

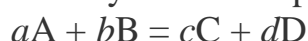
## Thermochemistry

Many chemical and physical processes of interest are carried out at atmospheric (essentially constant) pressure. Under this condition, the heat exchanged during the process equals the change in enthalpy according to equation  $Q_p = \Delta H$

It is also possible that a reaction takes place in a closed container; in such a case the heat exchanged equals the change in internal energy (i.e.,  $Q_v = \Delta E$ ).

## Heat of Formation

For any reaction represented by the chemical equation



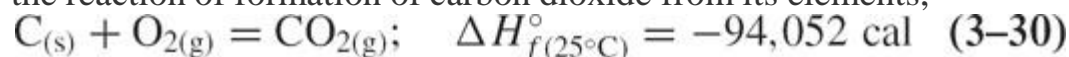
the enthalpy change can be written as

$$\Delta H = \sum \bar{H}_{\text{products}} - \sum \bar{H}_{\text{reactants}} \quad (3-28)$$

$$\Delta H = c\bar{H}_C + d\bar{H}_D - a\bar{H}_A - b\bar{H}_B \quad (3-29)$$

where  $\bar{H}$  = enthalpy per mole (called the molar enthalpy) and  $a$ ,  $b$ ,  $c$ , and  $d$  are stoichiometric coefficients.

the reaction of formation of carbon dioxide from its elements,



Here

$$\Delta H_{f(25^\circ C)}^\circ = \bar{H}(CO_2, g, 1 \text{ atm}) - \bar{H}(C, s, 1 \text{ atm}) - \bar{H}(O_2, g, 1 \text{ atm}) \quad (3-31)$$

If the  $\bar{H}$  values for the elements  $C_{(s)}$  and  $O_{2(g)}$  are chosen arbitrarily to be zero, then according to equation (3-31), the molar enthalpy of the compound,  $\bar{H}(CO_2, g, 1 \text{ atm})$ , is equal to the enthalpy of the formation reaction,  $\Delta H_{f(25^\circ C)}^\circ$ , for the process in equation (3-30) at 1 atm of pressure and 25°C.

The standard heat of formation of gaseous carbon dioxide is  $\Delta H_{f(25^\circ C)}^\circ = -94,052 \text{ cal}$ . The negative sign accompanying the value for  $\Delta H$  signifies that heat is evolved, that is, the reaction is exothermic.

## Standard Enthalpy

In thermodynamics, the convention of assigning zero enthalpy to all elements in their most stable physical state at 1 atm of pressure and 25°C is known as choosing a standard or reference state:

$$\bar{H}^\circ(\text{compound}) \equiv \Delta \bar{H}_f^\circ$$

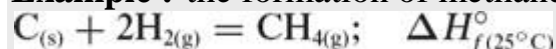
### Hess's Law and Heat of Combustion

**Hess's Law** :- $\Delta H$  depends only on the initial and final states of a system, *Hess's law of constant heat summation* and is used to obtain heats of reaction that are not easily measured directly.

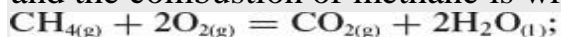
thermochemical equations for several steps in a reaction could be added and subtracted to obtain the heat of the overall reaction.

**heat of combustion**:- that is, the heat involved in the complete oxidation of 1 mole of a compound at 1 atm pressure, to convert the compound to its products

**Example** :-the formation of methane is written as



and the combustion of methane is written as

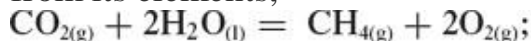


$$\Delta H_{\text{comb}(25^\circ\text{C})}^\circ = -212.8 \text{ kcal}$$

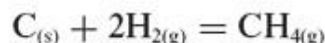
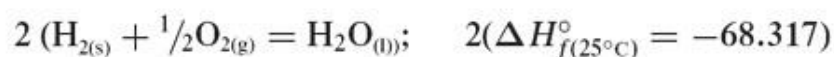
The enthalpies of formation of both  $\text{CO}_{2(g)}$  and  $\text{H}_2\text{O}_{(l)}$  have been measured with extreme accuracy; therefore,  $\Delta H_{f(25^\circ\text{C})}^\circ$  for methane gas can be obtained by subtracting  $\Delta H_{f(25^\circ\text{C})}^\circ$  of  $\text{CO}_{2(g)}$  and twice that of  $\text{H}_2\text{O}_{(l)}$  from the heat of combustion:

One can, for instance, choose the reaction of formation of carbon dioxide

from its elements,



$$\Delta H_{\text{comb}f(25^\circ\text{C})}^\circ = +212.8 \text{ kcal}$$



$$\Delta H_{f(25^\circ\text{C})}^\circ(\text{CH}_4, \text{g}) = -\Delta H_{\text{comb}}^\circ + \Delta H_f(\text{CO}_2, \text{g}) + 2 \times \Delta H_f(\text{H}_2\text{O}, \text{l})$$

$$= 212.8 \text{ kcal} + (-94.052 \text{ kcal}) + 2(-68.317 \text{ kcal})$$

$$= -17.886 \text{ kcal}$$

### Heats of Reaction from Bond Energies

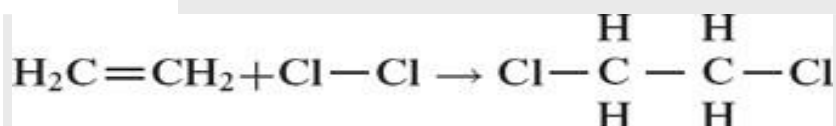
In a chemical reaction, bonds may be broken and new bonds may be formed to give rise to the product.

The net energy associated with the reaction

**heat of reaction**:- can be estimated from the bond

energies that are broken and the bond energies that are formed during the reaction process.

**Example :-** The covalent bonding energy in the reaction



can be calculated from knowing a C=C bond is broken (requiring 130 kcal), a Cl—Cl bond is broken (requiring 57 kcal), a C—C bond is formed (liberating 80 kcal), and two C—H bonds are formed (liberating  $2 \times 78$  or 156 kcal). Thus, the energy  $\Delta H$  of the reaction is  $\Delta H = 130 + 57 - 80 - 156 = -49$  kcal

Because  $1 \text{ cal} = 4.184 \text{ joules}$ ,  $-49 \text{ kcal}$  is expressed in SI units as  $-2.05 \times 10^5 \text{ joules}$ .

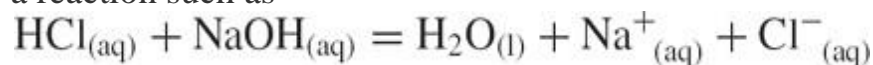
### **Applications of Thermochemistry**

1-Determination Heat-of-mixing data a reaction such as precipitation is occurring during the mixing of two salt solutions. If no reaction takes place when dilute solutions of the salts are mixed, the heat of reaction is zero.

2-Differentiation between strong acids and strong bases:- strong acids and strong bases are completely ionized in water so that heat of neutralization remain constant.



No combination occurs between any of the other species in a reaction such as



3-Determination of the number of calories obtained from various foods.

4-Thermodynamic measurements(binding affinity of drug) (Gibbs energy, enthalpy, entropy, heat capacity change) which can be applied to the drug development process.