

Thermodynamics – Born- Haber cycles

Born Haber cycles – Is when Hess's Law is extended towards ionic compounds. We usually calculate Enthalpy of formation for substances using bond energy data. But, we cannot find bond energy data available for Na-Cl or Mg-O or Al-Cl. Bond energy data are available only for the covalent bonds. Ex C-H (+415 kJmol⁻¹) C-C (346 kJmol⁻¹) . Afore mentioned compounds are ionic compounds. Therefore, we will have to calculate Enthalpy of formation for ionic compounds using other enthalpy data like lattice energy and ionization energies.

When we calculate enthalpy values using a lab experiments, the values we get for most of these enthalpies are less than listed data. That is basically due to energy losses happen during these experiments. Also, these listed data are calculated taking average values for the bonds in many compounds.

For example when you calculate C -Cl bond energy value it is an average of

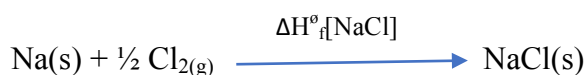
C-Cl bond in many compounds containing C-Cl like CCl₄ CH₃Cl CH₃C(CH₃)Cl

Depending on the other atoms attached to the central carbon atom, strength of the C-Cl bond can vary. You cannot get one single value for it due to electronegativity of different atom attached to it. Listed bond energy values are normally an average value for the particular bond (eg C-H bond) calculated considering C-H bond in many compounds.)

Useful definitions

Enthalpy of formation (ΔH°_f)

The change in enthalpy when one mole of a substance is formed under standard conditions (1atm pressure and 298K temperature) from its pure elements that are in standard conditions.



$$\Delta H^{\circ}_{\text{rn}} = \sum \Delta H^{\circ}_f[\text{Products}] - \sum \Delta H^{\circ}_f[\text{Ingredients}]$$

Bond Energy(Bond dissociation enthalpy) ΔH°_D

The amount of energy necessary to break one mole of bonds in a substance, by dissociating the substance into atoms of its elements in the gaseous state(under standard conditions)

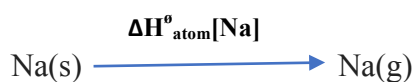


Enthalpy of atomization [$\Delta H^\circ_{\text{atom}}$]

Enthalpy of atomization is the amount of enthalpy change when a compound's bonds are broken and the component atoms are reduced to individual atoms

For Solids(Metals)

The enthalpy of atomization of an elemental solid is exactly the same as the enthalpy of sublimation for any elemental solid that becomes a monatomic gas upon evaporation.



For Diatomic Elements

When a diatomic element is converted to gaseous atoms, only half a mole of molecules will be needed, as the standard enthalpy change is based purely on the production of one mole of gaseous atoms.

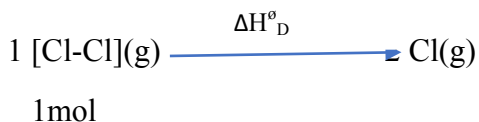


Standard enthalpy of atomization is the enthalpy change when 1 mol of gaseous atoms is formed from its element in its defined physical state under standard conditions (298.15K, 1 atm)

Bond Dissociation energy and Enthalpy of atomization

(At 298K and 1atm pressure) Bond dissociation will break **one mole of bonds to form 2 atoms**, whereas, Enthalpy of atomization will only make **1 mol of an atom from ½ mol of compound**. Therefore, bond dissociation of diatomic covalent compounds will make 2 atoms after breaking the 1mol of bond.

Therefore for diatomic covalent compounds => Bond enthalpy = 2(atomization energy)

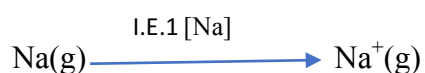


Ionization Energy (I.E)

Energy required to remove electrons from its element in gaseous state under standard conditions(1 atm and 298K)

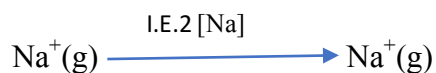
First Ionization energy(I.E.₁)

Energy required to remove 1 mol of electrons from its element in gaseous state to form 1 mol of unipositive ions.



Second Ionization energy (I.E.₂)

Energy required to form 1 mol of dipositive ion in gaseous state from gaseous unipositive ion by removing 1 mol of electrons is called EA₂

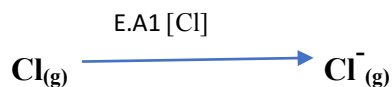


Electron Affinity (E.A)

Enthalpy change associated with an element or an ion to to form a negatively charged ion is called electron affinity.

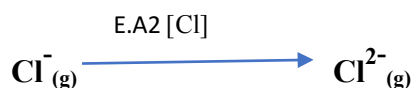
First electron affinity (E.A.₁)

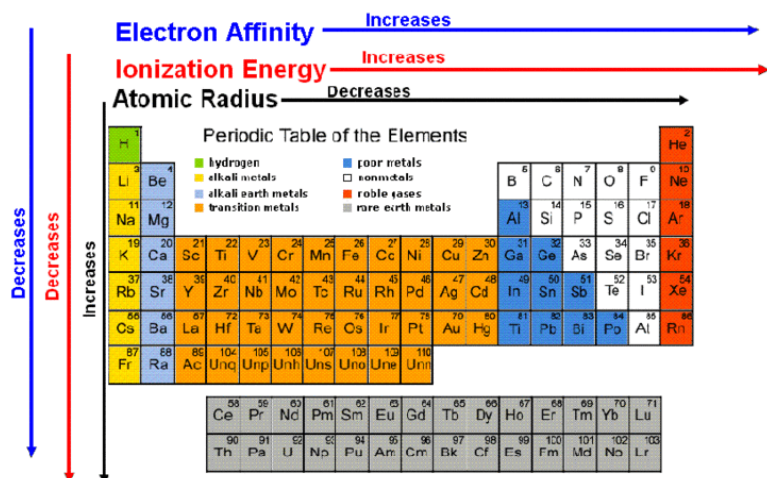
The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions.



Second Electron affinity(E.A.₂)

The second electron affinity is the energy released when 1 mole of gaseous uni-negative atoms each acquire an electron to form 1 mole of gaseous 2- (di-negative) ions.





Lattice Enthalpy ($\Delta H^{\circ}_{\text{Lattice}}$)

Lattice enthalpy is simply the change in Enthalpy associated with the formation of one mole of an ionic compound from its oppositely charged ions in their standard states under standard conditions.



Therefore:

- The enthalpy change will always be exothermic (negative)
- A more negative value shows greater electrostatic attraction and therefore a stronger bond in the solid

Trends in Lattice enthalpy

There are two factors that affect the lattice enthalpy of an ionic compound:

- The size of the ions
- The charge of the ions

This is because these are also the factors that affect charge density. Charge density of an ion will determine its "attracting power" and therefore the greater the charge density of the ions, the greater the electrostatic forces between them. So a larger ion will decrease the charge density and a more highly charged ion will increase the charge density.

Questions [\[edit\]](#)

1. Explain why the lattice enthalpy of NaBr is much less exothermic than MgCl_2
 2. How is Hess's law used to work out lattice enthalpy from born-haber cycle?
 3. What are the factors affecting lattice enthalpy?
 4. What is the definition of 1st electron affinity?
 5. What is the trend in decomposition temperatures of group two carbonates? why is this?
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1.

Na^+ has larger radius than Mg^{2+}

Br^- has larger radius than Cl^-

Na^+ has lower charge than Mg^{2+}

Therefore Stronger attraction between MgCl_2 ions

2. rearrange:

enthalpy change of formation = atomisation enthalpies + electron affinity + lattice enthalpy

3. The size of the ions The charge of the ions

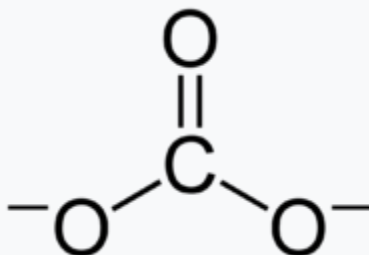
4. The first electron affinity is the enthalpy change when one electron is added to each gaseous atom in one mole, to form one mole of 1- ions

5. Increasing temperature down group, this is because down the group, ionic radius increase, so charge density decrease, so thermal stability increases down the group.

Distorted ion breaks down more easily

Thermal decomposition of group 2 carbonates

The Group 2 carbonates MgCO_3 , CaCO_3 , SrCO_3 and BaCO_3 all react in the same way when heated:



A Carbonate ion



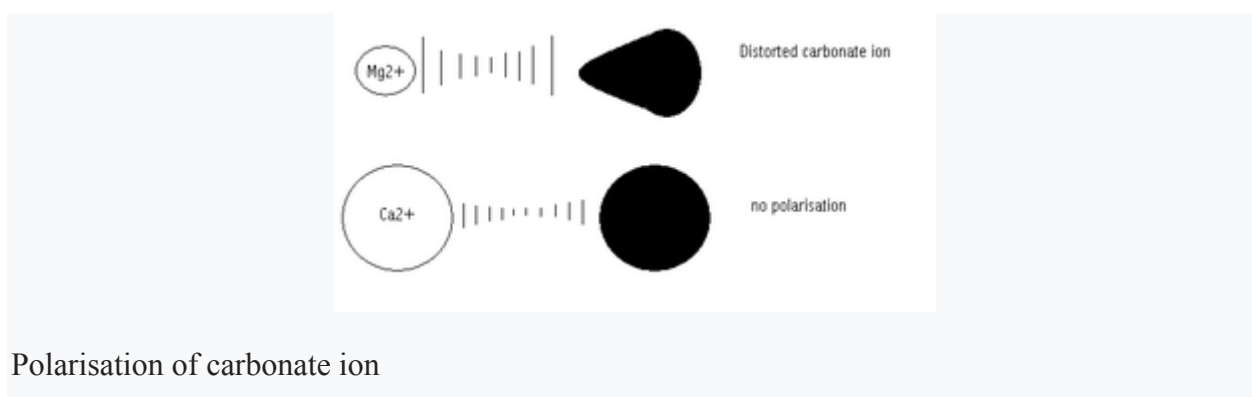
The decomposition temperatures for these reactions are as follows:

$$\text{MgCO}_3 = 350 \text{ }^\circ\text{C}$$

$$\text{CaCO}_3 = 832 \text{ }^\circ\text{C}$$

$$\text{SrCO}_3 = 1340 \text{ }^\circ\text{C}$$

$$\text{BaCO}_3 = 1450 \text{ }^\circ\text{C}$$



Polarisation of carbonate ion

A trend of increasing temperature down the group is evident. This may seem confusing because the magnesium cation is the smallest and they all have the same charge. Magnesium therefore has the greatest lattice enthalpy and the greatest attraction to the carbonate ion. However, this does not result in a higher decomposition temperature - the stronger pull of a smaller cation combined with the diffuse electron cloud of a carbonate ion causes much more polarisation of the carbonate ion to occur.

The change of shape is where the electrons are pulled onto one of the Oxygen atoms causing distortion in the carbonate ion. This change in shape reduces strength and causes the carbonate to break up when heated.

Magnesium Oxide is a particularly favourable product due to its high lattice enthalpy, this contributes to the ease of decomposition of magnesium carbonate and is why magnesium oxide is used as a refractory lining.