Thermodynamics of Inorganic Compounds

Enthalpy (H)

Enthalpy is the heat energy that is being absorbed or evolved during the progression of a chemical reaction.

It is equal to the internal energy of the system plus the product of pressure and volume.

The enthalpy of a thermodynamic system is defined as;

Most chemical reactions occur at constant P, so heat transferred at constant P is called q_p with,

$$q_p = \Delta H = \Delta E - w = \Delta E + P\Delta V = \Delta(E+PV)$$

where H = **Enthalpy** H is defined as $(E + PV)$

ΔH = heat transferred at constant P

ΔH = change in heat content of the system

$\Delta H = H_{final} - H_{initial}$

If $H_{final} > H_{initial}$ then ΔH is positive, Process is **Endothermic**

If $H_{final} < H_{initial}$ then ΔH is negative, Process is **Exothermic**

Enthalpy is a state function and independent of path.

The change in enthalpy associated with a particular chemical process. Most compounds have negative enthalpies of formation.

The standard enthalpy change (ΔH^o) of a reaction is the enthalpy change which occurs when equation quantities of materials react under standard conditions, and with everything in its standard state.

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad \Delta H^o_f = -572\,kJ\,mol^{-1}$$
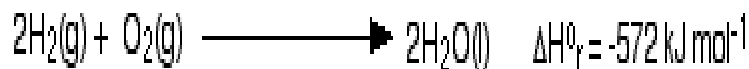
Gibbs Free Energy

It is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G = H - TS$$

Standard Gibbs free energy change is calculated:

$$\Delta G° = \Delta H° - T\Delta S°$$

The entropy change for the reaction

$$CH_{4(g)} + 2O_{2(g)} \longrightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$\Delta S°$ worked out as -242.2 $J\,K^{-1}mol^{-1}$. Convert this to kJ by dividing by 1000.

$$\Delta S° = -0.2422\ kJ\ K^{-1}mol^{-1}.$$

For the combustion of methane, the standard enthalpy of formation is,

$$\Delta H° = -890.4\ kJ\ mol^{-1}.$$

To calculate the Gibbs free energy change at, 298 K, put these values in eq.

$$\Delta G° = \Delta H° - T\Delta S°$$

$$\Delta G° = -890.4 - 298\ x\ (-0.2442) = -817.6\ kJ\ mol^{-1}$$

Bond energy

It is defined as the amount of energy required to break apart a mole of molecules into its component atoms. It is a measure of the strength of a chemical bond. Bond energies of some bond are given in the table.

Bond	Bond Energy (kJ mol⁻¹)
C-H	+413
Cl-Cl	+243
C-Cl	+346
H-Cl	+432

Lattice Enthalpy (Energy)

Lattice Enthalpy measures of the strength of the forces between the ions in an ionic solid.

The lattice energy is defined as the enthalpy change when 1 mole of solid crystal is formed from its scattered gaseous ions. Lattice formation enthalpies are always negative. For NaCl, the lattice formation enthalpy is -787 kJ mol^{-1}.

Or

The enthalpy change needed to convert 1 mole of solid crystal into its scattered gaseous ions. Lattice dissociation enthalpies are always positive. For NaCl, the lattice dissociation enthalpy is +787 kJ mol^{-1}.

| Compound	Lattice Energy
LiF	−1030 kJ/mol
NaCl	−786 kJ/mol
NaBr	−747 kJ/mol
CsCl	−657 kJ/mol
CsI	−600 kJ/mol
MgO	−3795 kJ/mol
CaO	−3414 kJ/mol
SrO	−3217 kJ/mol

Factors affecting lattice enthalpy

The two main factors affecting lattice enthalpy are the charges on the ions and the ionic radii (which affects the distance between the ions).

The charges on the ions

Sodium chloride and magnesium oxide have exactly the same arrangements of ions in the crystal lattice, but the lattice enthalpies are very different.

$$NaCl\text{---------------------------------------} -787.0 \text{ KJmole}^{-1}$$

$$MgO\text{---------------------------------------} -3795 \text{ KJmole}^{-1}$$
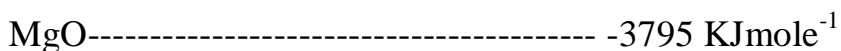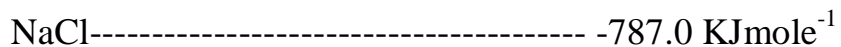
The lattice enthalpy of magnesium oxide is much greater than that of sodium chloride. That's because in magnesium oxide, 2+ ions are attracting 2- ions; in sodium chloride, the attraction is only between 1+ and 1- ions.

The radius of the ions

The lattice enthalpy of magnesium oxide is also increased relative to sodium chloride because magnesium ions are smaller than sodium ions, and oxide ions are smaller than chloride ions.

That means that the ions are closer together in the lattice, and that increases the strength of the attractions. For example, as we go down Group **7** of the Periodic Table from fluorine to iodine, we would expect the lattice enthalpies of their sodium salts to fall as the negative ions get bigger.

The most stable crystal structure of the compound is that with the greatest lattice enthalpy.

Significance of lattice energy

The higher the magnitude of lattice energy, the greater would be the stability of the ionic compound. The higher the magnitude of lattice energy means larger energy of attraction between the cations and anions. Hence, the magnitude of properties such as melting point, boiling point, enthalpy of formation, enthalpy of sublimation would be high for ionic compounds having high the magnitude of lattice energy.

Lattice enthalpies can explain trends in

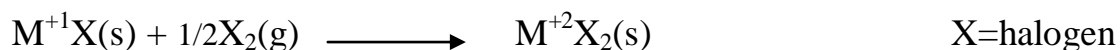- Thermal stability
- Oxidation state stability
- Solubility

Thermal stabilities of ionic solids

• Which carbonate will be more stable, $MgCO_3$ or $BaCO_3$?

$$MgCO_3 \qquad\qquad T_{decomp} \;=\; 573K$$

$$BaCO_3 \qquad\qquad T_{decomp} \;=\; 1573K$$

Stabilities of oxidation states

The same argument is used to account for the fact that high oxidation states are stabilized by small anions

$$M^{+1}X(s) + 1/2X_2(g) \longrightarrow M^{+2}X_2(s) \qquad\qquad X=halogen$$

CuF_2 exists, CuI_2 does not: F is smaller, thus the difference in lattice enthalpies is larger and F is able to stabilize the higher oxidation state

Solubilities

As lattice energy increases, solubility will decrease. The compound that requires the least amount of energy to break apart will be the most soluble compound.

$$MX(s) \longrightarrow M^+(aq) + X^-(aq)$$
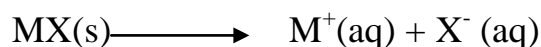
- Dissolution is a complicated process, but lattice enthalpies and hydration enthalpies play important roles.
- Generally, the larger the difference in radii, the more soluble in water.

   CsI is the least soluble compound among the following compounds.

Compound	Lattice Energy (KJ/mol)
LiI	-758
NaI	-704
KI	-658
RbI	-629
CsI	-603

Hess's Law of Constant Heat Summation

"The change in enthalpy is the same whether the reaction takes place in one step or in a series of steps"   or

The total enthalpy of combustion for the reactants is equal to the formation energy of the products plus the combustion energy of the products

The law for constant heat summation was derived in the year 1840, a Swiss-born German Henry Hess, derived a relationship in thermo-chemistry for calculating the standard reaction enthalpy for multistep reactions.
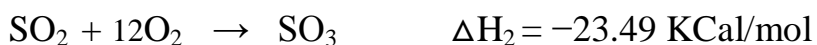
Application of Hess's Law

Consider the formation of SO_3 gas from Sulphur is a multistep reaction involving the formation of SO_2 gas. Let us find out the standard reaction enthalpy for the formation of SO_3 gas from Sulphur.
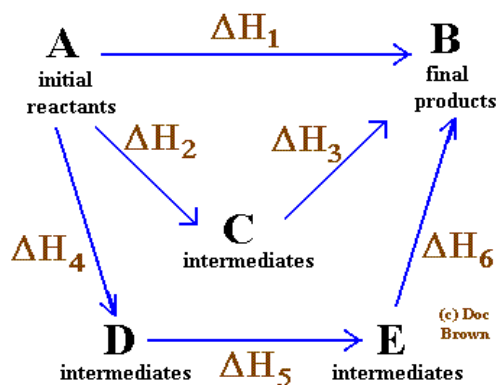
Step 1: Formation of Sulphur Dioxide gas

$$S + O_2 \rightarrow SO_2 \qquad \Delta H_1 = -70.96 \text{ KCal/mol}$$

Step 2: Conversion of SO_2 gas to SO_3 gas

$$SO_2 + 12O_2 \rightarrow SO_3 \qquad \Delta H_2 = -23.49 \text{ KCal/mol}$$

Standard reaction enthalpy as per Hess's Law:

$$\Delta HR = \Delta H_2 + \Delta H_1 = (-70.96) + (-23.49) = -94.95 \text{ KCal/mol}$$

Net reaction:

$$S + 3/2O_2 \rightarrow SO_3 \qquad \Delta H_R = -94.95 \text{KCal/mol}$$
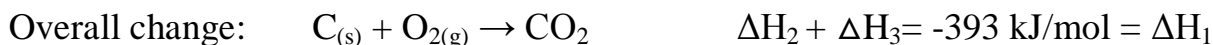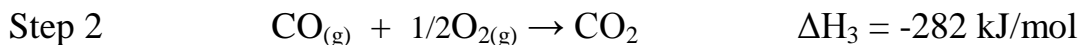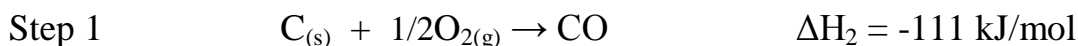
Hence, in simple words we can state:

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$$

Formation of carbon dioxide from carbon and oxygen can occur in one step or two steps. In two steps it can be formed via the production of carbon monoxide.
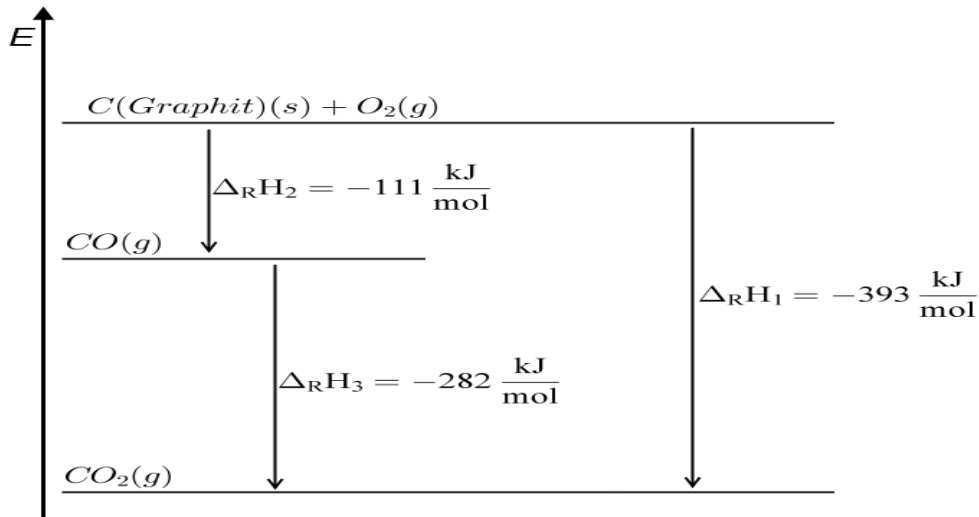
In one step,

$$C_{(s)} + O_{2(g)} \rightarrow CO_2 \qquad \qquad \Delta H_1 = \text{-393 kJ/mol} \ldots\ldots(i)$$

In two steps,

Step 1 $\qquad C_{(s)} + 1/2O_{2(g)} \rightarrow CO \qquad \qquad \Delta H_2 = \text{-111 kJ/mol}$

Step 2 $\qquad CO_{(g)} + 1/2O_{2(g)} \rightarrow CO_2 \qquad \qquad \Delta H_3 = \text{-282 kJ/mol}$

Overall change: $\qquad C_{(s)} + O_{2(g)} \rightarrow CO_2 \qquad \Delta H_2 + \Delta H_3 = \text{-393 kJ/mol} = \Delta H_1$

This is same as equation (i) and the heat change also matches with that. So,

$$\Delta H_1 = \Delta H_2 + \Delta H_3$$

Calculation of Lattice Energy

Lattice Energy of an ionic compound can be calculated by the following methods.

1. Born-Haber Cycles –Based on Hess Law
2. Born-Lande equation – Crystal structure are known
3. Kapustinskii equation – Crystal structure are not known

Born-Haber Cycle

The lattice energy of ionic crystal may be calculated by indirect method which is known as Born-Haber cycle. This method is based on Hess's law of thermo chemistry.
The Born-Haber cycle and calculation of lattice energy of few ionic compounds are shown below.

The Born-Haber cycle of sodium chloride crystal (NaCl)
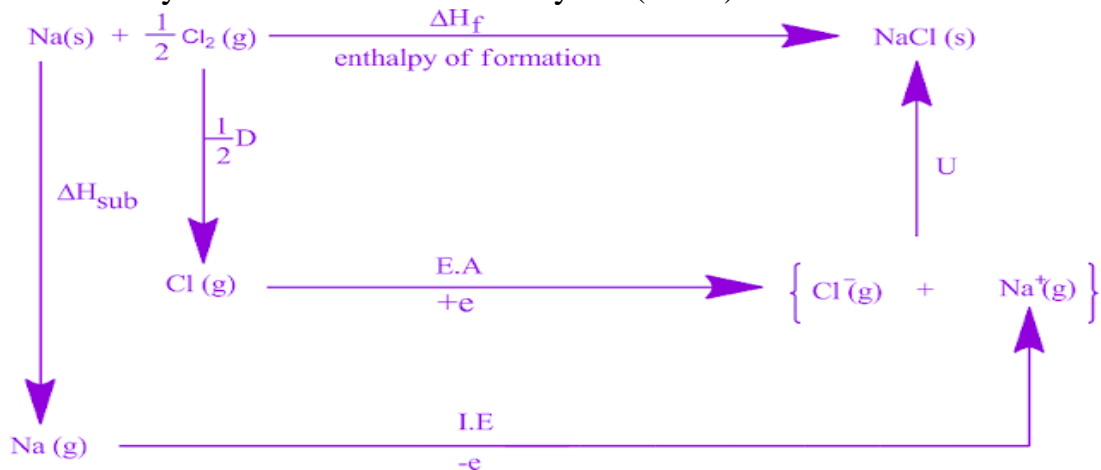
According to Hess's law,
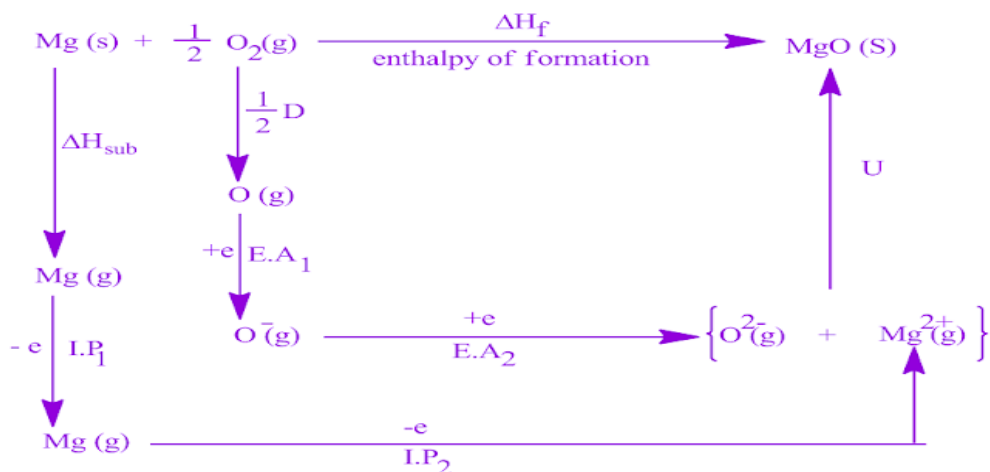
$$\Delta H_f = \Delta H_{sub} + I.E + \frac{1}{2} D + E.A + U$$

$$-411 = +107 + 496 + 122 - 349 + U$$

$$U = -411 - 107 - 496 - 122 + 349$$

$$U = -787 \text{ kJ mol}^{-1}$$

Born-Haber cycle of magnesium oxide, MgO

According to Hess's law,

$$\Delta H_f = \Delta H_{sub} + I.P_1 + I.P_2 + E.A_1 - E.A_2 + \frac{1}{2}D + U$$

8

Applications of Born – Haber cycle

i) It can be used to determine electron gain enthalpy , ionisation energy and lattice energy.

ii) It can be used to explain the stability of molecules.

Born–Landé Equation

The calculation of lattice energy of ionic compounds in direct method is not possible. But the theoretical value of lattice energy can be calculated by Born-Lande equation.

The Born-Lande equation is a mean of calculating the lattice energy of a crystalline ionic compound. In 1918, Max Born and Alfred Landé proposed that the lattice energy could be derived from the electrostatic potential of the ionic lattice and a repulsive potential energy term.

$$U_o = - \frac{N_A M z^+ z^- e^2}{4\pi\varepsilon_0 r_0} \left(1 - 1/n\right)$$

where:

- U_o = Lattice Energy
- N_A = Avogadro constant;
- M = Madelung constant, relating to the geometry of the crystal;
- z^+ = Numeric charge number of cation
- z^- = Numeric charge number of anion
- e = Elementary charge, 1.6022×10^{-19} C
- ε_0 = Permittivity of free space

    $4\pi\varepsilon_0 = 1.112 \times 10^{-10}$ C^2/(J·m)

- r_0 = Distance to closest ion
- n = Born exponent, typically a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically.

The Born–Landé equation shows that the lattice energy of a compound depends on a number of factors;

1. As the charges on the ions increase the lattice energy increases (becomes more -ve)
2. When ions are closer together the lattice energy increases (becomes more -ve)

For instance, Barium oxide (BaO), has the NaCl structure (FCC) and therefore the same Madelung constant, has a bond radius of 275 pm and a lattice energy of -3054 kJ/mol, while sodium chloride (NaCl) has a bond radius of 283 pm and a lattice energy of -786 kJ/mol.

Calculated Lattice Energies

The Born–Landé equation gives an idea to the lattice energy of a system.

Compound	Calculated	Experimental
NaCl	−756 kJ/mol	−787 kJ/mol
LiF	−1007 kJ/mol	−1046 kJ/mol
$CaCl_2$	−2170 kJ/mol	−2255 kJ/mol

Born Exponent

The Born exponent is typically between 5 and 12. Approximate experimental values are listed below:

Ion configuration	He	Ne	Ar, Cu^+	Kr, Ag^+	Xe, Au^+
n	5	7	9	10	12

Determination of Boron Exponent for BaO.

Ba^{+2} is isoelectronic with Xe, so $n = 12$

O^{-2} is isoelectronic with Ne, so $n = 7$

Therefore the value of n for BaO $= \dfrac{12 + 7}{2} = 9.5$

Kapustinskii Equation

Lattice energy, (U_o) of an ionic crystal can be calculated with reasonable accuracy if the structure is known. But how can we calculate U for a new or hypothetical compound of unknown structure?

Recall that the reduced Madelung constant is about the same for different crystal structures. Russian chemist A. F. Kapustinskii recognized this fact and devised a formula in 1956 that allows one to calculate U for any compound if we know the univalent radii of the constituent ions.

$$U_o = K \frac{v \cdot |z^+| \cdot |z^-|}{r^+ + r^-} \left(1 - d/r^+ + r^-\right)$$

Where,

U_o = Lattice Energy

$K = 1.20200 \times 10^{-4} \text{ J·m·mol}^{-1}$

$d = 3.45 \times 10^{-11} \text{ m}$

v = Number of ions in the empirical formula

z^+ and z^- are the numbers of elementary charge on the cation and anion, respectively

r^+ and r^- are the radii of the cation and anion, respectively, in meters

The calculated lattice energy gives a good estimation; the real value differs in most cases by less than 5%.

Furthermore, one is able to determine the ionic radii (or more properly, the thermo-chemical radius) using the Kapustinskii equation when the lattice energy is known. This is useful for rather complex ions like sulfate (SO_4^{2-}) or phosphate (PO_4^{3-})

Born-Mayer Equation

Born–Mayer equation is an equation that is used to calculate the lattice energy of a crystalline ionic compound. It is a refinement of the Born–Landé equation by using an improved repulsion term.

$$U_o = - \frac{N_A M z^+ z^- e^2}{4\pi\varepsilon_0\, r_0} \left(1 - \rho / r_0\right)$$

where:

- U_o = Lattice Energy

- N = Avogadro constant;

- M = Madelung constant, relating to the geometry of the crystal;

- z+ = Charge number of cation

- z− = Charge number of anion

- e = Elementary charge, 1.6022×10^{-19} C

- ε = Permittivity of free space

    $4\pi\varepsilon = 1.112 \times 10{-}10$ $C^2/(J{\cdot}m)$

- r = distance to closest ion
- ρ = A constant dependent on the compressibility of the crystal; 30 pm works well for all alkali metal halides

Kapustinskii observed that A/n is relatively constant but increases slightly with coordination number. Because coordination number also increases with d, the value of A/nd should also be relatively constant.

The Born-Mayer equation gives the total electrostatic interaction energy for a given structure in terms of the Madelung constant, A, for that structure. Something else that varies from structure to structure is the number of ions within the formula unit for a given structure.

Compound	Coord. No.	Madelung Constant, A	A/ν
			ν is the number of ions in the formula unit
Sodium Chloride (NaCl)	6:6	1.74756	0.88
Cesium Chloride (CsCl)	8:8	1.76267	0.87
Zinc Blende (ZnS)	4:4	1.638	0.82
Wurtzite (ZnS)	4:4	1.64132	0.82
Fluorite (CaF$_2$)	8:4	2.51939	0.84
Rutile (TiO$_2$)	6:3	2.408	0.80
Corundum (Al$_2$O$_3$)	6:4	4.1719	0.83

Kapustinskii noted that the ratio of the Madelung constant, A, to the total number of ions per formula unit for a series of compounds with different structures deviate by less than 10% from 0.87, the value found for the NaCl structure.

By replacing A with 0.87ν, taking the average value of n, and making the approximation that the internuclear separation is the sum of the ionic radii, he derived a new expression for the total electrostatic interaction from the Born-Lande equation. This is known as the Kapustinskii equation.