{NH_4ClO_4} - [\Delta_{diss(HClO_4)} + \Delta H_{IE} + \Delta H_{EA} + \Delta H_{PA(NH_3)}]$$

and,

$$U_{H_3OClO_4} = \Delta H_{H_3OClO_4} - [\Delta H_{diss(HClO_4)} + \Delta H_{IE} + \Delta H_{EA} + \Delta H_{PA(H_2O)}]$$

Equating the above relations, i.e. $U_{NH_4ClO_4} = U_{H_3OClO_4}$, we get :

$$\Delta H_{NH_4ClO_4} - \Delta H_{PA(NH_3)} = \Delta H_{H_3OClO_4} - \Delta H_{PA(H_2O)}$$

or,

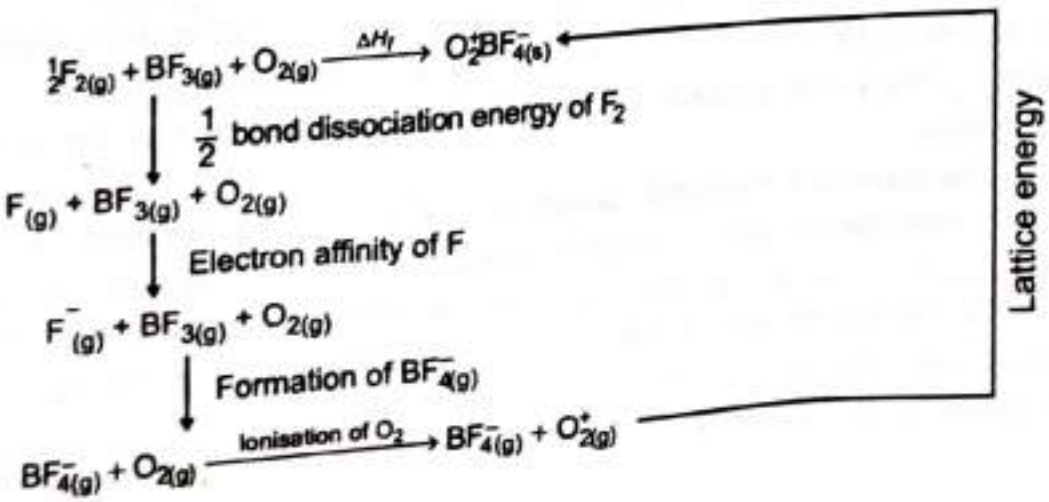
$$\Delta H_{PA(H_2O)} = \Delta H_{H_3OClO_4} - \Delta H_{NH_4ClO_4} + \Delta H_{PA(NH_3)}$$

Thus, by using the value of $\Delta H_{PA(NH_3)}$, the proton affinity of H_2O can be calculated. The proton affinities (in gas phase) of NH_3 and H_2O are 895 kJ mol^{-1} and 760 kJ mol^{-1} respectively. These values indicate the amounts of energy to be released in the concerned process of proton acceptance.

(iv) **Prediction of stability of an ionic compound :** By considering a suitable cycle, the enthalpy of formation of an ionic compound in question can be calculated. To evaluate the lattice energy, Born-Lande equation (see Sec. 11.7.1) can be used and for this purpose, the ionic radii can be obtained by Pauling's method (see Sec. 11.3.2). If the process is found to be endothermic, the corresponding ionic compound does not form while for the exothermic process it exists. For example, by using some approximations, ΔH_f for $NaCl_2$ has been found to be highly positive. Hence it cannot exist.

Let us consider the predictive stability of the compound ***dioxygenyl tetrafluoroborate***, $O_2^+BF_4^-$.

To evaluate the enthalpy of formation, let us consider the following Born-Haber cycle, in which the elemental fluorine is used as a vigorous oxidising agent to carry out the oxidation of oxygen molecule to dioxygenyl cation.



ΔH_f = ionisation energy of $O_2 + \frac{1}{2}$ bond dissociation energy of F_2 + electron affinity of F + enthalpy of formation of $BF_{4(g)}^-$ from $F_{(g)}^-$ and $BF_{3(g)}$ + lattice energy = $(1164 + \frac{1}{2} \times 158 - 326 - 385 - 500) = +32$ kJ mol^{-1}.

In calculating the lattice energy, the ionic radii of O_2^+ and BF_4^- are approximately taken as ~ 177 pm and ~ 218 pm respectively from thermochemical data (see Table 11.3.2.2). Then from the approximate knowledge of r_+/r_-, the lattice energy is calculated from the Born-Lande equation. It is found to be -500 ± 20 kJ mol^{-1}. The calculated ΔH_f is slightly positive. We are to mention that the lattice energy used is an approximate one. **Hence, we can conclude that if at all, the compound exists, it will have a low stability.** In fact, the compound has been synthesised and the prediction, i.e. low stability, has been verified experimentally.

A similar calculation helped Bartlett to predict the **existence of** $Xe^+PtF_6^-$ and it was ultimately realised.

Similarly, it can be shown that the compound dioxygenyl superoxide (i.e. $O_2^+O_2^-$) cannot exist because the corresponding ΔH_f is highly positive (~ + 600 kJ mol^{-1}).

(v) **Prediction of disproportionation of an ionic compound in its lower oxidation state :** Metals generally do not form ionic compounds in their lower oxidation states such as : $CaCl$, $MgCl$, AlO, Zn_2O, etc. Instead of these, they form $CaCl_2$, $MgCl_2$, Al_2O_3, ZnO respectively. From the standpoint of ionisation energies (which are endothermic in nature), formation of the compounds in the lower oxidation states appears to be more favourable compared to the involvement of the higher oxidation states which require more ionisation energies for their generation. But this disfavour in the participation of the higher oxidation states can be easily overcome in many cases through the enchanced lattice energy (which is exothermic) due to the higher charge and lower interionic separation.

For example, let us consider the relative thermodynamic stabilities (measured by ΔH_f) of CaF and CaF_2 : $\Delta H_{f(CaF)} = -260$ kJ mol^{-1}, $\Delta H_{f(CaF_2)} = -1243$ kJ mol^{-1}. These values are computed from the corresponding Born-Haber cycles (under some approximations). It is evident that independently, CaF should exist but with respect to the following disproportionation process leading to CaF_2 which is much stabler, CaF becomes nonexistent.

$$2CaF \rightarrow CaF_2 + Ca, \text{ (disproportionation)}$$

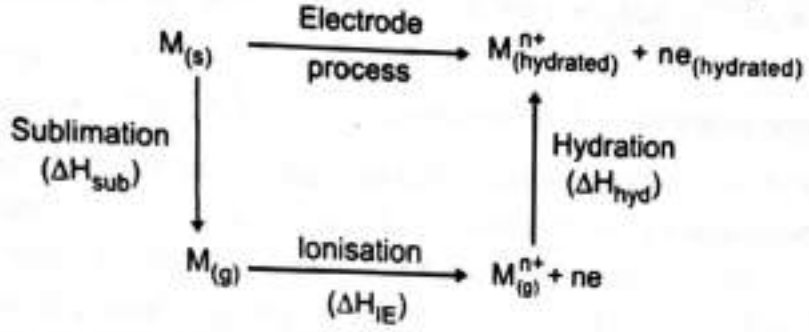
Here, the enthalpy change (ΔH) is given by, $\Delta H = \Delta H_{f(CaF_2)} - 2\Delta H_{f(CaF)} = -1243 - 2(-260) = -723$ kJ mol^{-1}. Here all the species are solid. Hence the effect of entropy change (ΔS) is of no significance to predict the direction of the above disproportionation process.

In some cases for the lower oxidation states, the lattice energy is too low to make the overall process exothermic.

(vi) **Prediction of the standard electrode potential (i.e. noblity of the metals) of the metals (cf. Sec. 16.5.1) :** Several factors are involved in measuring the electrode potential (E) of the process, $M_{(s)} \rightarrow M_{hydrated}^{n+} + ne$. In fact, to treat the problem, we are to consider the free energy change, ΔG ($= \Delta H - T\Delta S$) in the process, but for the sake of simplicity, to measure the potentials for a comparison we shall pay attention only to ΔH determined by a suitable Born-Haber cycle. Here it is worth mentioning that the reactant in the process is solid and the product remains in a

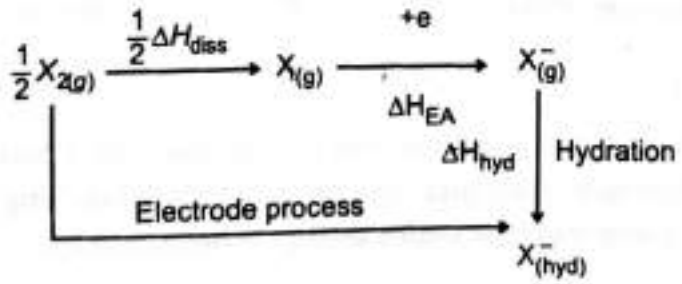
hydrated condition yielding an electrorestriction over the solvent molecules in the hydration sphere. As a result, the **contribution of ΔS is relatively small compared to that of ΔH** in determining the position of the process. Thus, $\Delta G = -nFE = \Delta H - T\Delta S \approx \Delta H$, F = faraday; i.e. E **is controlled mainly by ΔH.** In fact, for E^0, all the thermodynamic parameters are in standard states i.e. $\Delta G^0 = -nFE^0 = \Delta H^0 - T\Delta S^0$.

To compute the ΔH, we are to consider the following Born-Haber cycle :



Thus, under the approximation as stated above, E (electrode potential) is determined by the summation, $\Delta H_{sub} + \Delta H_{IE} + \Delta H_{hyd}$. Here both ΔH_{sub} and ΔH_{IE} are endothermic. Hence to favour the process, ΔH_{hyd} (which is exothermic) should be high. ***The metals having high sublimation and ionisation energies are noble.*** The heavy transition metals are in this group, and it is nicely reflected for the heavy metals like, *Ag*, *Au*, *Pt*, etc. On the other hand, **the low values of ΔH_{sub} and ΔH_{IE} make the alkali and alkaline earth metals more reactive.**

Abnormally high electrode potential of the $\frac{1}{2}F_2/F^-$ ***couple*** : The electron affinity of chlorine is higher than that of fluorine, but the electrode potential of $\frac{1}{2}Cl_2/Cl^-$ (E_0 = 1.33 V) is much smaller compared to that of $\frac{1}{2}F_2/F^-$ (E_0 = 2.87 V). Apparently it is contradictory but it can be explained by considering the involved Born-Haber cycle.



Though the electron affinity (ΔH_{EA}) favours the couple $\frac{1}{2}Cl_2/Cl^-$ more, **the exceedingly small bond dissociation energy of F_2 and high hydration energy of F^- can drive the cycle more in favour of the couple $\frac{1}{2}F_2/F^-$.**

(vii) **Prediction of solubility of a compound :** For an ionic compound, the Born-Haber cycle involving the hydration energies and lattice energy is very much important in predicting the solubility of the compound. This aspect will be discussed in Sec. 13.5.

Here we shall cite two interesting compounds, $AlCl_3$ (anhydrous) and HCl (anhydrous) which are covalent in nature, because ΔH_f values corresponding to the hypothetical ionic compounds

become positive. But these compounds in an aqueous solution dissociate into the constituent ions. **Actually the hydration energies of the ions can compensate the disfavour due to the high ionisation energies inivolved to produce the ions (i.e. H^+, Al^{3+}).** It is worth noting that though anhydrous $AlCl_3$ is covalent, the hydrated salt $AlCl_3$, $6H_2O$ is ionic. For such hydrated salts, in the Born-Haber cycle, hydration energy is to be incorporated in calculating ΔH_f.

$$Al_{(s)} + \frac{3}{2}Cl_{2(g)} \rightarrow AlCl_{3s}, \Delta H_f = +ve; Al_{(s)} + \frac{3}{2}Cl_{2(g)} + 6H_2O \rightarrow AlCl_3.6H_2O_{(s)}, \Delta H_f = -ve$$

(viii) **Halogen exchange reaction :** The reaction, $\diagdown\!\!\diagup C - Cl + MF \rightarrow \diagdown\!\!\diagup C - F + MCl$ is **most favoured for *CsF*.** If we construct a Born-Haber cycle for the reaction, then the overall enthalpy change will be approximately determined by the lattice energy difference of *MF* and *MCl*. *MF* will have the lowest lattice energy for *CsF* and the process will be most favoured.

(ix) **Participation of higher oxidation states in ionic bonding :** Generally to produce a cation of its higher oxidation states is disfavoured due to the gradual increase in ionisation energies. But in such cases, **oxygen and fluorine are highly promising to introduce the ionic character because of the facts:** (a) **high electron affinities** of oxygen and fluorine favour the exothermicity, (b) **low ionic radii** of the small anions favour the lattice energy, (c) in the case of fluorine, the **unusually low bond dissociation energy** makes the process more exothermic. It will be shown that ***oxidative halogenation*** is very much thermodynamically favoured by F_2.

(x) **Oxidative halogenation and reductive dehalogenation :** For the oxidative halogenation reaction, $\frac{1}{2}X_2 + MX \rightarrow MX_2$, the enthalpy change will be controlled mainly by the following factors :

- formation of X^- in the reaction $\frac{1}{2}X_2 + e \rightarrow X^-$; it will be favoured most for fluorine having **very low bond dissociation energy** and **high electron affinity** (though chlorine possesses slightly higher electron affinity), in fact, $\frac{1}{2}F_2 + e \rightarrow F^-$ is a more favourable process than $\frac{1}{2}Cl_2 + e \rightarrow Cl^-$;
- second ionisation energy of the metal and it is constant for a particular metal.
- *lattice energy difference of MX* and MX_2 for which the Madelung constants are different; the thermodynamic favour from the lattice energy is measured by :

$$\Delta U \propto \left| \frac{3}{r(M^{2+}) + r(X^-)} - \frac{1}{r(M^+) + r(X^-)} \right|, \text{(cf. Kaputinskii eqn.)}$$

$$\approx \left| \frac{2}{r(X^-)} \right|, \text{(assuming, } r(M^+) > r(M^{2+}) << r(X^-)$$

The above approximation is fairly correct because the anions are, in general, much larger than the cations. **Thus, the thermodynamic favour is maximum for flourine.**

For different halogens (considering the same *entropic effect* for all halogens), ***the process is favoured most when X = F because of both lattice energy factor and formation of X^-.*** In

Model Questions On Born-Haber Cycle

1. Calculate the electron affinity of chlorine with the help of the given data: ΔH_f = heat of formation of RbCl = $-441\ KJ\ mol^{-1}$, ΔH_{sub} = heat of sublimation of Rb = $80\ KJ\ mol^{-1}$, ΔH_{diss} = bond dissociation energy of Cl_2 = $243\ KJ\ mol^{-1}$, ΔH_{IE} = first ionisation energy of Rb = $403\ KJ\ mol^{-1}$, U = lattice energy of RbCl = $-680\ KJ\ mol^{-1}$.

2. Construct a relevant Born-Haber cycle using the following data:

$\Delta H_f (NaI) = -289\ KJ\ mol^{-1}$, $\Delta H_{sub(Na)} = 108.8\ KJ\ mol^{-1}$,

$\Delta H_{diss}(I_2) = 214.2\ KJ.mol^{-1}$, $\Delta H_{IE(Na)} = 497.3\ KJ.mol^{-1}$,

$U_{NaI} = -694.7\ KJ\ mol^{-1}$.

From the above data also calculate the value of Electron affinity of iodine.

References

1. Cotton, F.A., Wilkinson, G., Murillo, C.A. "Advanced Inorganic Chemistry.

2. Das Asim Kumar, "Fundamental Concepts of inorganic chemistry" Revised second Edition.