Unit 4: APPLICATIONS OF THE FIRST LAW

4.1-Thermodynamic cycle

A thermodynamic cycle is a sequence of successive transformations that starts with a thermodynamic system in a given state, transforms it and finally returns it to its initial state, so that the cycle can be restarted. During the cycle, the system's temperature, pressure and other state parameters change, while it exchanges work and carries out heat transfer with the outside world.

There are many thermodynamic cycles, including the following1.

- The **Carnot cycle** consists of isothermal compression, adiabatic compression, isothermal expansion and adiabatic expansion.

- The **Stirling cycle** consists of isochoric compression, isothermal expansion, isochoric expansion and isothermal compression.

- The **Brayton cycle** consists of adiabatic compression, isobaric expansion, adiabatic expansion and isobaric contraction.

- The **Diesel cycle** consists of adiabatic compression, isobaric expansion, adiabatic expansion and isochoric compression.

4.2-Thermochimie

4.2.1 ENTHALPY CHANGE, ΔrH OF A REACTION – REACTION ENTHALPY

In a chemical reaction, reactants are converted into products and is represented by,

$$\textbf{Reactants} \rightarrow \textbf{Products}$$

The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction, is given by the symbol $\Delta_r H$

$$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

$$\Delta_r H = \sum a\Delta H_{\text{products}} - \sum b\Delta H_{\text{reactants}}$$

(Here symbol ∑ (sigma) is used for summation and a and b are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation. For example, for the reaction

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

$$\Delta_r H = \sum a\Delta H_{\text{products}} - \sum b\Delta H_{\text{reactants}}$$

$$\Delta r\ H = \Delta r\ H(CO2.g) + 2\ \Delta r\ H(H_2O.l) - \Delta r\ H(CH_4.g) + 2\ \Delta r\ H(O_2.g)$$

Enthalpy change is a very useful quantity. Knowledge of this quantity is required when one needs to plan the heating or cooling required to maintain an industrial chemical reaction at constant temperature. It is also required to calculate temperature dependence of equilibrium constant.

(a) Standard enthalpy of reactions

Enthalpy of a reaction depends on the conditions under which a reaction is carried out. It is, therefore, necessary that we must specify some standard conditions. The standard enthalpy of reaction is the enthalpy change for a reaction when all the participating substances are in their standard states.

The standard state of a substance at a specified temperature is its pure form at 1 bar. For example, the standard state of liquid ethanol at 298 K is pure liquid ethanol at 1 bar; standard state of solid iron at 500 K is pur e iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript ° to the symbol ΔH, e.g., $\Delta H°$

(b) Enthalpy changes during phase transformations

Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).

$$H_2O\ (s) \rightarrow H_2O\ (l)\ ;\ \Delta_{fus}H° = 6\ KJ.mol^{-1}$$

Here $\Delta_{fus}H°$ is enthalpy of fusion in standard state. If water freezes, then process is reversed and equal amount of heat is given off to the surroundings.

The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called standard enthalpy of fusion or molar enthalpy of fusion, ΔH_{fus} .

Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point Tb and at constant pressure:

$$H_2O\ (l) \rightarrow H_2O\ (g)\ ;\ \Delta_{vap}H° = 40\ KJ.mol^{-1}$$

$\Delta_{vap}H°$ is the standard enthalpy of vaporization.

Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1bar) is called its standard enthalpy of vaporization or molar enthalpy of vaporization, $\Delta\ vapH°$.

The magnitude of the enthalpy change depends on the strength of the intermolecular interactions in the substance undergoing the phase transformations. For example, the strong hydrogen bonds between water molecules hold them tightly in liquid phase. For an organic liquid, such as acetone, the intermolecular dipole-dipole interactions are significantly weaker. Thus, it requires less heat to vaporize 1 mol of acetone than it does to vaporize 1 mol of water. Table 1 gives values of standard enthalpy changes of fusion and vaporization for some substances.

Table 4. 1. Standard enthalpy changes of fusion and vaporisation.

Substance	**Tf (°K)**	**ΔfusH°(kJ.mol^{-1})**	**Tb (°K)**	**ΔfusH°(kJ.mol^{-1})**
N_2	63.15	0.72	77.35	5.59
NH_3	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH_3COCH_3	177.8	5.72	329.4	29.1
CCl4	250.16	2.5	349.69	30.0
H_2O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C_6H_6	278.65	9.83	353.25	30.8

Problem: A swimmer coming out from a pool is covered with a film of water weighing about 18g. How much heat must be supplied to evaporate this water at 298 K? Calculate the internal energy of vaporization at 100°C. $\Delta_{vap}H°$ for water at 373K = 40.66 kJ mol^{-1}

Solution

We can represent the process of evaporation as vaporization

$$\mathbf{18g\ H_2O\ (l) \rightarrow 18g\ H_2O\ (g)}$$

No. of moles in 18 g H_2O(l) is 18g

n= m/M=18g/18 g mol^{-1} = 1 mol

$\Delta vapU° = \Delta\ vapH° - P\,\Delta V = \Delta_{vap}H° - \Delta n\,RT$

(assuming steam behaving as an ideal gas).

$\Delta\ vapH° - \Delta nRT = 40.66\ kJ\ mol^{-1} - (1)(8.314\ JK^{-1}\ mol^{-1})(373K)(10^{-3}kJ\ J^{-1})$

$\Delta vap\ U° = 40.66\ kJ\ mol^{-1} - 3.10\ kJ\ mol^{-1} = 37.56\ kJ\ mol^{-1}$

(c) Standard enthalpy of formation

The standard enthalpy change for the formation of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H°$, where the subscript ' f ' indicates that one mole of the compound in question has been formed in its standard state from its elements in their most stable states of aggregation. The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H_2 gas and those of dioxygen, carbon and sulphur are O_2 gas, $C_{graphite}$ and $S_{rhombic}$ respectively. Some reactions with standard molar enthalpies of formation are given below.

$$\mathbf{H_2\,(g) + \tfrac{1}{2}\, O_2(g) \rightarrow H_2O\,(l)\ ;\ \Delta_f H° = -285.8\ KJ.mol^{-1}}$$

$$\mathbf{C\,(graphite.s) + 2\, H_2(g) \rightarrow CH_4\,(g)\ ;\ \Delta_f H° = -74.81\ KJ.mol^{-1}}$$

$$\mathbf{C\,(graphite.s) + 3\, H_2(g) + \tfrac{1}{2}\, O_2 \rightarrow C_2H_5OH\,(l)\ ;\ \Delta_f H° = -277.7\ KJ.mol^{-1}}$$

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H°$, is just a special case of $\Delta rH°$, where one mole of a compound is formed from its constituent elements, as in the above three equations, where 1 mol of each, water, methane and ethanol is formed. In contrast, the enthalpy changes for an exothermic reaction:

$$\mathbf{CaO\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s)\ ;\ \Delta_r H° = -178.3\ KJ.mol^{-1}}$$

is not an enthalpy of formation of calcium carbonate, since calcium carbonate has been formed from other compounds, and not from its constituent elements. Also, for the reaction given below, enthalpy change is not standard enthalpy of formation, $\Delta_f H$ for HBr(g).

$$\mathbf{H_2(g) + Br_2(l) \rightarrow 2HBr\,(g)\ ;\ \Delta_r H° = -72.8\ KJ.mol^{-1}}$$

Here two moles, instead of one mole of the product is formed from the elements, i.e.,

$$\mathbf{\Delta_r H° = 2\Delta_f H°}$$

Therefore, by dividing all coefficients in the balanced equation by 2, expression for enthalpy of formation of HBr (g) is written as

$$\mathbf{\tfrac{1}{2}\, H_2(g) + \tfrac{1}{2}\, Br_2(l) \rightarrow HBr\,(g)\ ;\ \Delta_f H° = -72.8\ KJ.mol^{-1}}$$

Standard enthalpies of formation of some common substances are given in Table 2.

Table 4.2. Standard enthalpies of formation.

Substance	$\Delta_f H°$(kJ.mol^{-1})	Substance	$\Delta_f H°$(kJ.mol^{-1})
Al_2O_3(s)	-1675.7	HI(g)	+26.48
$BaCO_3$(s)	-1216.3	KCl(s)	-436.75
Br_2(l)	0	KBr(s)	-393.8
Br_2(g)	+30.91	MgO(s)	-601.7
$CaCO_3$(s)	-1206.92	$Mg(OH)_2$(s)	-924.54
C (diamond)	+1.89	NaF(s)	-573.65
C (graphite)	0	NaCl (s)	-411.15
CaO(s)	-635.09	NaBr(s)	-361.06
CH_4(g)	-74.81	NaI(s)	-287.78
C_2H_4(g)	52.26	NH_3(g)	-46.31
CH_3OH(l)	-238.86	NO(g)	+90.25
C_2H_5OH(l)	-277.69	NO_2(g)	+33.18
C_6H_6(l)	+52.26	PCl_3(l)	-319.7
CO(g)	-110.53	PCl_5(s)	-443.5
CO_2(g)	-393.51	SiO2(s) (quartz)	-910.94
C_2H_6(g)	-84.68	$SnCl_2$(s)	-325.1
Cl_2(g)	0	$SnCl_4$(l)	-511.3
C_3H_8(g)	-103.85	SO_2(g)	-296.83
n-C_4H_{10}(g)	-126.15	SO_3(g)	-395.72
HgS(s) red	-58.2	SiH_4(g)	+34
H_2(g)	0	$SiCl_4$(g)	-657.0
H_2O(g)	-241.82	C(g)	+716.68
H_2O(l)	-271.1	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	Fe_2O_3(s)	-824.2
HBr(g)	-36.4		

By convention, standard enthalpy for formation, $\Delta_f H°$, of an element in reference state, i.e., its most stable state of aggregation is taken as zero.

Suppose, you are a chemical engineer and want to know how much heat is required to decompose calcium carbonate to lime and carbon dioxide, with all the substances in their standard state.

$$\mathbf{CaO\ (s) + CO_2\ (g) \rightarrow\ CaCO_3\ (s)\ ;\ \Delta_rH° = ?}$$

Here, we can make use of standard enthalpy of formation and calculate the enthalpy change for the reaction. The following general equation can be used for the enthalpy change calculation.

$$\mathbf{\Delta r\ H\ \ = \sum a\Delta\ H\ products - \sum\ b\Delta H\ reactants}$$

where a and b represent the coefficients of the products and reactants in the balanced equation. Let us apply the above equation for decomposition of calcium carbonate. Here, coefficients 'a' and 'b' are 1 each.

Therefore,

$$\mathbf{\Delta_rH° = \Delta_fH°(CaO(s)) +\Delta_fH°(CO_2(g)) - \Delta_fH°(CaCO_3(s))}$$

$$= 1(-635.1) + 1(-393.5) – (-1206.9)\ \ = 178.3\ KJ.mol-1$$

Thus, the decomposition of $CaCO_3$ (s) is an endothermic process and you have to heat it for getting the desired products.

(d) Thermochemical equations

A balanced chemical equation together with the value of its Δr H is called a thermochemical equation. We specify the physical state (alongwith allotropic state) of the substance in an equation. For example:

$$\mathbf{C_2H_5OH\ (l)\ )+ 3\ O_2(g) \rightarrow\ 2CO_2(g) + 3\ H_2O(l)\ ;\ \Delta_rH° = -1367\ KJ.mol^{-1}}$$

The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

It would be necessary to remember the following conventions regarding thermo- chemical equations.

1. The coefficients in a balanced thermo- chemical equation refer to the number of moles (never molecules) of reactants and products involved in the reaction.

2. The numerical value of Δr H° refers to the number of moles of substances specified by an equation. Standard enthalpy change ΔrH° will have units as kJ mol^{-1}.

To illustrate the concept, let us consider the calculation of heat of reaction for the following reaction:

$$\mathbf{Fe_2O_3(s)\ ) + 3\ H_2\ (g) \rightarrow\ 2\ Fe\ (s) + 3\ H_2O(l)\ ;}$$

From the Table (2) of standard enthalpy of formation (Δ_f H), we find :

$\Delta_f H°$ (H_2O,l) = -285.83 $KJ.mol^{-1}$

$\Delta_f H°$ (Fe_2O_3,s) = -824.2 $KJ.mol^{-1}$

Also ; $\Delta_f H°$ (Fe,s) = 0 $KJ.mol^{-1}$ and ; $\Delta_f H°$ (H_2,g) = 0 $KJ.mol^{-1}$

Then

$\Delta_r H°1$ = 3(-285.83)-1(-824.2)= -33.3 $KJ.mol^{-1}$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for Δr H° is kJ mol-1 , which means per mole of reaction. Once we balance the chemical equation in a particular way, as above, this defines the mole of reaction. If we had balanced the equation differently, for example,

$$\mathbf{\tfrac{1}{2}\, Fe_2O_3(s)\,) + 3/2\; H_2\, (g) \rightarrow\; Fe\; (s) + 3/2\; H_2O(l)\; ;}$$

then this amount of reaction would be one mole of reaction and Δ rH° would be

$\Delta_r H°2$ = 3/2(-285.83)-1/2(-824.2)= -16.6 $KJ.mol^{-1}$ = ½ $\Delta_r H°1$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of Δr H° is reversed in sign. For example

$$\mathbf{N_2(g)\; + 3\, H_2\, (g) \rightarrow\; 2NH_3(g)\; ;\; \Delta_r H° = -91.8\; KJ.mol^{-1}}$$

$$\mathbf{2NH_3(g) \rightarrow\; N_2(g)\; + 3\, H_2\, (g);\; \Delta_r H° = +91.8\; KJ.mol^{-1}}$$

(e) Hess's Law of Constant Heat Summation

We know that enthalpy is a state function; therefore the change in enthalpy is independent of the path between initial state (reactants) and final state (products). In other words, enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of Hess's Law.

If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature.

Let us understand the importance of this law with the help of an example

Consider the enthalpy change for the reaction

$$\mathbf{C\; (graphite.s) + 1/2\; O_2(g)\; \rightarrow\; CO(g)\; ;\; \Delta_r H° = ?}$$

Although CO(g) is the major product, some CO_2 gas is always produced in this reaction. Therefore, we cannot measure enthalpy change for the above reaction directly. However, if we can find some other reactions involving related species, it is possible to calculate the enthalpy change for the above reaction.

Let us consider the following reactions:

$$\mathbf{C\ (graphite.s) + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta_r H°1 = -393.5\ KJ.\ mol^{-1}}$$

$$\mathbf{CO\ (g) + 1/2\ O_2(g) \rightarrow CO_2(g)\ ;\ \Delta_r H°2 = -\ 283.0\ KJ.mol^{-1}}$$

We can combine the above two reactions in such a way so as to obtain the desired reaction. To get one mole of CO(g) on the right, we reverse equation (ii). In this, heat is absorbed instead of being released, so we change sign of ΔrH^0 value

$$\mathbf{CO_2(g) \rightarrow CO\ (g) + 1/2\ O_2(g)\ ;\ \Delta_r H°3 = +\ 283.0\ KJ.mol^{-1}}$$

Adding equation (1) and (3), we get the desired equation,

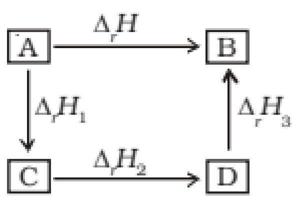
$$\mathbf{C\ (graphite.s) + 1/2\ O_2(g) \rightarrow CO(g)\ ;}$$

For which $\Delta_r H° = (-393.5+283.0) = -110.5$ KJ.mol^{-1}

In general, if enthalpy of an overall reaction A→B along one route is $\Delta r\ H$ and ΔrH_1, ΔrH_2, ΔrH_3 ..... representing enthalpies of reactions leading to same product, B along another route, then we have

$\Delta\ rH = \Delta\ rH_1 + \Delta r\ H_2 + \Delta r\ H_3$ ...

It can be represented as:



4.2.2 ENTHALPIES FOR DIFFERENT TYPES OF REACTIONS

It is convenient to give name to enthalpies specifying the types of reactions.

(a) Standard enthalpy of combustion (symbol : $\Delta cH°$)

Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the reactants and products being in their standard states at the specified temperature.

Cooking gas in cylinders contains mostly butane ($C_4 H_{10}$). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:

$$\mathbf{C_4H_{10}\,(g) + 13/2\ O_2\,(g) \rightarrow 4\ CO_2(g) + 5H_2O\,(l)\ ;\ \Delta_cH^\circ = -2658\ KJ.mol^{-1}}$$

Similarly, combustion of glucose gives out 2802.0 kJ/mol of heat, for which the overall equation is :

$$\mathbf{C_6H_{12}\,(g) + 6\ O_2\,(g) \rightarrow 6\ CO_2(g) + 5H_2O\,(l)\ ;\ \Delta_cH^\circ = -2802\ KJ.mol^{-1}}$$

Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

Problem

The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, CO_2(g) and H_2O (1) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, ΔfH° of benzene. Standard enthalpies of formation of CO_2(g) and H_2O(l) are –393.5 kJ mol^{-1} and – 285.83 kJ mol^{-1} respectively.

Solution

The formation reaction of Benzene is given by

$6\ C\ (graphite.s) + 3\ H_2(g) \rightarrow C_6H_6\ (l);\ \Delta_fH^\circ = ?$ …………1

The enthalpy of combustion of 1 mole of Benzene is.

$C_6H_6\ (l) + 15/2\ O_2\ (g) \rightarrow 6\ CO_2(g) + 3H_2O\ (l)\ ;\ \Delta_cH^\circ = -3267\ KJ.mol^{-1}$ …… 2

The enthalpy of formation of 1 mole of CO_2 is.

$C\ (graphite.s) + O_2(g) \rightarrow CO_2(g)\ ;\ \Delta_fH^\circ = -393.5\ KJ.\ mol^{-1}$ ……….3

The enthalpy of formation of 1 mole of H_2O is.

$H_2\ (g) + ½\ O_2(g) \rightarrow H_2O\ (l)\ ;\ \Delta_fH^\circ = -285.83\ KJ.\ mol^{-1}$ ……….4

Multiplying eqn 3 by 6 and eqn 4 by 3 we get:

$6\ C\ (graphite.s) + 6\ O_2(g) \rightarrow 6\ CO_2(g)\ ;\ \Delta_fH^\circ = -2361\ KJ.\ mol^{-1}$ ……….3

$3\ H_2\ (g)+3/2\ O_2(g) \rightarrow 3H_2O\ (l)\ ;\ \Delta_fH° = -857.49\ KJ.\ mol^{-1}$ ……….4

Summing up the above two equations :

$6\ C\ (graphite.s)\ +3H_2 + 15/2\ O_2(g) \rightarrow 6\ CO_2(g)+ 3H_2O\ ;\ \Delta_fH° = -3218.49\ KJ.\ mol^{-1}$ 5

Reversing equation 2

$6\ CO_2(g)\ +3H_2O\ (l) \rightarrow C_6H_6\ (l) + 15/2\ O_2\ (g)\ ;\ \Delta_cH° = 3267\ KJ.mol^{-1}$ …… 6

Adding equations 5 and 6 we get:

$6\ C\ (graphite.s)\ +3H_2 \rightarrow C_6H_6\ (l)\ ;\ \Delta_fH° = 48.51\ KJ.mol^{-1}$

(b) Enthalpy of atomization (symbol:ΔaH°)

Consider the following example of atomization of dihydrogen

$$\mathbf{H_2\ (g) \rightarrow 2H(g);\ \Delta a\ H° = 435.0\ kJ\ mol^{-1}}$$

You can see that H atoms are formed by breaking H–H bonds in dihydrogen. The enthalpy change in this process is known as enthalpy of atomization, Δa H°. It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase.

In case of diatomic molecules, like dihydrogen (given above), the enthalpy of atomization is also the bond dissociation enthalpy. The other examples of enthalpy of atomization can be

$$\mathbf{CH_4(g) \rightarrow C(g) + 4H(g);\ \Delta a\ H° = 1665\ kJ\ mol^{-1}}$$

Note that the products are only atoms of C and H in gaseous phase. Now see the following reaction:

$$\mathbf{Na(s) \rightarrow Na(g)\ ;\ \Delta a\ H° = 108.4\ kJ\ mol^{-1}}$$

In this case, the enthalpy of atomization is same as the enthalpy of sublimation.

(c) Bond Enthalpy (symbol: $\Delta_{bond}H$)

Chemical reactions involve the breaking and making of chemical bonds. Energy is required to break a bond and energy is released when a bond is formed. It is possible to relate heat of reaction to changes in energy associated with breaking and making of chemical bonds. With reference to the enthalpy changes associated with chemical bonds, two different terms are used in thermodynamics.

(i) Bond dissociation enthalpy

(ii) Bond Lattice enthalpy

Let us discuss these terms with reference to diatomic and polyatomic molecules. Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H2) are broken:

$$\mathbf{H_2(g) \rightarrow 2H(g)\ ;\ \Delta_{H-H}H^\circ = 435.0\ kJ\ mol^{-1}}$$

The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

Note that it is the same as the enthalpy of atomization of dihydrogen. This is true for all diatomic molecules. For example:

$$\mathbf{Cl_2(g) \rightarrow 2Cl(g)\ ;\ \Delta_{Cl-Cl}H^\circ = 242\ kJ\ mol^{-1}}$$

$$\mathbf{O_2(g) \rightarrow 2O(g)\ ;\ \Delta_{O=O}H^\circ = 428\ kJ\ mol^{-1}}$$

In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule. Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4. The overall thermochemical equation for its atomization reaction is given below:

$$\mathbf{CH_4(g) \rightarrow C(g) + 4H(g);\ \Delta a\ H^\circ = 1665\ kJ\ mol^{-1}}$$

In methane, all the four C – H bonds are identical in bond length and energy. However, the energies required to break the individual C – H bonds in each successive step differ :

$$\mathbf{CH_4(g) \rightarrow CH_3(g) + H(g);\ \Delta_{bond}\ H^\circ = +427\ kJ\ mol^{-1}}$$

$$\mathbf{CH_3(g) \rightarrow CH_2(g) + H(g);\ \Delta_{bond}\ H^\circ = +427\ kJ\ mol^{-1}}$$

$$\mathbf{CH_2(g) \rightarrow CH_1(g) + H(g);\ \Delta_{bond}\ H^\circ = +427\ kJ\ mol^{-1}}$$

$$\mathbf{CH_1(g) \rightarrow C(g) + H(g);\ \Delta_{bond}\ H^\circ = +427\ kJ\ mol^{-1}}$$

Therefore

$$\mathbf{CH_4(g) \rightarrow C(g) + 4\ H(g);\ \Delta_a\ H^\circ = 1665\ kJ\ mol^{-1}}$$

In such cases we use mean bond enthalpy of C – H bond. For example in CH_4 , $\Delta_{C-H} H^\circ$ is calculated as:

$$\mathbf{\Delta_{C-H}H^\circ = 1/4(\Delta\ aH^\circ) = 1/4\ (1665\ kJ\ mol\text{-}1) = 416\ kJ\ mol\text{–}1}$$

We find that mean C–H bond enthalpy in methane is 416 kJ/mol. It has been found that mean C–H bond enthalpies differ slightly from compound to compound, as in

CH_3CH_2Cl, CH_3NO_2, etc, but it does not differ in a great deal*. Using Hess's law, bond enthalpies can be calculated. Bond enthalpy values of some single and multiple bonds are given in Table 6.3. The reaction enthalpies are very important quantities as these arise from the changes that accompany the breaking of old bonds and for mation of the new bonds. We can predict enthalpy of a reaction in gas phase, if we know different bond enthalpies. The standard enthalpy of reaction, $\Delta r\ H°$ is related to bond enthalpies of the reactants and products in gas phase reactions as:

$$\mathbf{\Delta r\ H = \sum bond\ \Delta\ H\ reactants - \sum bond\ \Delta H\ products}$$

This relationship is particularly more

useful when the required values of $\Delta f\ H$ are not available. The net enthalpy change of a reaction is the amount of energy required to break all the bonds in the reactant molecules minus the amount of energy required to break all the bonds in the product molecules. Remember that this relationship is approximate and is valid when all substances (reactants and products) in the reaction are in gaseous state.

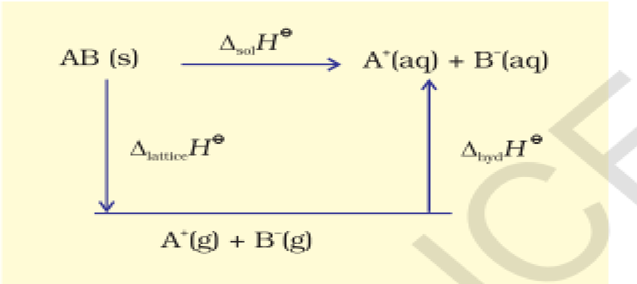
Table. 4.3. Some mean single bond Enthalpies in $kJ.mol^{-1}$ at 298K

H	C	N	O	F	Si	P	S	Cl	Br	I	
435.8	414	389	464	569	293	318	339	431	368	297	H
	347	293	351	439	289	264	259	330	276	238	C
		159	201	272		209		201	243		N
			138	184	368	351		205		201	O
				155	540	490	327	255	197		F
					176	213	230	331	272	213	Si
						213	230	331	272	213	P
							213	251	213		S
								243	218	209	Cl
									192	180	Br
										151	I

(d) Enthalpy of Solution (symbol : $\Delta_{sol}H$)

Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

When an ionic compound dissolves in a solvent, the ions leave their ordered positions on the crystal lattice. These are now more free in solution. But salvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, AB (s)



The enthalpy of solution of AB(s), Δ solH° , in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{lattice}H°$ and enthalpy of hydration of ions, Δ_{hyd} H as:

$$\Delta_{sol}H° = \Delta_{lattice}H° + \Delta_{hyd} H°$$

For most of the ionic compounds, Δ_{sol} H° is positive and the dissociation process is endothermic. Therefore the solubility of most salts in water increases with rise of temperature. If the lattice enthalpy is very high, the dissolution of the compound may not take place at all. Why do many fluorides tend to be less soluble than the corresponding chlorides? Estimates of the magnitudes of enthalpy changes may be made by using tables of bond energies (enthalpies) and lattice energies (enthalpies).

(e) Lattice Enthalpy

The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

$$\mathbf{Na^+Cl^-(s) \rightarrow Na^+(g) + Cl^-(g); \Delta_a H° = +788\ kJ\ mol^{-1}}$$

Since it is impossible to determine lattice enthalpies directly by experiment, we use an indirect method where we construct an enthalpy diagram called a Born-Haber Cycle (Figure).

Let us now calculate the lattice enthalpy of Na^+,Cl^- (s) by following steps given below :

1. Na(s) $\rightarrow$ Na(g) sublimation of sodium metal, Δ_{sub} H° = 108.4 kJ mol^{-1}

2. $Na(g) \rightarrow Na^{+}(g) + e^{-}(g)$ the ionization of sodium atoms, ionization enthalpy $\Delta_i H° =$ 496 kJ mol^{-1}

3. $1/2\ Cl_2(g) \rightarrow 1/2\ Cl(g)$ the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy.

$1/2\ \Delta_{bond} H = 121$ kJ mol^{-1}

4. $Cl(g) + e^{-}(g) \rightarrow Cl^{-}(g)$ electron gained by chlorine atoms. The electron gain enthalpy,

$\Delta_{eg} H° = -348.6$ kJ mol

You have learnt about ionization enthalpy and electron gain enthalpy in Unit 3. In fact, these terms have been taken from thermodynamics. Earlier terms, ionization energy and electron affinity were in practice in place of the above terms.

5. $Na^{+}(g) + Cl^{-}(g) \rightarrow Na^{+},Cl^{-}(s)$

The sequence of steps is shown in Fig. 4.1, and is known as a Born-Haber cycle. The importance of the cycle is that, the sum of the enthalpy changes round a cycle is zero.

Applying Hess's law, we get,

$\Delta_{lattice} H° = 411.2 + 108.4 + 121 + 496 - 348.6$

$\Delta_{lattice} H° = +788$ kJ

for : $NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$

Internal energy is smaller by 2RT (because $\Delta n = 2$) and is equal to + 783 kJ mol .

Now we use the value of lattice enthalpy to calculate enthalpy of solution from the expression:

$\Delta_{sol} H° = \Delta_{lattice} H° + \Delta_{hyd} H°$

For one mole of NaCl(s), lattice enthalpy = + 788 kJ mol–1 and $\Delta_{hyd} H° = -784$ kJ mol–1 (from the literature)

$\Delta_{sol} H° = +788$ kJ mol^{-1} $- 784$ kJ mol^{-1} $= +4$ kJ mol^{-1}

The dissolution of NaCl(s) is accompanied by very little heat change.

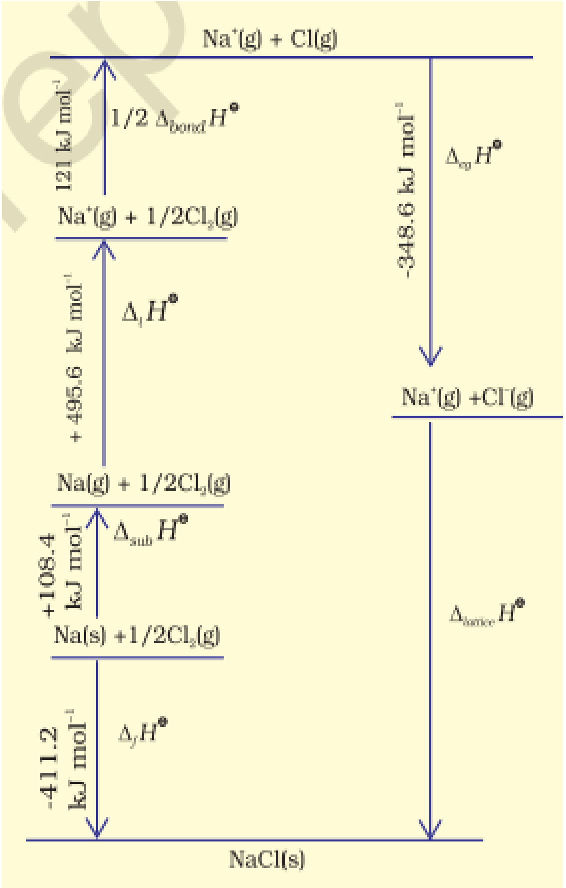


Fig 4.1. Enthalpy diagram for lattice enthalpy of NaCl.