## 1.5.1 Standard Enthalpy of Combustion-

Standard enthalpy of combustion is defined as the enthalpy change when one mole of a compound is completely burnt in oxygen with all the reactants and products in their standard state under standard conditions at 250 C i.e298K and 1 atmospheric pressure.Solution decreases, reaction is endothermic, and ΔH is positive.

Standard enthalpy of combustion is defined as the enthalpy change when one mole of a compound is completely burnt in oxygen with all the reactants and products in their standard state under standard conditions (298K and 1 atm pressure).

 For example:

H2(g)+12O2(g)→H2O(l);ΔcH°=−286kJmol−1

C4H10(g)+132O2(g)→4CO2(g)+5H2O(l);ΔcH°=−2658kJmol−1

Standard enthalpy of reaction

N2(g)​+3H2(g)​→2NH3(g)​

Given:
Bond energyN≡NΔH=946

H−HΔH=435

N−HΔH=989

Standard enthalpy of reaction=∑ΔHreactant−∑ΔHproduct

=∑ΔHN≡N​+3ΔHH−H​−∑6ΔHN−H​

=[946+3×(435)]−[6×389]

=946+1305−2334

## =−83kJ/mol

The enthalpy change for reaction−83kJ/mol.

**Problem:**

The heat of combustion of CH4 (g) at 298K is found to be -885.4KJ/mole. Find the value of enthalpy change.

**Solution:**

The combustion of methane may be represented as-

CH4 (g) +2O2 (g)→ CO2 (g) + 2H2O (l)

ΔE = ΔHC = -885.4KJ/mole

Δn =1 -3 = -2 mole.

Δ H = ΔE + ΔnRT

= -885.4 + (-2) (8.3/4 (298)

= - 885.4 – 4.955

Δ H =- 890.35 KJ

**Problem:**

i) H2 (g) +1/2O2 (g) →H2O (l) ΔHc°=−286kJmol−1

ii)C4H10(g)+13/2 O2(g)→4CO2(g)+5H2O(l);ΔHc°=−2658kJmol−1

## iii) CH4 + 2O2⟶CO2 + 2H2OΔHc° = - 890kJ mol-1

## iv) Calculate the enthalpy of combustion of methane,if the standard enthalpies of formation of methane, carbon dioxide, water are -74.85,-393.5 and -286kJ mol-1?

Theenthalpyassociated with the combustion reaction.

CH4(g)+O2(g)→CO2(g)+2H2O(l)

Now it is a fact that,

ΔHc°=ΣΔH°f(products)−ΣΔH°f(reactants)

Given the appropriate data,

ΔHc°={(−393.5−2×286)−(−74.85)}⋅kJ⋅mol−1

=−890.7⋅kJ⋅mol−1

**1.5.2 Standard Enthalpy ofNeutralization-**

The standard enthalpy change of neutralizationis theenthalpy changewhen solutions of an acid and an alkali react together understandardconditions to produce 1 mole of water. Enthalpy change of neutralizationis always measured per mole of water formed.

The enthalpy of neutralization (ΔHn​) is the change in enthalpy that occurs when one equivalent of an acid and one equivalent of a base undergo a neutralization reaction to form water and a salt. It is a special case of the enthalpy of reaction. It is defined as the

HCl(aq)+ NaOH(aq)→ NaCl(aq)+ H2O(l)ΔHn​=−55.2 kJ/mole

The standard enthalpy change of neutralization is theenthalpy change when solutions of an acid and an alkali react together under standard conditions i.e. at 250C (298 0K) and one atmospheric pressure to produce 1 mole of water.

Strong Monobasic Base andStrong Dibasic Acid

HCl(aq)+ NaOH(aq)→ NaCl(aq)+ H2O(l)ΔHn​=−55.2 kJ/mole

H2SO4(aq)+ 2NaOH(aq)→ Na2SO4(aq)+ 2H2O(l)ΔHn​=−55.8 kJ/mole

**1.6 Integral and differential enthalpies of solution and dilution:**

**I.** Integral Enthalpy of Solution is the heat absorbed or released when a solute is dissolved in a definite amount of solvent. The heat of solution depends on the nature of the solute and on its concentration in the final solution. The integral heat of solution when one mole of solute is added to an infinite amount of solvent is sometimes written as delta infinitysoln.

**II.** Differential heat of solution is the partial derivative of the total heat of solution with respect to the molal concentration of one component of the solution, when the concentration of the other component or components, the pressure, and the temperature are held constant.

**III.** Enthalpy of dilution is the enthalpy change associated with the dissolution of a substance in a solvent at constant pressure resulting in infinite dilution. Enthalpy of dilution is most often expressed in kJ/mol at constant temperature. The energy change can be regarded as being made of three parts, the endothermic breaking of bonds within the solute and within the solvent, and the formation of attractions between the solute and the solvent. An ideal solution has an enthalpy of solution of zero.

Enthalpy of dilution, also known as the heat of dilution, can be defined as the change in enthalpy that is associated with the dilution of a specific component of a solution when the pressure is kept constant. Usually, the enthalpy of dilution of a component in a solution is expressed in terms of energy per amount of substance. However, this quantity can also be expressed in terms of energy per unit mass. The most common units used to express enthalpy of dilution are joules per mole (J/mol) and kilojoules per mole (kJ/mol).

**1.6.1 Enthalpy of Dilution – Differential and Integral--**

Enthalpy of dilution can be defined in two different ways – in terms of integral heat and in terms of differential heat. When it comes to differential heat of dilution, the enthalpy is considered at a very small scale. Here, change in enthalpyassociated with the addition of a very small quantity of the solvent to a relatively huge quantity of the solution. The molar differential enthalpy of dilution can be defined as the change in enthalpy associated with the addition of one mole of the solvent to a comparatively large amount of solution when the pressure and the temperature of the environment are kept constant.

The integral perspective, the enthalpy of dilution is calculated by considering the solution at the macroscopic scale. A dilution process is considered where the solution is diluted from a specific initial concentration to a specific final concentration. Therefore, the molar integral enthalpy of dilution can be evaluated by calculating the total enthalpy change associated with the change in the dilution of the solution and normalizing this value by the number of moles of the solute.

## 1.6.2Molar enthalpy of solution-

## Molar enthalpy of solution is the energy released or absorbed per mole of solute being dissolved in solvent. If heat is absorbed when the solute dissolves, temperature of solution decreases, reaction is endothermic, and ΔH is positive.

Enthalpy changes also occur when a solute undergoes the physical process of dissolving into a solvent.

CaCl2(s)→Ca2+(aq)+2Cl−(aq) +82.8kJ

The**molar heat of solution**(ΔHsoln)of a substance is the heat absorbed or released

when one mole of the substance is dissolved in water.

Example- Calcium chloride ΔHsoln=−82.8kJ/mol

Use ammonium nitrate, which absorbs heat from the surroundings when it

dissolves.

NH4NO3(s)+25.7kJ→NH+4(aq)+NO−3(aq)

As the ammonium nitrate dissolves, it absorbs heat from the body and helps to

limit swelling. For ammonium nitrate,olΔHsoln=25.7kJ/mol.

**1.7Bond Energy:**

Bond energy (E)is defined as the amount ofenergyrequired to break apart a[mole](https://www.thoughtco.com/mole-definition-in-chemistry-606377)ofmoleculesinto its component [atoms](https://www.thoughtco.com/definition-of-atom-and-examples-604373). It is a measure of the strength of a chemical bond. Bond energy is also known as bond enthalpy (H) or simply as bond strength.

Bond energy is based on an average of bond dissociation values for species in the gas phase at a temperature of 298Kelvin. It may be measuring or calculating the enthalpy change of breaking a molecule into its component atoms and ions and dividing the value by the number of chemical bonds.

**Example-**

The enthalpy change of breaking methane (CH4) into a carbon atom and four hydrogen ions, divided by four (the number of C-H) bonds, yields the bond energy.Bond energy is not the same thing as bond-dissociation energy. Bond energy values are an average of the bond-dissociation energies within a molecule.

**1.7.1 Calculation of Bond Energy:**

**i) Bond Dissociation Energy:**

Bond dissociation energy is defines as the amount ofenergywhich is required to homolytically fracture a chemical [bond](https://www.thoughtco.com/definition-of-bonds-in-chemistry-604392). A homolytic fracture usually produces radical species. Shorthand notation for this energy is BDE,D0, orDH°. Bond dissociation energy is often used as a measure of the strength of a chemical bond and to compare different bonds.

**a)** Bond dissociation energy is the energy required to break a chemical bond.

**b)** It is one means of quantifying the strength of a chemical bond.

**c)**Bond dissociation energy equals bond energy only for diatomic molecules.

**d)** The strongest bond dissociation energy is for the Si-F bond. The weakest energy is for a covalent bond and is comparable to the strength of intermolecular forces.

**ii) Bond Dissociation Energy versus Bond Energy**

Bond dissociation energy is only equal to bond energy fordiatomic molecules. This is because the bond dissociation energy is the energy of a single chemical bond, while bond energy is the average value for all the bond dissociation energies of all bonds of a certain type within a molecule.

**Example-**

Consider removing successive hydrogen atoms from a methane molecule. The first bond dissociation energy is 105 kcal/mol, second is 110 kcal/mol, third is 101 kcal/mol, and final is 81 kcal/mol. So, the bond energy is the average of the bond dissociationenergies, or 99 kcal/mol. In fact, the bond energy doesn't equal the bond dissociation energy for any of the C-H bonds in the methane molecule.

**1.8 Effect of Temperature onHeat of Reaction:**

**The Kirchhoff Equation**

Theheatchange accompanying chemical or physical processes depends on the temperature at which the process takes place. This dependence is mathematically expressed in the form is known as Kirchhoff equation.

Kirchhoff’s Equation is equality expressing the temperature dependence of the thermal quantities linked with a chemical reaction through the difference in heat capacities between the products and reactants. The same reaction, when carried at dissimilar temperatures, the enthalpies of reaction are different.

Kirchhoff equation relates the heat of reaction with the definite heats of a structure before and after the reaction. Kirchhoff equation is represented as

dQ/dt = C – C’

Where, Q is the heat energy evolved throughout the procedure at temperature‘t’ without modifying in volume and C is the specific heats of the reactants and C’ is the specific heats of products.

Consider the process in which the reactants in state ‘A’ at temperature T1 are converted into products in state ‘B’ a temperature T2. Assume that all operations are carried out at constant pressure. The conversion may be carried out in two ways but according to Hess’s law, the total heat change must be the same in both cases.

**(1)** The reactants in state (A) at temperature T1are heated to a temperature T2. The heat absorbed is (∆T) (CP)A. where ∆T = T2– T1, and (CP)Ais the heat capacity of the reactants in the state (A). The reaction is now allowed to take place at this temperature and the heat change for the process is (HB– HA)2= ∆H2

The total heat change for the process =**(∆T) (CP)A+ ∆H2.**

**(2)** The reactants in state (A) at temperature T1 are considered to products in state B at the same temperature. The heat cement change = (HB– HA)1= ∆H1. The temperature of the products is then raised from T1to T2and the heat absorbed is (∆T) (CP)B, where (CP)Bis the heat capacity of the products.

The total heat change for the process =**(∆T) (CP)B+ ∆H1.**

From Hess’s law,

**(∆T) (CP)A+ ∆H2= (∆T) (CP)B+ ∆H1**

or, ∆H2– ∆H1= [(CP)B– (CP)A] x (∆T)

= ∆CP(∆T)

where, ∆CP= (CP)B– (CP)A

or,**[∆H2– ∆H1] / ∆T = ∆CP**

For an infinitesimally small change in temperature, one can write,

**[d∆H / dT] = ∆CP** (1)

Similarly, it may be shown that if the process is carried out at constant volume the relationship is;

**[d∆U / dT] = ∆C**  (2)

The relationships (1) and (2) are different forms of the Kirchhoff equation. The equations are useful for calculating the heat of reactions at a given temperature when the value is known at another temperature provided the heat capacities of the reactants and products are also known.

A temperature transform occurs when the temperature is increased or decreased by the flow of heat. This shifts the chemical equilibrium toward the products or reactants, which can be resolute by studying the reaction and deciding whether it is endothermic or exothermic.

**Example**

The heat of reaction (**∆H) for the formation ofNH3.N2 +3H2 = 2NH3 at**

**270C was found to be -91.95KJ.What will be the heat of reaction** (**∆H) at 500C. The molar heat capacities at constant pressure and at 270C for N2, H2 and NH3 are 28.45,28.32 and 37.07joules respectively.**

**Solution: Applying Kirchhoff’s equation at constant pressure.**

**∆H2 - ∆H1 =∆Cp (T2- T1) T1 = 27 +273 = 300K**

**∆H1 = -91.95KJ T2 = 50 +273 = 323K**

**T2 - T1 = 323 -300 =23K**

∆CP= (Heat capacity of products) – ( Heat capacity of reactants)

 **= ( 2 x 37.07) – ( 28.45 +3 x 28.32) = -39.28 J = - 39.28 x10-3 KJ**

∴**∆H2 = ∆H1 + ∆Cp (T2 - T1)**

 **= - 91.94 + ( -39.28 x10-3 x 23 )**

∴**∆H2 = - 91.94 – 0.904 = - 92.84 KJ**