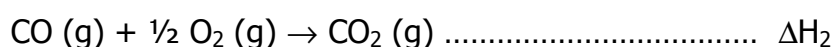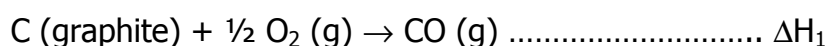## Hess's Law

Heat of reaction is an enthalpy change. Since enthalpy is a state function, the change in enthalpy depends upon the initial and final states of the system. A chemical reaction can be carried out with different ways. As long as the reactants and the products are the same, the heat of reaction will be the same. The heat of reaction does not depend upon side reactions or intermediate reactions. It does not depend upon the path between the reactants and the products.

Hess's Law is based on the properties of enthalpy. According to this law, chemical reactions are considered as algebraic equations in thermochemical calculations. They can be added, subtracted or multiplied by certain numbers. The operation should be applied to the heats of reaction.
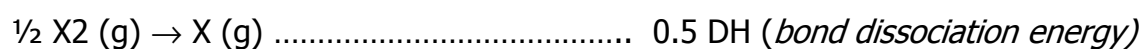
C (graphite) + ½ O_2 (g) $\rightarrow$ CO (g) .... ΔH_1

CO (g) + ½ O_2 (g) $\rightarrow$ CO_2 (g) .... ΔH_2

Net change is;

C (graphite) + O_2 (g) $\rightarrow$ CO_2 (g) .... $\Delta H_3 = \Delta H_1 + \Delta H_2$

Born-Haber Cycle

Born-Haber cycle depends upon Hess's Law. It is used to calculate the cohesive energy of ionic crystals (MX). The cohesive energy of an ionic crystal is the energy of the crystal relative to the infinitely separated ions. So, the ions are gases, M^+(g) and X^-(g). Cohesive energy can not be measured directly, it is calculated for the below changes using Hess's Law.

M (s) $\rightarrow$ M (g) .... ΔH_{sub} (*sublimation energy*)

M (g) $\rightarrow$ M^+(g) + e- (g) .... IP (*ionization potential)*

½ X2 (g) $\rightarrow$ X (g) .... 0.5 DH (*bond dissociation energy)*

X (g) + e- (g) $\rightarrow$ X^-(g) .... $-$EA (*electron affinity)*

X^-(g) + M^+(g) $\rightarrow$ MX (s) .... $-$CE (*cohesive energy)*

Heat of formation of the ionic crystal may be obtained by adding all these equations;

ΔH (MX) = ΔH$_{sub}$ + IP + 0.5 DH − EA − CE

and this equation can be solved for the cohesive energy.

Dependence of ΔH$_r$ on Temperature

For a chemical reaction, the standard heat of reaction may be written as;

ΔH^o_r = H$^o_{products}$ - H$^o_{reactants}$

In order to find how ΔH^o_r changes with temperature, we differentiate this equation with respect to T;

$$\frac{d\Delta H^{o}{}_{r}}{dT} = \frac{dH^{o}{}_{P}}{dT} - \frac{dH^{o}{}_{R}}{dT}$$

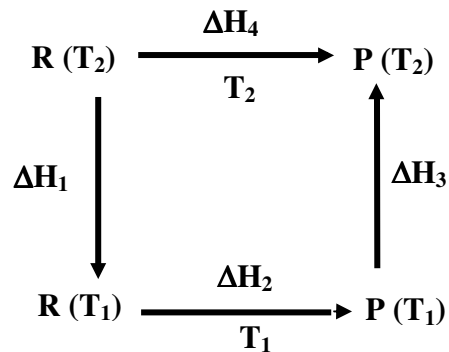dH^O/dT is the change in enthalpy with temperature at constant pressure. It is constant pressure heat capacity C$_p{}^o$

$$\frac{d\Delta H^{O}{}_{r}}{dT} = (C_p{}^o)_{products} - (C_p{}^o)_{reac\tan ts} = \Delta C_p{}^o$$

Integrating between limits we obtain;

$$\int_{T_1}^{T_2} d\Delta H^o{}_r = \int_{T_1}^{T_2} \Delta C_p{}^o dT$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p{}^o dT$$

This equation indicates that the reaction takes place according to the below cycle;

$$R\ (T_2) \xrightarrow[T_2]{\Delta H_4} P\ (T_2)$$

$$\Delta H_1 \downarrow \qquad \uparrow \Delta H_3$$

$$R\ (T_1) \xrightarrow[T_1]{\Delta H_2} P\ (T_1)$$

Since ΔH is independent of the path, the heat of reaction at T_2 is;

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

$$= \int_{T_1}^{T_2} (C_p^{\ o})_R\, dT + \Delta H_{T_1} + \int_{T_1}^{T_2} (C_p^{\ o})_P\, dT$$

$$= \Delta H_{T_1} + \int_{T_1}^{T_2} [(C_p^{\ o})_P - (C_p^{\ o})_R]\, dT = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p^{\ o}\, dT$$

where;

$$\Delta C_p^{\ o} = \sum_P n_i \overline{C}_{p,i}^{\ o} - \sum_R n_i \overline{C}_{p}{}^{,}{}_i^{\ o}$$

If the temperature range is small, C_p is a constant. However, C_p is a function of T and generally given as;

$$C_p = a + bT + cT^2$$

Heat of Solution

The heat of solution is the enthalpy change associated with the addition of a specified amount of solute to a specified amount of solvent at constant T and P.

If the force of attraction between solute molecules is large, then energy is needed to dissolve the solute. Such processes are **"endothermic".** If force of attraction between a solute molecule and a solvent molecule is large then the system emits energy to the surroundings. The solution process is **"exothermic".**

Integral heat of solution is the enthalpy change associated with the addition of 1 mole of solute to n moles of solvent.

Heat of solution depends upon the concentration of the resulting solution. As the concentration of the solution decreases, the heat of solution approaches a limiting value, **heat of solution in the infinitely dilute solution.**

Heat of dilution is the enthalpy change associated with the addition of a specified amount of solvent to a specified amount of solution. Heat of dilution depends upon the concentrations of the initial and final solutions.

Heat of Formation of a solution is the sum of the integral heat of solution and the heat of formation of the solute.

Calculation of ΔH_r by using Bond Energies

In cases where heats of formation of the substances are unknown, bond energies are used to calculate heats of reaction. **Standard bond dissociation energy** is the enthalpy change of the system when 1 mole of the bond is broken at 1 atm pressure and 25°C. In this change, the reactants and the products are assumed to be gases at 1 atm and 25°C. Bond dissociation of the bond A − B is the enthalpy change of the following reaction;
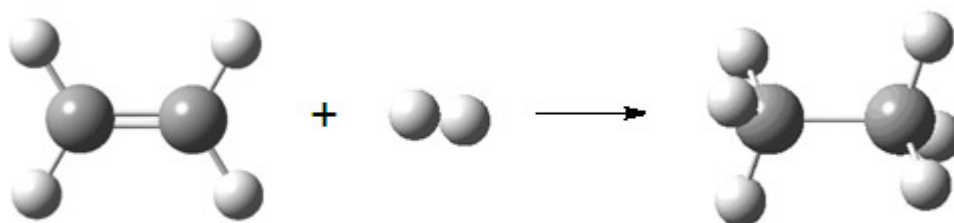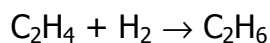
A − B (g) $\rightarrow$ A (g) + B (g) ………………………….. DH^o (A − B)
DH^o (A − B) = $\Delta H^o_{f,A} + \Delta H^o_{f,B} - \Delta H^o_{f,AB}$

When a bond is broken, heat is transferred from the surroundings to the system $\Delta H > 0$. Conversely, when a bond is formed, the system emits energy to the surroundings $\Delta H < 0$.

H_2O (g) $\rightarrow$ 2H (g) + O (g) .... ΔH^{o}_{25} = 221.14 kcal

So, bond dissociation energy of 1 mole O − H bond is ½ (221.14) = 110.57 kcal

In the hydrogenation of ethylene,

$C_2H_4 + H_2 \rightarrow C_2H_6$

the changes that take place during the reaction are;

H − H bond is broken .... $\Delta H = DH^{o}$ (H-H) = 103.2 kcal
C = C bond is broken .... $\Delta H = DH^{o}$ (C=C) = 145.0 kcal
C − C bond is formed .... $\Delta H = - DH^{o}$ (C- C) = -80.5 kcal
2 (C − H) bonds are formed .... $\Delta H = -2DH^{o}$ (C-H) = -196.4 kcal

Total enthalpy change is ΔH_r = -29.0 kcal

Adiabatic Flame Temperature

Adiabatic flame temperature is the temperature which would be attained if the compound were burned adiabatically. In fact, it is the highest temperature that could be attained in a chemical reaction.

If exothermic reactions are carried out adiabatically, the products will be at a very high temperature. We suppose the adiabatic reaction occurs in two steps;

Reactants (T_o, P) $\rightarrow$ Products (T_o, P) .... $\Delta H_{To} = \Delta H_1$

Products (T_o, P) $\rightarrow$ Products (T_f, P) .... $\Delta H = \Delta H_{To} + \int_{T_o}^{T_f} C_p(P)dT$

Since the reaction is adiabatic and the pressure is constant;

$Q_p = \Delta H = 0$

$-\Delta H_{To} = \int_{T_o}^{T_f} C_p(P)dT$

In exothermic reactions, the heat emitted to the surroundings is spent to increase the temperature of the products in adiabatic conditions.