

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Thermodynamics: part 3
Module Id	kech_10603
Pre-requisites	Enthalpy and types of chemical reactions.
Objectives	After going through this module, the learner will be able to <ol style="list-style-type: none">1. Describe the standard state for thermodynamic functions2. Explain sign of enthalpy change for changes of state3. Calculate enthalpy changes for reactions4. Use bond energies to estimate heats of reaction5. Apply Hess's law to calculate reaction enthalpy6. Understand Born Haber process
Keywords	Enthalpy change , bond enthalpy , Hess's law , Born Haber cycle

2. Development Team

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Table of Contents:

1. Introduction
2. Reaction Enthalpy
3. Thermochemical Equations
4. Hess's law
5. Lattice Enthalpy from Born Haber cycle
6. Conclusion

1. Introduction

Enthalpy change is a very useful and important quantity to study various chemical reactions. 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. The enthalpy change is studied here in this module from the viewpoint of types of reactions.

2. Enthalpy Change, $\Delta_r H$ of a Reaction – Reaction Enthalpy

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

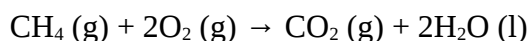
Reactants \rightarrow Products

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

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

$$\Delta_r H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

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



$$\Delta_r H = \sum_i a_i H_{\text{products}} - \sum_i b_i H_{\text{reactants}}$$

$$= [H_m (\text{CO}_2, \text{g}) + 2H_m (\text{H}_2\text{O}, \text{l})] - [H_m (\text{CH}_4, \text{g}) + 2H_m (\text{O}_2, \text{g})]$$

where H_m is the molar enthalpy.

(i) 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 pure iron at 1 bar. Usually data are taken at 298 K.

Standard conditions are denoted by adding the superscript \ominus to the symbol ΔH , e.g.,

(ii) Enthalpy changes during phase transformations

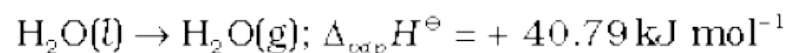
Phase transformations also involve energy changes. Ice, for example, requires heat for melting. Normally this melting takes place at constant pressure (atmospheric pressure) and during phase change, temperature remains constant (at 273 K).



Here $\Delta_{\text{fus}}H^\ominus$ 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, $\Delta_{\text{fus}}H^\ominus$.

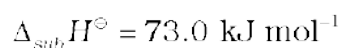
Melting of a solid is endothermic, so all enthalpies of fusion are positive. Water requires heat for evaporation. At constant temperature of its boiling point T_b and at constant pressure:



$\Delta_{\text{vap}}H$ 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, $\Delta_{\text{vap}}H^\ominus$.

Sublimation is direct conversion of a solid into its vapour. Solid CO_2 or 'dry ice' sublimates at 195K with $\Delta_{\text{sub}}H^\ominus = 25.2 \text{ kJ mol}^{-1}$; naphthalene sublimates slowly and for this



Standard enthalpy of sublimation, $\Delta_{\text{sub}}H^\ominus$ is the change in enthalpy when one mole of a solid substance sublimates at a constant temperature and under standard pressure (1bar).

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 vaporise 1 mol of acetone than it does to vaporize 1 mol of water. Table 1 gives values of standard enthalpy changes of fusion and vaporisation for some substances.

Table 1 Standard Enthalpy Changes of Fusion and Vaporisation

Substance	T_f/K	Δ_{fus}H[⊖]/(kJ mol⁻¹)	T_b/K	Δ_{vap}H[⊖]/(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 ₃ COCH ₃	177.8	5.72	329.4	29.1
CCl ₄	250.16	2.5	349.69	30.0
H ₂ O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C ₆ H ₆	278.65	9.83	353.25	30.8

(T_f and T_b are melting and boiling points, respectively)

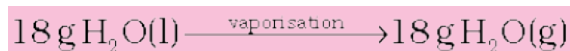
Example 1

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 vaporisation at 100°C.

for water at 373K = 40.66 kJ mol⁻¹

Solution

We can represent the process of evaporation as



No. of moles in 18 g H₂O(l) is

$$\Delta_{\text{vap}}U = \Delta_{\text{vap}}H^\ominus - p\Delta V = \Delta_{\text{vap}}H^\ominus - \Delta n_g RT$$

(assuming steam behaving as an ideal gas).

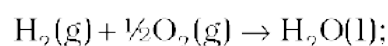
$$\Delta_{\text{vap}}H^\ominus - \Delta n_g RT = 40.66 \text{ kJ mol}^{-1} \\ - (1)(8.314 \text{ JK}^{-1}\text{mol}^{-1})(373\text{K})(10^{-3} \text{ kJ J}^{-1})$$

$$\Delta_{\text{vap}}U^\ominus = 40.66 \text{ kJ mol}^{-1} - 3.10 \text{ kJ mol}^{-1} \\ = 37.56 \text{ kJ mol}^{-1}$$

(iii) 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 $\Delta_f H^\ominus$, 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.

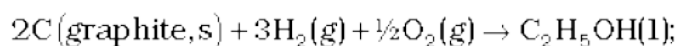
The reference state of an element is its most stable state of aggregation at 25°C and 1 bar pressure. For example, the reference state of dihydrogen is H₂ gas and those of dioxygen, carbon and sulphur are O₂ gas, C_{graphite} and S_{rhombic} respectively. Some reactions with standard molar enthalpies of formation are given below.



$$\Delta_f H^\ominus = -285.8 \text{ kJ mol}^{-1}$$

C (graphite, s)

$$\Delta_f H^\ominus = -74.81 \text{ kJ mol}^{-1}$$

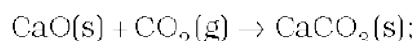


$$\Delta_f H^\ominus = -277.7 \text{ kJ mol}^{-1}$$

Table 2 Standard Molar Enthalpies of Formation ($\Delta_f H^\ominus$) at 298K of a Few Selected Substances

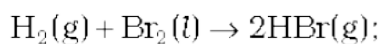
Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$	Substance	$\Delta_f H^\ominus / (\text{kJ mol}^{-1})$
Al ₂ O ₃ (s)	-1675.7	HI(g)	+26.48
BaCO ₃ (s)	-1216.3	KCl(s)	-436.75
Br ₂ (l)	0	KBr(s)	-393.8
Br ₂ (g)	+30.91	MgO(s)	-601.70
CaCO ₃ (s)	-1206.92	Mg(OH) ₂ (s)	-924.54
C (diamond)	+1.89	NaF(s)	-573.65
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 ₂ H ₄ (g)	52.26	NH ₃ (g)	-46.11
CH ₃ OH(l)	-238.86	NO(g)	+90.25
C ₂ H ₅ OH(l)	-277.69	NO ₂ (g)	+33.18
C ₆ H ₆ (l)	+49.0	PCl ₃ (l)	-319.70
CO(g)	-110.53	PCl ₅ (s)	-443.5
CO ₂ (g)	-393.51	SiO ₂ (s) (quartz)	-910.94
C ₂ H ₆ (g)	-84.68	SnCl ₂ (s)	-325.1
Cl ₂ (g)	0	SnCl ₄ (l)	-511.3
C ₃ H ₈ (g)	-103.85	SO ₂ (g)	-296.83
n-C ₄ H 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 ₂ O(g)	-241.82	C(g)	+716.68
H ₂ O(l)	-285.83	H(g)	+217.97
HF(g)	-271.1	Cl(g)	+121.68
HCl(g)	-92.31	Fe ₂ O ₃ (s)	-824.2
HBr(g)	-36.40		

It is important to understand that a standard molar enthalpy of formation, $\Delta_f H^\ominus$, is just a special case of $\Delta_r H^\ominus$, 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 change for an exothermic reaction:



$$\Delta_r H^\ominus = -178.3 \text{ kJ mol}^{-1}$$

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, $\Delta_f H^\ominus$ for HBr(g).



$$\Delta_r H^\ominus = -72.8 \text{ kJ mol}^{-1}$$

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

$$\Delta_r H^\ominus = 2\Delta_f H^\ominus$$

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

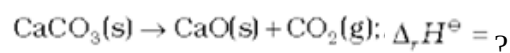


$$\Delta_r H^\ominus = -36.4 \text{ kJ mol}^{-1}$$

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

By convention, standard enthalpy for formation, $\Delta_f H^\ominus$, 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.



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.

$$\Delta_r H^\ominus = \sum_i a_i \Delta_f H^\ominus(\text{products}) - \sum_i b_i \Delta_f H^\ominus(\text{reactants})$$

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,

$$\Delta_r H^\ominus = \Delta_f H^\ominus[\text{CaO}(\text{s})] + \Delta_f H^\ominus[\text{CO}_2(\text{g})] \\ - \Delta_f H^\ominus[\text{CaCO}_3(\text{s})]$$

$$= 1(-635.1 \text{ kJ mol}^{-1}) + 1(-393.5 \text{ kJ mol}^{-1})$$

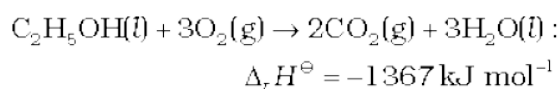
$$- 1(-1206.9 \text{ kJ mol}^{-1})$$

$$= 178.3 \text{ kJ mol}^{-1}$$

Thus, the decomposition of $\text{CaCO}_3(\text{s})$ is an endothermic process and you have to heat it for getting the desired products.

3. Thermochemical equations

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

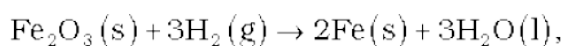


The above equation describes the combustion of liquid ethanol at constant temperature and pressure. The negative sign of enthalpy change indicates that this is an exothermic reaction.

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 $\Delta_r H^\ominus$ refers to the number of moles of substances specified by an equation. Standard enthalpy change $\Delta_r H^\ominus$ will have units as kJ mol^{-1} .

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



From the Table (1) of standard enthalpy of formation ($\Delta_f H^\ominus$), we find:

$$= -285.83 \text{ kJ mol}^{-1};$$

$$= -824.2 \text{ kJ mol}^{-1};$$

Also $\Delta_f H^\ominus(\text{Fe}, s) = 0$ and

$$\Delta_f H^\ominus(\text{H}_2, g) = 0 \text{ as per convention}$$

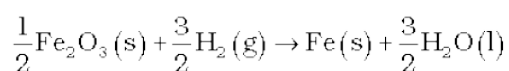
Then,

$$\Delta_r H_1^\ominus = 3(-285.83 \text{ kJ mol}^{-1}) - 1(-824.2 \text{ kJ mol}^{-1})$$

$$= (-857.5 + 824.2) \text{ kJ mol}^{-1}$$

$$= -33.3 \text{ kJ mol}^{-1}$$

Note that the coefficients used in these calculations are pure numbers, which are equal to the respective stoichiometric coefficients. The unit for $\Delta_r H^\ominus$ 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,

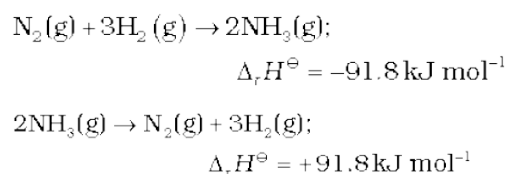


then this amount of reaction would be one mole of reaction and $\Delta_r H^\ominus$ would be

$$\begin{aligned}\Delta_r H_2^\ominus &= \frac{3}{2}(-285.83 \text{ kJ mol}^{-1}) \\ &\quad - \frac{1}{2}(-824.2 \text{ kJ mol}^{-1}) \\ &= (-428.7 + 412.1) \text{ kJ mol}^{-1} \\ &= -16.6 \text{ kJ mol}^{-1} = \frac{1}{2} \Delta_r H_1^\ominus\end{aligned}$$

It shows that enthalpy is an extensive quantity.

3. When a chemical equation is reversed, the value of $\Delta_r H^\ominus$ is reversed in sign. For example



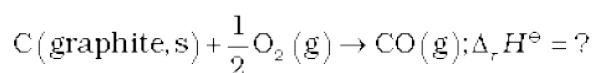
4. Hess's Law of Constant Heat Summation

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.

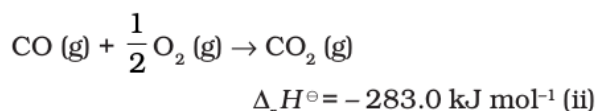
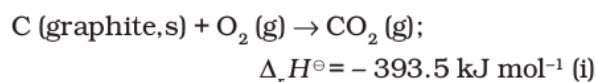
Consider the enthalpy change for the reaction



Although CO(g) is the major product, some CO₂ 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.

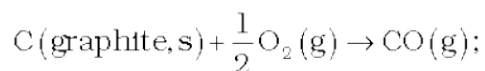
Let us consider the following reactions:



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 $\Delta_r H^\ominus$ value

$$\Delta_r H^\ominus = +283.0 \text{ kJ mol}^{-1} \text{ (iii)}$$

Adding equation (i) and (iii), we get the desired equation,

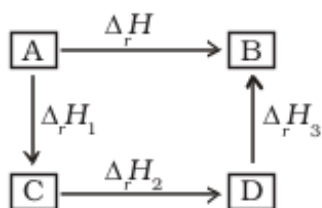


for which $\Delta_r H^\ominus = (-393.5 + 283.0)$
 $= -110.5 \text{ kJ mol}^{-1}$

In general, if enthalpy of an overall reaction $A \rightarrow B$ along one route is $\Delta_r H$ and $\Delta_r H_1$, $\Delta_r H_2$, $\Delta_r H_3$,..... representing enthalpies of reactions leading to same product, B along another route, then we have

$$\Delta_r H = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3 \dots \text{ (3)}$$

It can be represented as:



Enthalpies for different types of reactions

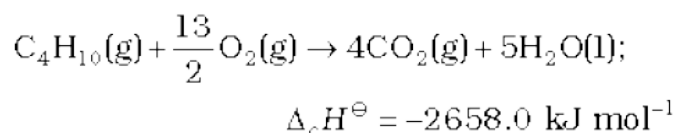
It is convenient to give name to enthalpies specifying the types of reactions.

(i) Standard enthalpy of combustion (symbol : $\Delta_c H^\ominus$)

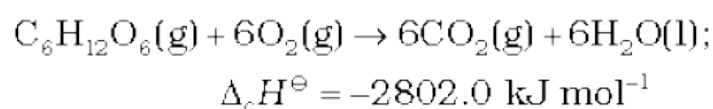
Combustion reactions are exothermic in nature. These are important in industry, rocketry, and other walks of life. Standard enthalpy of combustion is defined as the enthalpy change per mole

(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 (C₄H₁₀). During complete combustion of one mole of butane, 2658 kJ of heat is released. We can write the thermochemical reactions for this as:



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



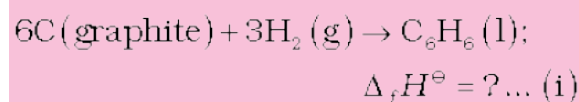
Our body also generates energy from food by the same overall process as combustion, although the final products are produced after a series of complex bio-chemical reactions involving enzymes.

Example 2

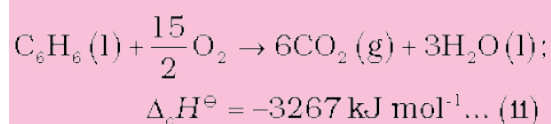
The combustion of one mole of benzene takes place at 298 K and 1 atm. After combustion, CO₂(g) and H₂O (l) are produced and 3267.0 kJ of heat is liberated. Calculate the standard enthalpy of formation, Δ_f H[⊖] of benzene. Standard enthalpies of formation of CO₂(g) and H₂O are -393.5 kJ mol⁻¹ and -285.83 kJ mol⁻¹ respectively.

Solution

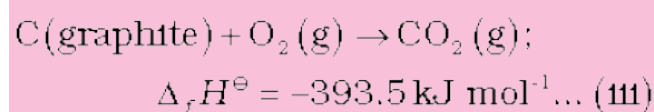
The formation reaction of benzene is given by:



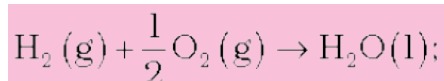
The enthalpy of combustion of 1 mol of benzene is:



The enthalpy of formation of 1 mol of CO₂(g) :

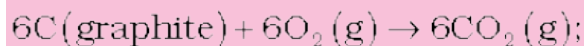


The enthalpy of formation of 1 mol of H₂O(l) is :

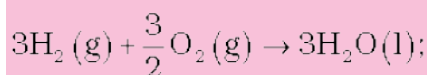


$$\Delta_f H^\ominus = -285.83 \text{ kJ mol}^{-1} \dots \text{(iv)}$$

multiplying eqn. (iii) by 6 and eqn. (iv) by 3 we get:

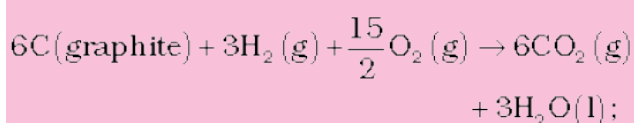


$$\Delta_f H^\ominus = -2361 \text{ kJ mol}^{-1}$$



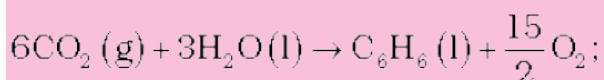
$$\Delta_f H^\ominus = -857.49 \text{ kJ mol}^{-1}$$

Summing up the above two equations:



$$\Delta_f H^\ominus = -3218.49 \text{ kJ mol}^{-1} \dots \text{(v)}$$

Reversing equation (ii);



$$\Delta_f H^\ominus = 3267.0 \text{ kJ mol}^{-1} \dots \text{(vi)}$$

Adding equations (v) and (vi), we get



$$\Delta_f H^\ominus = 48.51 \text{ kJ mol}^{-1}$$

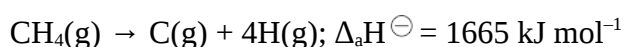
(ii) Enthalpy of atomization (symbol: $\Delta_a H^\ominus$)

Consider the following example of atomization of dihydrogen



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, $\Delta_a H^\ominus$. 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



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



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

(iii) Bond Enthalpy (symbol: $\Delta_{\text{bond}}H^{\ominus}$)

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) Mean bond enthalpy

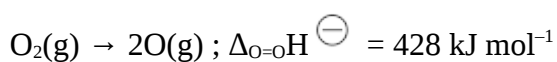
Let us discuss these terms with reference to diatomic and polyatomic molecules.

Diatomic Molecules: Consider the following process in which the bonds in one mole of dihydrogen gas (H_2) are broken:



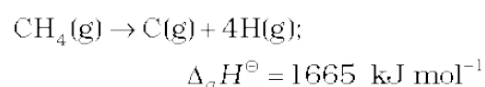
The enthalpy change involved in this process is the bond dissociation enthalpy of H–H bond. The bond dissociation enthalpy is the change in enthalpy when one mole of covalent bonds of a gaseous covalent compound is broken to form products in the gas phase.

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

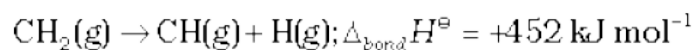
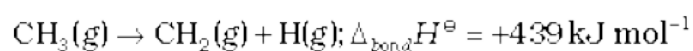
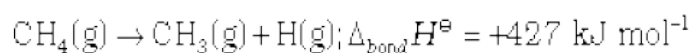


In the case of polyatomic molecules, bond dissociation enthalpy is different for different bonds within the same molecule.

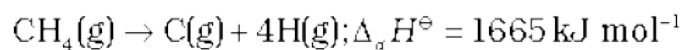
Polyatomic Molecules: Let us now consider a polyatomic molecule like methane, CH_4 . The overall thermochemical equation for its atomization reaction is given below:



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:



Therefore,



In such cases we use **mean bond enthalpy of C – H bond**.

For example in CH_4 , $\Delta_{\text{C-H}} H^\ominus$ is calculated as:

$$\begin{aligned} \Delta_{\text{C-H}} H^\ominus &= \frac{1}{4}(\Delta_{\alpha} H^\ominus) = \frac{1}{4} (1665 \text{ kJ mol}^{-1}) \\ &= 416 \text{ kJ mol}^{-1} \end{aligned}$$

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 $\text{CH}_3\text{CH}_2\text{Cl}$, 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 formation 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, $\Delta_r H^\ominus$ is related to bond enthalpies of the reactants and products in gas phase reactions as: (4)

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.

(iv) Enthalpy of Solution (symbol : $\Delta_{\text{sol}} H^\ominus$)

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.

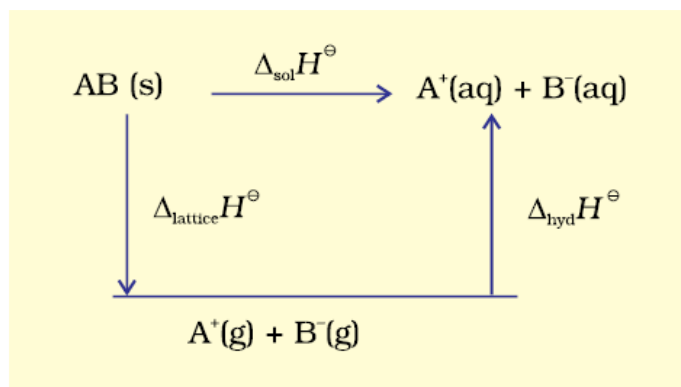
Table 3(a) Some Mean Single Bond Enthalpies in kJ mol^{-1} at 298 K

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	226	360	289	213	Si
						213	230	331	272	213	P
							213	251	213	-	S
								243	218	209	Cl
									192	180	Br
										151	I

Table 3(b) Some Mean Multiple Bond Enthalpies in kJ mol^{-1} at 298 K

$\text{N} = \text{N}$	418	$\text{C} = \text{C}$	611	$\text{O} = \text{O}$	498
$\text{N} \equiv \text{N}$	946	$\text{C} \equiv \text{C}$	837		
$\text{C} = \text{N}$	615	$\text{C} = \text{O}$	741		
$\text{C} \equiv \text{N}$	891	$\text{C} \equiv \text{O}$	1070		

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 solvation of these ions (hydration in case solvent is water) also occurs at the same time. This is shown diagrammatically, for an ionic compound, $\text{AB}(\text{s})$



The enthalpy of solution of $\text{AB}(\text{s})$, $\Delta_{\text{sol}}H^{\ominus}$, in water is, therefore, determined by the selective values of the lattice enthalpy, $\Delta_{\text{lattice}}H^{\ominus}$ and enthalpy of hydration of ions, $\Delta_{\text{hyd}}H^{\ominus}$ as

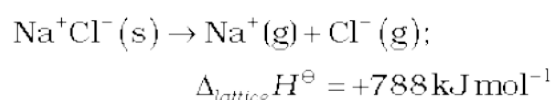
$$\Delta_{\text{sol}}H^{\ominus} = \Delta_{\text{lattice}}H^{\ominus} + \Delta_{\text{hyd}}H^{\ominus}$$

For most of the ionic compounds, $\Delta_{\text{sol}}H^{\ominus}$ 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).

5. Lattice Enthalpy from Born-Haber Cycle

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.



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** (Fig. 1).

Let us now calculate the lattice enthalpy of $\text{Na}^+\text{Cl}^-(\text{s})$ by following steps given below:

1. $\text{Na}(\text{s}) \rightarrow \text{Na}(\text{g})$, sublimation of sodium metal,
2. $\text{Na}(\text{g}) \rightarrow \text{Na}^+(\text{g}) + \text{e}^-(\text{g})$, the ionization of sodium atoms, ionization enthalpy $\Delta_i H^\ominus = 496 \text{ kJ mol}^{-1}$
3. $\frac{1}{2} \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$, the dissociation of chlorine, the reaction enthalpy is half the bond dissociation enthalpy. $\frac{1}{2} \Delta_{\text{bond}} H^\ominus = 121 \text{ kJ mol}^{-1}$

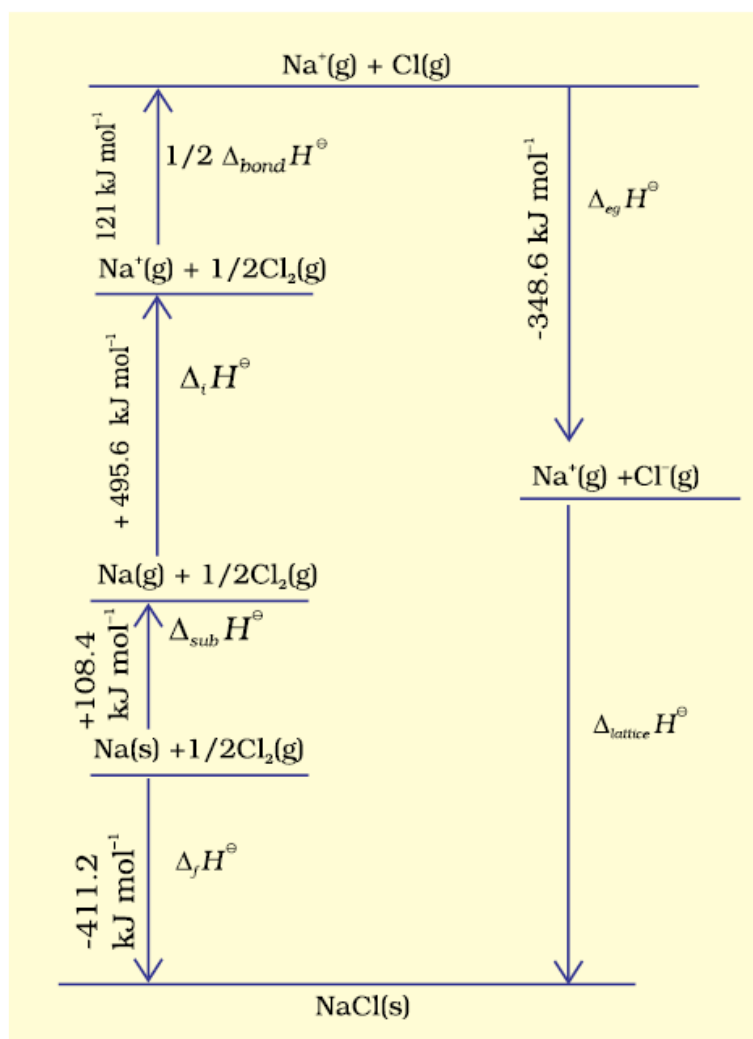


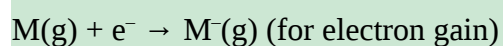
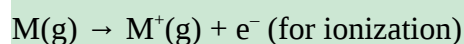
Fig. 1 Enthalpy diagram for lattice enthalpy of NaCl

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

The electron gain enthalpy, $\Delta_{\text{eg}}H^{\ominus} = -348.6 \text{ kJ mol}^{-1}$.

Ionization Energy and Electron Affinity

Ionization energy and electron affinity are defined at absolute zero. At any other temperature, heat capacities for the reactants and the products have to be taken into account. Enthalpies of reactions for



at temperature, T is

$$\Delta_{\text{r}}H^{\ominus}(\text{T}) = \Delta_{\text{r}}H^{\ominus}(0) +$$

The value of C_p for each species in the above reaction is $5/2 R$ ($C_v = 3/2R$)

So, $\Delta_r C_p^\ominus = + 5/2 R$ (for ionization)

$\Delta_r C_p^\ominus = - 5/2 R$ (for electron gain)

Therefore,

$\Delta_r H^\ominus$ (ionization enthalpy) = E_0 (ionization energy) + $5/2 RT$

$\Delta_r H^\ominus$ (electron gain enthalpy) = $- A$ (electron affinity) – $5/2 RT$

5. The sequence of steps is shown in Fig. 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,

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

$$\Delta_{lattice} H^\ominus = +788 \text{ kJ}$$

for

Internal energy is smaller by $2RT$ (because $\Delta n_g = 2$) and is equal to $+ 783 \text{ kJ mol}^{-1}$.

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

$$\Delta_{sol} H^\ominus = \Delta_{lattice} H^\ominus + \Delta_{hyd} H^\ominus$$

For one mole of NaCl(s) ,

lattice enthalpy = $+ 788 \text{ kJ mol}^{-1}$

and $\Delta_{hyd} H^\ominus = - 784 \text{ kJ mol}^{-1}$ (from the literature)

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

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

6. Conclusion:

There are varieties of enthalpy changes. Changes of phase such as melting, vaporization and sublimation usually occur at constant temperature and can be characterized by enthalpy changes which are always positive. Enthalpy of formation, combustion and other enthalpy changes can be calculated using Hess's law. Enthalpy change for chemical reactions can be determined by

$$\Delta_r H^0 = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$$

and in gaseous state by

$$\Delta_r H^0 = \Sigma \text{ bond enthalpies of the reactants} - \Sigma \text{ bond enthalpies of the products.}$$