

THERMOCHEMISTRY

1.2 INTRODUCTION

All physical and chemical changes are associated with a certain amount of heat exchange. In thermochemistry, we study the heat exchange that takes place between the system and the surroundings during a change, more specifically a chemical reaction undergoing inside a system. The whole subject matter of thermochemistry is based on the first law of thermodynamics.

Amount of heat exchanged during a process depends on the path taken by the system for the change. It is convenient to express the heat exchanged during a change in terms of path independent quantities such as ΔU and ΔH . So instead of heat exchange, we will talk about internal energy change or enthalpy change during a reaction. If the reaction occurs at constant volume, the heat produced or absorbed by the reaction (q_v) can be considered as *internal energy of reaction*:

$$\Delta U = q_v$$

If the reaction occurs at constant pressure, the heat produced or absorbed by the reaction (q_p) can be considered as *enthalpy of reaction*:

$$\Delta H = q_p$$

If we know ΔU or ΔH of a reaction, then we can predict the heat of reaction. As most reactions are carried out in open atmosphere or at constant pressure, enthalpy of reaction is usually used to express the heat of reaction.

A reaction that releases heat is called *exothermic reaction*. For exothermic reactions, $\Delta H < 0$.

A reaction that absorbs heat is called *endothermic reaction*. For endothermic reactions, $\Delta H > 0$.

1.2 IMPORTANCE

Heat change during a chemical reaction is mainly due to the breaking and making of chemical bonds. Bond breaking requires input of energy and bond formation takes place with the release of energy. Thermochemistry can give us valuable information about bond energies. Direct measurement of some very important quantities such as lattice energy, electron affinity, resonance energy, etc is almost impossible. We can estimate such quantities from thermochemical data.

1.3 ENTHALPY OF CHEMICAL CHANGES

1.3.1 ENTHALPY OF REACTION (ΔH)

Enthalpy of reaction is the amount of heat exchanged between the system and the surroundings during the transformation of the reactants at a particular temperature and pressure into the products in the same temperature and pressure. Heat exchanged during a reaction depends on the physical states of the reactants and products, so the states must be mentioned in the thermochemical equation. Enthalpy of reaction is an extensive property. For example, for the reaction $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) = 2 \text{NO}(\text{g})$, enthalpy of reaction, $\Delta H = + 180.7 \text{ kJ}$ but for $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{NO}(\text{g})$, enthalpy of reaction, $\Delta H = + 90.4 \text{ kJ}$.

1.3.1.1 RELATION BETWEEN ΔU and ΔH

By definition of enthalpy, $H = U + PV$; so, for a gaseous chemical reaction occurring at constant T and P ,

$$\begin{aligned}\Delta H &= H_{\text{product}} - H_{\text{reactant}} \\ &= U_p + (PV)_p - U_r - (PV)_r \\ &= (U_p - U_r) + \{(PV)_p - (PV)_r\} \\ &= \Delta U + \{(nRT)_p - (nRT)_r\} \quad [\text{since } PV = nRT] \\ &= \Delta U + RT(n_p - n_r) \\ &= \Delta U + RT \times \Delta n_g\end{aligned}$$

$\therefore \Delta H = \Delta U + RT \times \Delta n_g$ for gaseous reactions at constant temperature and pressure. It can also be written as

$$q_p = q_v + RT \times \Delta n_g \quad [\text{since, } \Delta H = q_p \text{ and } \Delta U = q_v]$$

For reactions having any type of reactants and products (solid, liquid or gas), at constant T and P ,

$$\begin{aligned}\Delta H &= H_{\text{product}} - H_{\text{reactant}} \\ \Rightarrow \Delta H &= U_p + (PV)_p - U_r - (PV)_r \\ \Rightarrow \Delta H &= (U_p - U_r) + P(V_p - V_r) \\ \Rightarrow \Delta H &= \Delta U + P\Delta V\end{aligned}$$

For reactions having solid and liquid reactants at constant T and P ,
 $\Delta V \approx 0$, $\therefore \Delta H = \Delta U$

Try these problems

1. Under what condition, heat of reaction is equal to enthalpy change?
2. What is the relation between ΔH and ΔU in
 - (i) the fusion process?
 - (ii) the evaporation process?
3. Find out a relationship between heat of reaction at constant pressure and heat of reaction at constant volume in the Haber synthesis of $\text{NH}_3(\text{g})$. Assume that all the reactants and products behave ideally.
4. Internal energy change at constant volume associated with the conversion of one mole of $\text{SO}_2(\text{g})$ into $\text{SO}_3(\text{g})$ is $-97.027 \text{ kJ mol}^{-1}$ at 298 K. Calculate the enthalpy of reaction at constant pressure.

1.3.2 STANDARD STATE

Standard state of a substance at a specified temperature is its pure form at a pressure of 1 bar.

- Standard state of a solid at a given temperature is the pure solid at one bar pressure.
- Standard state of a liquid at a given temperature is the pure liquid at 1 bar pressure.
- Standard state of a gas at a given temperature is the ideal gas at a pressure of 1 bar.

Enthalpy or internal energy at standard state is denoted by placing a superscript degree to H or U . e.g. standard molar enthalpy of $\text{H}_2\text{O}(\text{l})$ at 273 K expressed as $H^\circ_{\text{m}}(\text{H}_2\text{O}, \text{l}, 273 \text{ K})$.

1.3.3 STANDARD ENTHALPY CHANGES

The standard enthalpy change, ΔH^0 for a process is defined as the change in enthalpy when the initial species in their standard states are transformed into the products in their standard states.

1.3.3.1 STANDARD REACTION ENTHALPY ($\Delta_r H^0$)

Standard reaction enthalpy, $\Delta_r H^0$, is the change in enthalpy when reactants in their standard states at temperature T are converted to products in their standard states at temperature T . For example, for the reaction,
 $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$,

$$\Delta_r H^0(298 \text{ K}) = -890 \text{ kJ mol}^{-1}$$

In general, for the reaction, $a A + b B \rightarrow c C + d D$,

$$\Delta_r H^0 = \{c H_m^0(C) + d H_m^0(D)\} - \{a H_m^0(A) + b H_m^0(B)\}$$

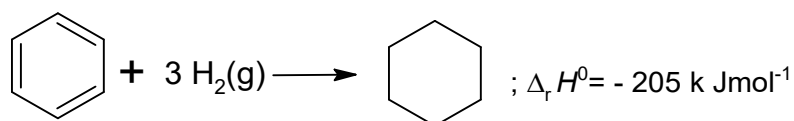
where H_m^0 's are standard molar enthalpy of the reactants and products.

Depending on the type of reaction, a specific name is given to the enthalpy of reaction. Some of the types of enthalpies of reaction are introduced below:

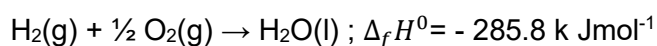
(a) *Standard Enthalpy of Combustion* ($\Delta_c H^0$): Standard enthalpy of combustion, $\Delta_c H^0$, of a compound or element is the enthalpy change associated with the complete combustion of 1 mole of the substance in its pure form at 1 bar to produce $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{N}_2(\text{g})$ if the compound contains C, H, O and N. For example, for the reaction, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$,

$$\Delta_c H^0(298 \text{ K}) = -2808 \text{ k J mol}^{-1}$$

(b) *Standard Enthalpy of Hydrogenation*: Standard enthalpy of hydrogenation of a substance is the enthalpy change involved in the hydrogenation of one mole of the substance in standard state to produce products in their standard states. For example, standard enthalpy of hydrogenation of benzene is



(c) *Standard Enthalpy of Formation* ($\Delta_f H^0$): Standard enthalpy of formation of a substance is defined as the enthalpy change associated with the formation of one mole of the substance in its standard state from its elements in their standard state. For example, standard enthalpy of formation of liquid water is:



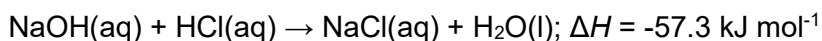
Standard enthalpy of formation of an element is always taken as zero. Standard enthalpy of reaction can be expressed in terms of standard enthalpy of formation of the reactants and products taking part in a reaction. For the general reaction, $a A + b B \rightarrow c C + d D$, standard reaction enthalpy is given by

$$\Delta_r H^0 = \{c \Delta_f H^0(C) + d \Delta_f H^0(D)\} - \{a \Delta_f H^0(A) + b \Delta_f H^0(B)\}$$

where $\Delta_f H^0$'s are standard enthalpy of formation of the reactants and products.

(c) *Standard Enthalpy of Neutralisation*: Enthalpy of neutralisation of an acid is the change in enthalpy associated with the neutralisation of one mole of the acid by a base in dilute solutions at 1 bar pressure. Similarly, enthalpy of neutralisation

of a base is the change in enthalpy associated with the neutralisation of one mole of the base by an acid in dilute solutions at 1 bar pressure. For example,

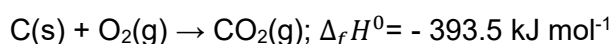


Try these problems

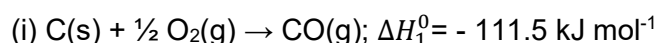
5. What is the standard state for carbon?
6. Write the thermochemical equation for the formation of $\text{CH}_4(\text{g})$.
7. The enthalpy change associated with the reaction,
 $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ is $-92.2 \text{ kJ mol}^{-1}$. What is the enthalpy of formation of ammonia gas?
8. Enthalpies of formation of $\text{CO}(\text{g})$, $\text{CO}_2(\text{g})$, $\text{N}_2\text{O}(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are -110, -393, -81, and 9.7 kJ mol^{-1} , respectively. Calculate $\Delta_r H$ for the following reaction:
$$\text{N}_2\text{O}_4(\text{g}) + 3 \text{CO}(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + 3 \text{CO}_2(\text{g}).$$
9. Can enthalpy of combustion be positive?
10. At 298 K, standard enthalpy of combustion of glucose, $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ is $-2816 \text{ kJ mol}^{-1}$. Calculate standard enthalpy of formation of glucose. Given that standard enthalpy of formation ($\Delta_f H^0$) of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -393.5 and $-285.9 \text{ kJ mol}^{-1}$, respectively at 298 K.
11. If the combustion of 1 g of graphite produces 20.7 kJ of heat, what is the enthalpy of combustion of graphite?
12. Standard enthalpy of combustion of benzene is $-3264.6 \text{ kJ mol}^{-1}$. Calculate the enthalpy change associated with burning of 39 g of benzene.
13. Calculate the value of $\Delta H - \Delta U$ for the reaction,
$$\text{C}_3\text{H}_8(\text{g}) + 5 \text{O}_2(\text{g}) \rightarrow 3 \text{CO}_2(\text{g}) + 4 \text{H}_2\text{O}(\text{l})$$
 at temperature T.

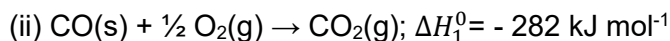
1.4 HESS'S LAW OF CONSTANT HEAT SUMMATION

Statement: If it is possible to divide a reaction into two or more than two individual reactions, then overall standard enthalpy of the reaction is the sum of the standard enthalpies of the individual reactions. To illustrate, let us consider the formation of $\text{CO}_2(\text{g})$. One way of forming $\text{CO}_2(\text{g})$ is



Another way of forming $\text{CO}_2(\text{g})$ is to first convert the starting materials [C(s) and $\text{O}_2(\text{g})$] into $\text{CO}(\text{g})$, then converting it into the final product $\text{CO}_2(\text{g})$:





It is clear here that $\Delta H_1^0 + \Delta H_2^0 = \Delta_f H^0(\text{CO}_2, g)$, satisfying the Hess's law.

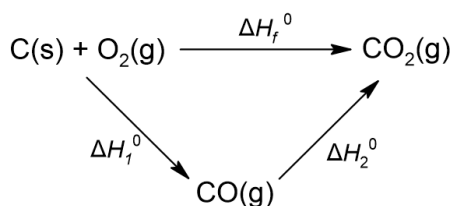


Figure 1.1 Alternative pathways for the formation of $\text{CO}_2(\text{g})$

Enthalpy is a state function, so change in enthalpy, ΔH in a process is independent of the path taken by the reacting system. ΔH depends only on the initial (Here, C(s) and $\text{O}_2(\text{g})$) and final state ($\text{CO}_2(\text{g})$) of the system.

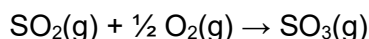
1.4.1 APPLICATIONS OF HESS'S LAW

Most important consequence of Hess's law is that thermochemical equations can be treated like algebraic equations. Algebraic equations can be added, subtracted, multiplied or divided by an integer to get the desired thermochemical equation. This is reflected in the numerical examples that follow.

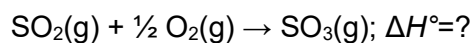
1.4.1.1 CALCULATION OF ENTHALPY OF REACTION

This can be illustrated by the following example.

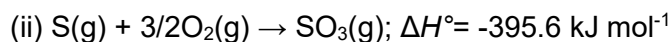
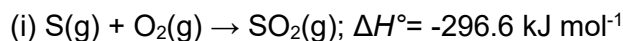
Example: Standard enthalpies of formation of $\text{SO}_2(\text{g})$ and $\text{SO}_3(\text{g})$ are $-296.6 \text{ kJ mol}^{-1}$ and $-395.5 \text{ kJ mol}^{-1}$, respectively. Estimate ΔH° for the following reaction:



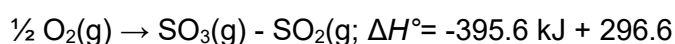
Solution: The required thermochemical equation is:



Given,



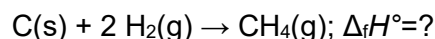
Subtracting equation (i) from (ii), we get



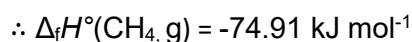
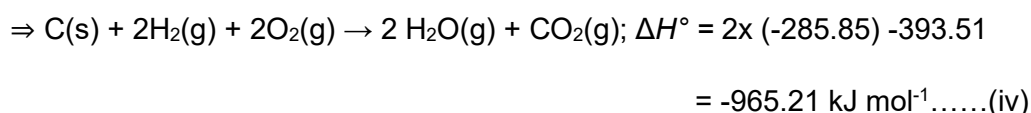
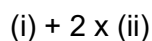
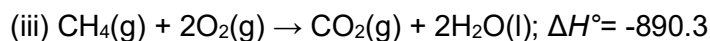
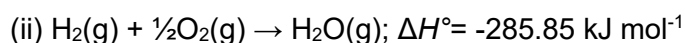
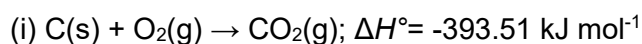
1.4.1.2 CALCULATION OF ENTHALPY OF FORMATION

Example: At 298 K, enthalpy of combustion of carbon(graphite), hydrogen(g) and methane(g) are -393.51, -285.85 and -890.3 kJ mol⁻¹, respectively. Calculate enthalpy of formation of methane(g) at 298 K.

Solution: The required thermochemical equation is:



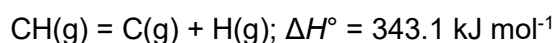
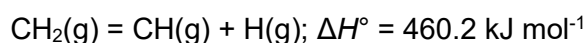
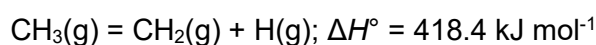
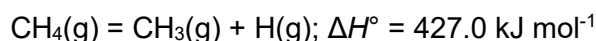
Given,



1.5 BOND ENTHALPY

Bond dissociation enthalpy of a given bond is the enthalpy change associated with the dissociation of one mole of the bond in a given compound into isolated atoms or radicals in the gaseous state. Bond dissociation enthalpy depends on the structure of the rest of the molecule. On the other hand, bond enthalpy is an average property. Bond enthalpy of a given bond is the average of enthalpies associated with the dissociation of the same bond in different gaseous compounds into isolated atoms or radicals in the gaseous state.

Let us take the example of methane molecule to distinguish the two concepts. The C—H bond dissociation enthalpies for the CH₄(g) in four different stages are:

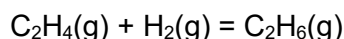


Therefore, bond enthalpy of C—H bond is the average of four enthalpies associated with the dissociation of C—H bond, i.e., $\frac{427.0+418.4+460.2+343.1}{4} = 412.2 \text{ kJ mol}^{-1}$.

1.5.1 CALCULATION OF ENTHALPY OF REACTION

This can be illustrated by the following example.

Example: Calculate enthalpy change for the reaction:



using the following data:

$$\Delta H(\text{C—C}) = 336.81 \text{ kJ mol}^{-1}; \Delta H(\text{C=C}) = 606.68 \text{ kJ mol}^{-1}$$

$$\Delta H(\text{C—H}) = 410.87 \text{ kJ mol}^{-1}; \Delta H(\text{H—H}) = 431.79 \text{ kJ mol}^{-1}$$

Solution: In this reaction, four C—H bonds and one C=C break in $\text{C}_2\text{H}_4(\text{g})$; one H—H bond breaks in $\text{H}_2(\text{g})$. In the product, six C—H bonds and one C—C bond is formed. Bond breaking is an energy requiring process and bond formation is an energy releasing process. Therefore,

$$\begin{aligned} \Delta_r H &= 4 \Delta H(\text{C—H}) + \Delta H(\text{C=C}) + \Delta H(\text{H—H}) - 6 \Delta H(\text{C—H}) - \Delta H(\text{C—C}) \\ &= 4 \times 410.87 + 606.68 + 431.79 - 6 \times 410.87 - 336.81 \\ &= 2681.95 - 2802.03 \\ &= -120.08 \text{ kJ mol}^{-1} \end{aligned}$$

1.5.2 CALCULATION OF BOND ENTHALPY

Bond enthalpies can be calculated from thermochemical data.

Example: Standard Bond dissociation enthalpies of $\text{H}_2(\text{g})$ and $\text{N}_2(\text{g})$ are 436 kJ mol^{-1} and $941.3 \text{ kJ mol}^{-1}$, respectively. If standard enthalpy of formation of ammonia gas is $-46.0 \text{ kJ mol}^{-1}$, calculate bond enthalpy of N—H bond in ammonia gas.

Solution: Given,

$$(i) \text{N}_2(\text{g}) = 2 \text{N}(\text{g}); \Delta H^\circ = 941.3 \text{ kJ mol}^{-1}$$

$$(ii) \text{H}_2(\text{g}) = 2 \text{H}(\text{g}); \Delta H^\circ = 435.0 \text{ kJ mol}^{-1}$$

$$(iii) \frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) = \text{NH}_3(\text{g}); \Delta H^\circ = -46.0 \text{ kJ mol}^{-1}$$

Multiplying equation (i) by $\frac{1}{2}$ and equation (ii) by $\frac{3}{2}$ and adding gives

$$\begin{aligned} (iv) \frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) &= \text{N}(\text{g}) + 3\text{H}(\text{g}); \Delta H^\circ = \frac{1}{2} \times 941.3 + \frac{3}{2} \times 436.0 \\ &= 1124.6 \text{ kJ mol}^{-1} \end{aligned}$$

Subtracting equation (iii) from (iv), we get

$$\text{NH}_3(\text{g}) = \text{N}(\text{g}) + 3\text{H}(\text{g}); \Delta H^\circ = 1124.6 + 46.0 = 1170.6 \text{ kJ mol}^{-1}$$

Average bond dissociation enthalpy of N—H bond is obtained by dividing the above ΔH° by 3:

$$\Delta H^\circ(\text{N—H}) = \frac{1170.6}{3} = 390.2 \text{ kJ mol}^{-1}$$

1.5.3 ENTHALPY OF FORMATION FROM BOND ENTHALPY

Enthalpy of formation of a compound of known structure can be estimated from bond enthalpy data. Let us calculate the approximate enthalpy of formation of $\text{H}_2\text{O}(\text{g})$ from its constituent elements, $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ according to the reaction: $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{g})$. The enthalpy of formation of $\text{H}_2\text{O}(\text{g})$,

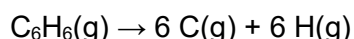
$$\Delta_f H(\text{H}_2\text{O}, \text{g}) = \Delta H(\text{H—H}) + \frac{1}{2} \Delta H(\text{O=O}) - 2 \Delta H(\text{O—H})$$

Putting the bond enthalpy values in the above equation, we get

$$\Delta_f H(\text{H}_2\text{O}, \text{g}) = 431.79 + \frac{1}{2} \times 493.7 - 2 \times 464.4 = -250.16 \text{ kJ mol}^{-1}$$

1.5.4 RESONANCE ENERGY FROM BOND ENTHALPY

Values of enthalpy of formation calculated from bond enthalpy data generally agree well with the experimentally determined values. In the case of compounds exhibiting resonance, experimental values do not match with the calculated values. This difference of experimental and calculated values gives a measure of the resonance energy of the compound. To illustrate, let us consider the example of benzene. Enthalpy change associated with the dissociation of benzene can be estimated using the following reaction:

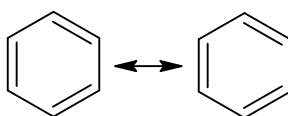


Considering the Kekule's structure of benzene (three C—C single bonds, three C—H single bonds and three C=C double bonds), dissociation enthalpy can be estimated as

$$\begin{aligned} \Delta_d H &= 3 \Delta H(\text{C—C}) + 3 \Delta H(\text{C=C}) + 6 \Delta H(\text{C—H}) \\ &= 3 \times 347.69 + 3 \times 615.05 + 6 \times 413.38 \\ &= 5368.5 \text{ kJ mol}^{-1} \end{aligned}$$

Experimental dissociation energy is found to be $5535.1 \text{ kJ mol}^{-1}$. So, benzene is more stable by $166.6 \text{ kJ mol}^{-1}$ than it is represented by the Kekule's structure.

This stability is gained by the compound because of resonance:



Thus, estimated resonance energy of benzene is $166.6 \text{ kJ mol}^{-1}$.

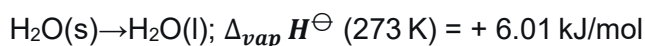
1.6 STANDARD ENTHALPIES OF PHYSICAL CHANGES

(1) Enthalpy of transition (standard), $\Delta_{trs} H^\ominus$: Standard enthalpy change in the transformation of one mole of a substance from one state to another state is known as the standard enthalpy of transition, $\Delta_{trs} H^\ominus$. It includes —

(a) Standard enthalpy of vaporization, $\Delta_{vap} H^\ominus$: This is the enthalpy change per mole when a pure liquid at 1 bar, vaporizes to a gas at 1 bar, e.g.,



(b) Standard enthalpy of fusion, $\Delta_{fus} H^\ominus$: This is the enthalpy change accompanying the conversion of one mole of a pure solid at 1 bar to a pure liquid at 1 bar, e.g.,



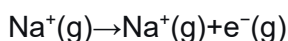
(c) Standard enthalpy of sublimation, $\Delta_{sub} H^\ominus$: This is the enthalpy change for a pure substance in which one mole of a pure solid at 1 bar is directly converted into a vapor at 1 bar, e.g.,



(2) Standard Enthalpy of solution, $\Delta_{sol} H^\ominus$: The standard enthalpy of solution of a substance is the enthalpy change when one mole of the pure solute at 1 bar dissolves in a specified quantity of the solvent. Limiting enthalpy of solution of a substance is the enthalpy change when one mole of the pure solute at 1 bar dissolves in an infinite amount of solvent and the interaction between the ions (or solute molecules) are negligible. For HCl,



(3) Enthalpy of Ionisation, $\Delta_{ion} H^\ominus$: The enthalpy of ionisation is the standard enthalpy change per mole for the removal of an electron from a species in the gas phase (e.g.,



Here, $\Delta n_g = 2 - 1 = +1 \text{ mol}$

$$\therefore \Delta H = \Delta U + \Delta n_g \times RT$$

$$\therefore \Delta_{ion} H^\ominus = \Delta_{ion} U^\ominus + RT$$

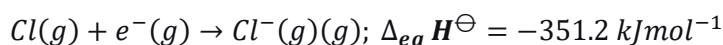
or

$$\Delta_{ion} H^\ominus = E_i + RT$$

where E_i the ionization energy or molar internal energy of ionization. Because $RT = 2.5 \text{ kJ mol}^{-1}$ at room temperature, in approximate work it is reasonable to consider

$$\Delta_{ion} H^\ominus = E_i$$

(4) Electron gain enthalpy, $\Delta_{eg} H^\ominus$: The standard enthalpy change accompanying electron attachment to one mole of atom, ion or molecule in the gas phase is the electron gain enthalpy, $\Delta_{eg} H^\ominus$.



Here, $\Delta n_g = -1 \text{ mol}$

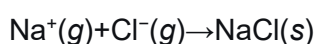
$$\therefore \Delta_{eg} H^\ominus = \Delta_{eg} U^\ominus - RT$$

The negative of the corresponding internal energy change is widely called the electron affinity, E_{ea} .

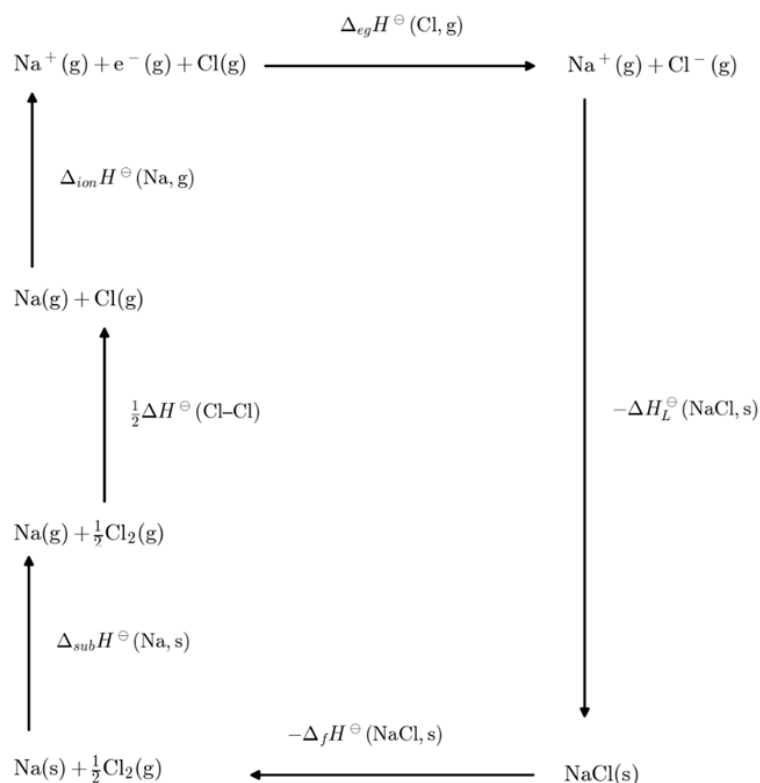
$$\Delta_{eg} H^\ominus = -E_{ea} - RT$$

The Born–Haber Cycle: The enthalpy of formation of a solid compound may be considered as an outcome of several contributions. For instance, solid sodium chloride can be regarded as the outcome of five steps:

1. Sublimation of Na(s): $Na(s) \rightarrow Na(g)$
2. Ionisation of Na(g): $Na(g) \rightarrow Na^+(g) + e^-(g)$
3. Dissociation of $\frac{1}{2} Cl_2(g)$: $\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$
4. Electron gain by Cl(g): $Cl(g) + e^-(g) \rightarrow Cl^-(g)$
5. Formation of NaCl from $Na^+(g)$ and $Cl^-(g)$:



A thermochemical cycle obtained from the above process is known as Born–Haber cycle: In a cycle, the sum of enthalpy changes is zero. If all but one of the enthalpy changes in a thermochemical cycle are known, then the unknown enthalpy change may be found.



For the cycle,

$$\Delta_{sub}H^{\ominus}(\text{Na}, s) + \frac{1}{2}\Delta H^{\ominus}(\text{Cl}-\text{Cl}) + \Delta_{ion}H^{\ominus}(\text{Na}, g) + \Delta_{eg}H^{\ominus}(\text{Cl}, g) - \Delta H_L^{\ominus}(\text{NaCl}, s) - \Delta_f H^{\ominus}(\text{NaCl}, s) = 0$$

Prob: Calculate the lattice enthalpy of NaCl(s) using a Born-Haber cycle from the following data:

$$\frac{1}{2}\Delta H^{\ominus}(\text{Cl}-\text{Cl}) = +121.68 \text{ kJ mol}^{-1}$$

$$\Delta_{sub}H^{\ominus}(\text{Na}, s) = +107.32 \text{ kJ mol}^{-1}$$

$$\Delta_{ion}H^{\ominus}(\text{Na}, g) = +493.3 \text{ kJ mol}^{-1}$$

$$\Delta_{eg}H^{\ominus}(\text{Cl}, g) = -351.2 \text{ kJ mol}^{-1}$$

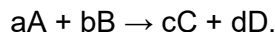
$$\Delta_f H^{\ominus}(\text{NaCl}, s) = -411.15 \text{ kJ mol}^{-1}$$

$$[\text{Ans: } \Delta H_L^{\ominus} = +787.2 \text{ kJ mol}^{-1}]$$

1.7 VARIATION OF ENTHALPY OF REACTION WITH TEMPERATURE (KIRCHHOFF'S EQUATION)

Enthalpy change associated with any process is a temperature dependent quantity. Temperature dependence of enthalpy change is expressed in terms of Kirchhoff's equation which can be derived in the following way:

For the general reaction



enthalpy of reaction is given by

$$\begin{aligned} \Delta_r H &= \sum H_{products} - \sum H_{reactants} \\ &= \{cH_m(C) + dH_m(D)\} - \{aH_m(A) + bH_m(B)\} \dots \dots \dots (i) \end{aligned}$$

Differentiating with respect to T, keeping P constant,

$$\left[\frac{\delta(\Delta_r H)}{\delta T} \right]_P = c \left(\frac{\delta H_m(C)}{\delta T} \right)_P + d \left(\frac{\delta H_m(D)}{\delta T} \right)_P - a \left(\frac{\delta H_m(A)}{\delta T} \right)_P - b \left(\frac{\delta H_m(B)}{\delta T} \right)_P$$

Using the definition of C_P , i.e., $C_P = \left(\frac{\delta H}{\delta T} \right)_P$

$$\begin{aligned} \left[\frac{\delta(\Delta_r H)}{\delta T} \right]_P &= \{cC_{P,m}(C) + dC_{P,m}(D)\} - \{aC_{P,m}(A) + bC_{P,m}(B)\} \\ \therefore \left[\frac{\delta(\Delta_r H)}{\delta T} \right]_P &= \Delta_r C_P \dots \dots \dots (ii) \end{aligned}$$

Where $C_{P,m}$ denotes molar heat capacity of the substance specified within bracket.

From (ii), $d(\Delta_r H) = \Delta_r C_p dT \dots \dots \dots (iii)$

Integrating equation (iii) within the temperature limits T_1 and T_2 ,

$$\int_{T_1}^{T_2} d(\Delta_r H) = \int_{T_1}^{T_2} \Delta_r C_p dT$$

$$\Rightarrow \Delta_r H(T_2) - \Delta_r H(T_1) = \int_{T_1}^{T_2} \Delta_r C_p dT \dots \dots \dots (iv)$$

This equation is known as the Kirchhoff's equation.

Two possibilities arise here as discussed below.

- (a) When $\Delta_r C_p$ is independent of temperature. In such a case, Kirchhoff's equation becomes,

$$\Delta_r H(T_2) - \Delta_r H(T_1) = \Delta_r C_p (T_2 - T_1) \dots \dots \dots (v)$$

- (b) When $\Delta_r C_p$ is dependent on temperature.

The variation of molar heat capacity with temperature is usually given as

$$C_{p,m} = \alpha + \beta T + \gamma T^2$$

where α , β , and γ are constants for a specific reactant or product.

$$\begin{aligned} \therefore \Delta_r C_p &= [(c\alpha_C + d\alpha_D) - (a\alpha_A + b\alpha_B)] + [(c\beta_C + d\beta_D) - (a\beta_A + b\beta_B)]T + \\ &[(c\gamma_C + d\gamma_D) - (a\gamma_A + b\gamma_B)]T^2 + \dots \dots \dots \\ &= \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \dots \dots \dots (vi) \end{aligned}$$

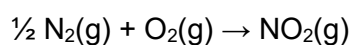
Substituting equation (vi) in equation (iv),

$$\int_{T_1}^{T_2} d(\Delta_r H) = \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \dots) dT$$

$$\Rightarrow \Delta_r H(T_2) - \Delta_r H(T_1) = \Delta\alpha(T_2 - T_1) + \frac{1}{2}\Delta\beta(T_2^2 - T_1^2) + \frac{1}{3}\Delta\gamma(T_2^3 - T_1^3) + \dots$$

Try this

14. Calculate standard enthalpy of reaction at 373 K for



Use the following data:

$$\Delta_r H^\circ(298 \text{ K}) = -33.18 \text{ kJ mol}^{-1}; C_{p,m}(\text{NO}_2, \text{g}) = 37.20 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_{p,m}(\text{O}_2, \text{g}) = 29.36 \text{ J K}^{-1} \text{ mol}^{-1}; C_{p,m}(\text{N}_2, \text{g}) = 29.13 \text{ J K}^{-1} \text{ mol}^{-1}$$

1.7 ANSWERS TO TRY THESE PROBLEMS

Ans to Q No1: When $\Delta V \approx 0$, $\Delta H = \Delta U$. For reactions having solid and liquid reactants at constant T and P , $\Delta V \approx 0$.

Ans to Q No 2: Here we use the equation $\Delta H = \Delta U + P\Delta V$

(i) In a fusion process, the volume change $\Delta V = V_l - V_s \approx 0$; so, $\Delta H = \Delta U$

(ii) In an evaporation process, the volume change $\Delta V = V_g - V_l$ is considerable; so, ΔH is greater than ΔU .

Ans to Q No 3: The relevant equation is $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$.

Here, $\Delta n_g = 2 - (3+1) = -2 \therefore q_p = q_v - 2RT$

Ans to Q No 4: Relevant equation is $\text{SO}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$

Here, $\Delta n_g = 1 - (1+\frac{1}{2}) = -\frac{1}{2}$

Hence, $\Delta H = \Delta U + RT \times \Delta n_g$

$$= (-97.027 \text{ kJ mol}^{-1}) + (-\frac{1}{2})(8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298 \text{ K})$$

$$= -98.3 \text{ kJ mol}^{-1}$$

Ans to Q No 5: Pure graphite at 1 bar

Ans to Q No 6: $\text{C}(\text{s}) + 2 \text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$; $\Delta_r H^\circ = ?$

Ans to Q No 7: $\Delta_r H = -46.1 \text{ kJ mol}^{-1}$

Ans to Q No 8: $\Delta_r H = -777.7 \text{ kJ mol}^{-1}$

Ans to Q No 9: No, enthalpy of combustion is always negative.

Ans to Q No 10: $\Delta_r H (\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) = -1260.4 \text{ kJ mol}^{-1}$

Ans to Q No 11: $\Delta_c H (\text{graphite}, \text{s}) = -248.4 \text{ kJ mol}^{-1}$

Ans to Q No 12: $\Delta_c H (\text{C}_6\text{H}_6, \text{l}) = -1632.3 \text{ kJ mol}^{-1}$

Ans to Q No 13: $\Delta H - \Delta U = -3RT$

Ans to Q No 14: $\Delta_r H^\circ(373 \text{ K}) = -33.68 \text{ kJ mol}^{-1}$

1.8 MODEL QUESTIONS

14. Fill in the blanks:

- (i) A reaction that releases heat is called
- (ii) Enthalpy of formation is the enthalpy change when one mole of a compound is formed from its

15. Derive a relationship between enthalpy change and internal energy change of a reaction.

16. Select the correct answer:

Enthalpy of formation of a compound is:

- (i) positive
- (ii) zero
- (iii) may be positive or negative
- (iv) always negative

17. Define standard state. What is the standard state of a solid?

18. Define and give example of the following terms:

- (i) Standard reaction enthalpy
- (ii) Standard enthalpy of combustion
- (iii) Standard enthalpy of formation
- (iv) Standard enthalpy of neutralisation

19. Explain, giving reason:

Enthalpy of neutralisation of a strong monobasic acid by a strong base is always equal to $-57.3 \text{ kJ mol}^{-1}$.

20. State Hess's law of constant heat summation. Justify the statement- "Hess's law is a direct consequence of the first law of thermodynamics."

21. Calculate the bond enthalpy of C—O bond in methanol from the following data:

- (i) $\text{C(s)} + 2 \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) = \text{CH}_3\text{OH}(\text{g}); \Delta H^\circ = -200.0 \text{ kJ mol}^{-1}$
- (ii) $\text{C(s)} = \text{C(g)}; \Delta H^\circ = 716.8 \text{ kJ mol}^{-1}$
- (iii) $2 \text{H}_2(\text{g}) = 4 \text{H(g)}; \Delta H^\circ = 872.0 \text{ kJ mol}^{-1}$
- (iv) $\frac{1}{2} \text{O}_2(\text{g}) = \text{O(g)}; \Delta H^\circ = 249.0 \text{ kJ mol}^{-1}$

22. State whether the following statement is true or false:

Bond enthalpy and bond dissociation enthalpy are same for diatomic molecules.

23. How would you determine resonance energy from bond enthalpy?

24. Derive Kirchhoff's equation to show the variation of reaction enthalpy with temperature.