2. Energetics

Content

2.1 Basic terms in thermochemistry and thermodynamics

2.1.1 System, surrounding and boundary

2.1.2 Types of systems
- Open system
- Closed system
- Isolated system
- Homogeneous and heterogeneous systems

2.1.3 Properties of a system
- Microscopic properties
- Macroscopic properties
  - Extensive properties
  - Intensive properties

2.1.4 State of a system
- Spontaneous processes
- Non-spontaneous processes
- Reversible process
- Irreversible process

2.1.5 Enthalpy (*H*)

2.1.6 Heat
- Specific heat and heat capacity

2.2 Enthalpy changes and standard enthalpy changes associated with different thermochemical processes/ reactions

2.2.1 Exothermic and endothermic processes
- Standard enthalpy changes

2.2.2 Thermochemical equations

2.2.3 Enthalpy diagrams

2.2.4 Enthalpy changes and standard enthalpy changes
- Standard enthalpy change of formation, ΔH_f^{θ}
- Standard enthalpy change of combustion, ΔH_c^{θ}
- Standard enthalpy change of bond dissociation, ΔH_D^{θ}
- Standard enthalpy change of neutralization, ΔH_{neu}^{θ}
- Standard enthalpy change of solvation, ΔH_{sol}^{θ}
- Standard enthalpy change of hydration, ΔH_{hyd}^{θ}
- Standard enthalpy change of dissolution, $\Delta H_{dissolution}^{\theta}$
- Standard enthalpy change of sublimation, ΔH_{sub}^{θ}
- Standard enthalpy change of evaporization, ΔH_{evap}^{θ}
- Standard enthalpy change of fusion, ΔH_{fus}^{θ}
- Standard enthalpy change of atomization, ΔH_{at}^{θ}
- Standard enthalpy change of first ionization, ΔH_{IE1}^{θ}
- Standard enthalpy change of electron gain, ΔH_{EG}^{θ}
- Standard lattice enthalpy change of an ionic compound, ΔH_L^{θ}

2.2.5 Indirect determination of $\Delta H (\Delta H^{\theta})$: Hess law
- Standard enthalpy of reaction

2.3 Lattice enthalpy or enthalpy of formation of an ionic compound: Born-Haber cycle

2.4 Spontaneity of chemical reactions
- Standard entropy change of a chemical reaction
- Gibbs free energy (*G*) and spontaneity of a reaction

Introduction

This unit discusses the study of the role or changes of energy in the form of heat. Almost all chemical reactions absorb or release energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. **Heat** is *the transfer of thermal energy between two bodies that are at different temperatures* and we often speak of "heat flow" from a hot object to a cold one. Although the term "heat" by itself implies transfer of energy when describing the energy changes that occur during a process, we customarily talk of "heat absorbed" or "heat released". **Thermochemistry** is *the study of heat change in chemical reactions* and when considering thermochemical events they are usually in reference to a state of standard state.

This chapter is concerned with the study of energy changes at the molecular level and the consequences to the changes of that system. In this regard, the basic terms appearing in thermochemistry must first be defined and understood. The significance of mathematical symbols "+" and "-" specified with the energy change must also be understood in respect of the amount of energy produced or supplied and this will be used to explain types of reactions such as endothermic and exothermic reactions. Thereafter, the discussion will move into the definition of enthalpies of different chemical events/reactions and expanded to the standard state. The basic laws in thermochemistry (Hess Law) will be used to perform calculations for chemical events as appropriate. Finally, the tendency for the occurrence of a reaction will be discussed with entropy, enthalpy and Gibbs free energy relation ($\Delta G = \Delta H - T\Delta S$) and hence to the spontaneity of reactions.

2.1 Basic terms in thermochemistry and thermodynamics

2.1.1 System, surrounding and boundary

It is useful to define and understand important terms that are used to define and explain the basic concepts and laws of thermochemistry.

- **System**

  A thermochemical system is defined as any portion of matter or universe under consideration which is separated from the rest of the universe. (or simply the object under study is defined as the system).

- **Surroundings**

  Everything in the universe (or the rest) that is not a part of the system and can interact with it is called surroundings (or simply everything outside the system).

- **Boundary**

  It is anything (for example wall of flask) which separates the system from its surroundings.

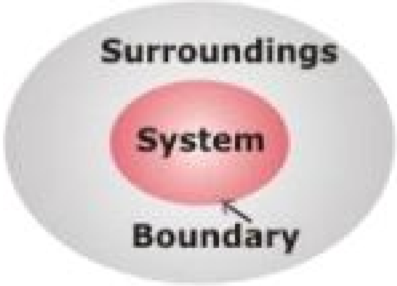


Figure 2.1 Schematic representation of a system, surroundings and boundary

2.1.2 Types of systems

There are different types of systems which can be defined depending on the interactions/processes between the system and the surroundings.

- **Open system**

  A system is said to be open if it can exchange both energy and matter/ mass with its surroundings. For example, an open bottle containing an aqueous salt solution represents an open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings or separately from the surroundings to the system.

- **Closed system**

  A system which permits the exchange of energy but not matter/ mass, across the boundary with its surroundings is called a closed system. For example, a liquid in equilibrium with its vapour in a sealed bottle represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

- **Isolated system**

  A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated system.

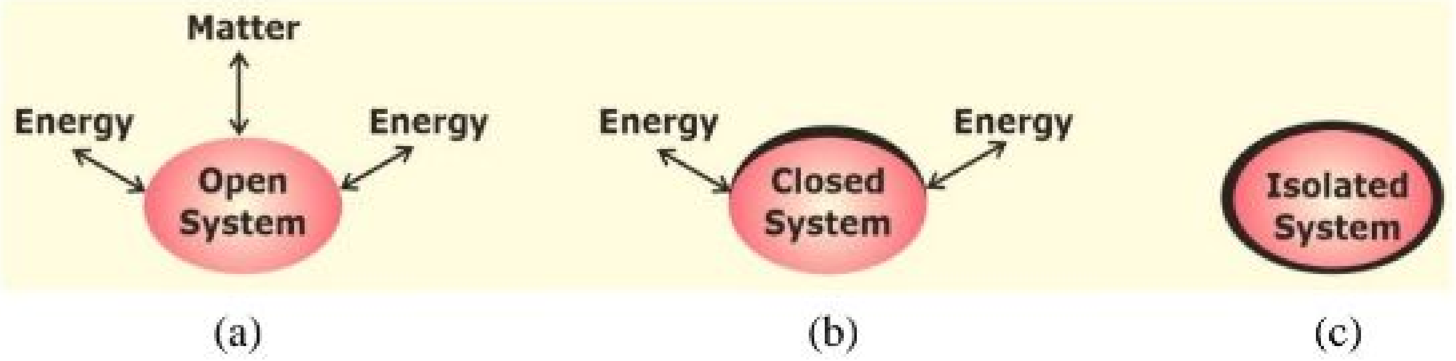


Figure 2.2 Schematic view of (a) open, (b) closed and (c) isolated systems

- **Homogeneous and heterogeneous systems**

  A system is said to be **homogeneous** if the physical states of all its matter are uniform. For example mixtures of gases, mixtures of completely miscible liquids, etc.

A system is said to be **heterogeneous**, if its contents do not possess the same physical state (phase). For example, immiscible liquids, solid in contact with an immiscible liquid, solid in contact with a gas, etc.

2.1.3 Properties of a system

- **Microscopic properties**
  A system is called a microscopic system if it is roughly of atomic dimensions i.e. on the atomic or molecular scale the properties must be determined by an indirect method(s) such as kinetic energy, speed, etc. of atoms/molecules in a closed container.

- **Macroscopic properties**
  The properties which are associated with bulk or macroscopic state of the system such as pressure, volume, temperature, concentration, density, viscosity, surface tension, refractive index, colour, etc. are called macroscopic properties.

Macroscopic properties of a system can be divided into two types.

- **Extensive properties**
  The properties that depend on the amount or size of a system (extent of a system) are called extensive properties. (For example, volume, number of moles, mass, energy, internal energy etc.). The value of the extensive property is equal to the sum of extensive properties of smaller parts into which the system is divided. Suppose masses $\mathbf{m_1}$ g, $\mathbf{m_2}$ g and $\mathbf{m_3}$ g are mixed in a system. Then the total mass of the system is equal to $(\mathbf{m_1}+\mathbf{m_2}+\mathbf{m_3})$ g. Thus mass is an extensive property.

- **Intensive properties**
  The properties that are independent of the amount or size of the system (extent of a system) are known as intensive properties. (For example, refractive index, surface tension, density, temperature, boiling point, freezing point, etc.), of the system. These properties do not depend on the number of moles of the substance in the system.

  If any extensive property is expressed per mole (mol^{-1}) or per gram (g^{-1}) or per cm^3 (cm^{-3}) or per cm^2 (cm^{-2}), it becomes an intensive property. For example, mass, volume, heat capacity are extensive properties while density, molar volume, specific heat capacity are intensive properties.

2.1.4 State of a system

A system is said to be in a particular physical state when specific values of the macroscopic properties of the system are known. For example, the gaseous state of matter can be described by parameters pressure (P), volume (V) and temperature (T) etc. The values of these parameters change when the matter is in liquid state. Thus, the

state of a system is defined by specific measurable macroscopic properties of the system.

The **initial state** of system refers to the starting state of the system before any kind of interaction with its surroundings.

The **final state** of system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter, heat, energy or all.

The variables like P, V, T and composition (or amount of moles or 'n') that are used to describe the state of a system are called **state variables** or **state functions**. When the state of the system changes, the values of the state variables of the system also change. Thus, state functions depend only on the initial state and the final state of the system and not on how the changes occur. Also, if the values of state functions of a system are known, all other properties like mass, viscosity, density, etc. of the system become specified. For specifying a state of the system, it is not necessary to know all the state variables, since they are interdependent and only a few of them (state variables) are sufficient.

Standard state

It is needed to refer to a reference pressure or the standard pressure denoted by P^{Θ} *at a specified temperature when heat changes in a system is considered. The standard pressure has a constant value in any given application. The IUPAC recommended the value for* P^{Θ} *as 1 atm (101325 Pa). (Note that there is no defined standard temperature, however, 298 K is used sometimes as specified.) A standard state of a pure substance is a particular reference state appropriate for the phase and is described by intensive variables. For example, standard state of solid iron is pure iron at 1 atm and at a given temperature (500 K). Standard conditions are denoted by adding the superscript* Θ *to the symbol of the quantity* (ΔH^{Θ}, ΔG^{Θ}, ΔS^{Θ} *etc.) It has to be noted that when solutions are involved, a concentration is 1 mol* dm^{-3}.

- **Spontaneous processes**

  These are occurring on their own accord. For example heat flow from a hotter end of a metal rod to a colder end. In these processes, the transformation of the system from the initial, to the final state is favourable in a particular direction only. Many of the spontaneous processes are natural processes and are also, irreversible processes.

- **Non-spontaneous processes**
  These are not occurring on their own accord. For example, although carbon burns in air evolving heat to form carbon dioxide, on its own carbon does not catch fire and an initial heat supply is required.

- **Reversible process**
  In a reversible process the series of changes carried out on the system during its transformation from initial to final state may be possibly reversed in an exact manner. This is possible when the changes are carried out very slowly in many smaller steps on the system during its change from initial to final state. Under such conditions the initial and final states of the system become reversible completely. For example, when ice melts a certain amount of heat is absorbed. The water formed can be converted back to ice if the same amount of heat is removed from it.

- **Irreversible process**
  An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings. Many of the spontaneous processes are irreversible in nature. For example biological ageing is an irreversible process. Water flowing down a hill on its own accord is an irreversible process.

2.1.5 Enthalpy (*H*)

Most of the physical and chemical changes take place or are carried out under the constant pressure conditions. For example in the laboratory, reactions are generally carried out in beakers, flasks, or test tubes that remain open to their surroundings and hence to a pressure of approximately one atmosphere (1 atm, $\sim 10^5$ Pa). To quantify the heat flow into or out of a system in a constant pressure process, chemists use a property called **enthalpy,** represented by the symbol ***H***. i.e. at constant pressure chemist use the relation, heat change equals to enthalpy change. Enthalpy is an extensive property; its magnitude depends on the amount of the substance present. It is impossible to determine the enthalpy of a substance, so it is the change in enthalpy, ΔH, that we actually measure.

The **enthalpy change of reaction, *ΔH*,** *is the difference between the total enthalpies of the products and the total enthalpies of the reactants.*

$$\boxed{\Delta H = H_{(\text{products})} - H_{(\text{reactants})}}$$

2.1.6 Heat

As the enthalpy is equal to the heat (q) at constant pressure, we may consider the measurement of heat changes. In the laboratory heat changes in physical and chemical processes are measured with a calorimeter, a closed container designed specifically for this purpose. To estimate heat changes we first need to have an understanding of specific heat and heat capacity.

Specific heat and heat capacity

The **specific heat (c)** of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius. The **heat capacity (C)** of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Specific heat is an intensive property, whereas heat capacity is an extensive property. The relationship between the heat capacity and specific heat of a substance is

$$\boxed{C = m\,c}$$

where, m is the mass of the substance in grams.
Note: *sometimes* **s** *is used to denote specific heat.*

For example, the specific heat of water is 4.184 J g^{-1} °C^{-1} and the heat capacity of 100.0 g of water is (100.0 g) × (4.184 J g^{-1} °C^{-1}) = 418.4 J °C^{-1}.

Note: *Specific heat has the units* J g^{-1} °C^{-1} *(or* J g^{-1} K^{-1}*) and heat capacity has the units* J °C^{-1} *(or* J K^{-1}*).*

Knowing the specific heat, the mass of a substance and the change in the sample's temperature Δt (temperature in °C) or ΔT (temperature in K), the amount of heat (Q) that has been absorbed or released in a particular process can be calculated by the equation;

$$\boxed{Q = m\,c\Delta t \quad \text{or} \quad Q = m\,c\Delta T}$$

where m is the mass of the sample and Δt is the temperature change i.e. $\Delta t = t_{\text{final}} - t_{\text{initial}}$
The sign convention for q is the same as that for enthalpy change; q is positive for endothermic processes and negative for exothermic processes.

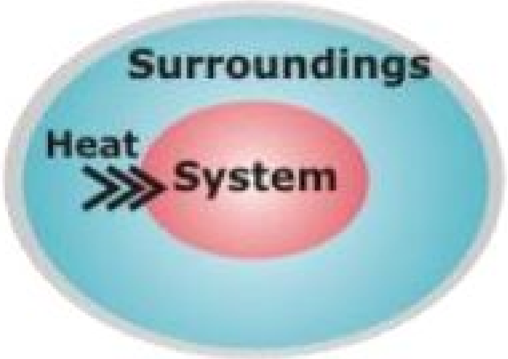
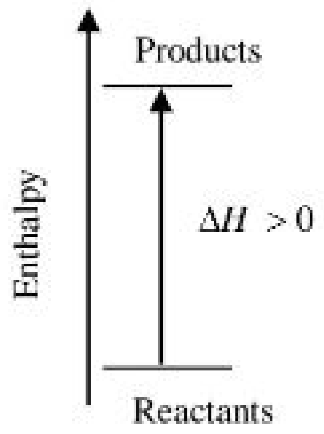
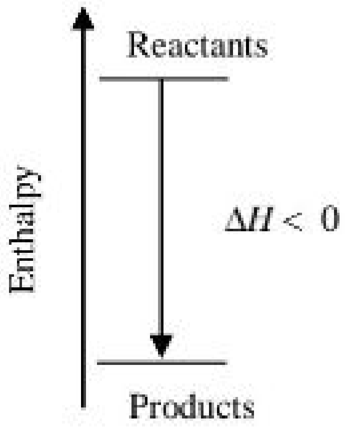
2.2 Enthalpy changes and standard enthalpy changes associated with different thermochemical processes/ reactions

ΔH represents the heat given off or absorbed during a reaction. The enthalpy of reaction can be positive or negative, depending on the process. Enthalpy change is directly proportional to the amounts of substances in a system.

2.2.1 Exothermic and endothermic processes

When a thermodynamic process is a chemical reaction or a physical transformation, it is classified as either exothermic or endothermic depending on the nature of heat change involved in the overall process. These two processes are differentiated as follows:

Table 2.1 Comparison between endothermic and exothermic processes

Endothermic processes	**Exothermic processes**
A process that transforms a system from initial to final state by absorption of heat is called an endothermic process.	A process that transforms a system from initial to final state by evolution of heat is called an exothermic process.
The final state of the system possesses higher energy than the initial state. The energy needed is absorbed as heat by the system from the surroundings. Example: Dissolving ammonium chloride in water.	The final state of the system possesses lower energy than the initial state. The excess energy is released as heat to the surrounding. Example: All combustion processes are exothermic.
Generally in a physical transformation which is endothermic, heat is supplied to bring about the change from initial to final state. Example: melting of a solid by supplying heat is an endothermic process.	If the physical transformation is exothermic heat is removed to bring about the change from the initial to final state. Example: Freezing of a liquid at its freezing point is an exothermic process.
Reactant + Energy(Heat) → Products $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + 90\text{ kJ} \rightarrow NO(g)$	Reactant → Products + Energy(Heat) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + 242\text{ kJ}$
	
For an endothermic process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$)	For an exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$)
	

Heat effects measured at constant pressure indicate changes in enthalpy of a system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Standard enthalpy changes

The measured enthalpy change for a reaction has a unique value only if the initial state (reactants) and final state (products) are precisely described. If we define a standard state (10^5 Pa pressure and a temperature of interest) for the reactants and products, we can then say that the standard enthalpy change is the enthalpy change in a reaction in which the reactants and products are in their standard states. This so-called **standard enthalpy of reaction** is denoted with a degree symbol, ΔH^θ. Although temperature is not a part of the definition of a standard state, it still must be specified in tabulated values because it depends on temperature. The standard temperature values given in this text are all 298.15 K or 25 °C unless otherwise stated.

Simply, we can say;

> *The standard enthalpy change of a reaction is the enthalpy change which occurs when the given quantities in a reaction react under standard conditions to form products in the standard state.*

2.2.2 Thermochemical equations

A balanced chemical equation together with standard conventions adopted and including the value of ΔH (or ΔH^θ) of the reaction is called a thermochemical equation. The following conventions are necessarily adopted in a thermochemical equation.

(i) The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

(ii) The enthalpy change of a reaction has unit **kJ mol^{-1}** and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

(iii) When a chemical reaction is reversed the value of ΔH is reversed in sign with the magnitude remaining the same.

(iv) Physical states of all species is important and must be specified in a thermochemical equation since ΔH (or ΔH^θ) depends on states (phases) of reactants and products.

(v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number.

(vi) The negative sign of ΔH^o indicates an exothermic reaction and a positive sign of ΔH^θ indicates an endothermic reaction.

Example:

Consider the following reactions.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \boldsymbol{\Delta H^\theta = -\ 483.7\ \mathrm{kJ\ mol^{-1}}}$$

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \boldsymbol{\Delta H^\theta = -\ 571.6\ \mathrm{kJ\ mol^{-1}}}$$

First reaction in the above thermochemical equations can be interpreted in several ways.

- 483.7 kJ given off per mole of the reaction*
- 483.7 kJ given off per 2 moles of $H_2(g)$ consumed
- 483.7 kJ given off per mole of $O_2(g)$ consumed

- 483.7 kJ given off per 2 moles of water vapour formed

ΔH^θ tells how much the enthalpy change would be, if the number of moles reacting is the same as the stoichiometric coefficients.

* **Note:** *In this case, 483.7 kJ mol*$^{-1}$*means that 483.7 kJ of heat is evolved when 2 moles of hydrogen gas were to react with 1 mole of oxygen gas to form 2 moles of gaseous water*

Sometimes the above reaction is written as;

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \mathbf{\Delta H^\theta = -\ 483.7\ kJ}$$

* **Note:** *In this case, 483.7 kJ of heat is evolved when a defined extent of reaction occurs as written and gives the units in* ***kJ****. Extent of reaction has the unit of mol. For the above reaction ;* $\boldsymbol{\Delta H} = \boldsymbol{\Delta H^\theta} \times \mathbf{mol} = \mathbf{-\ 483.7\ kJ\ mol^{-1}} \times \mathbf{mol} = \mathbf{-\ 483.7\ kJ}$

For example if we write the reaction as;

$$4H_2(g) + 2O_2\ (g) \rightarrow 4H_2O(g)$$

then we write ΔH of the reaction as $2 \times \Delta H^\theta$ **= - 967.4 kJ**

That means the original ΔH^θ value has to be multiplied by 2 or in other words the value of ΔH is multiplied by the amount (mol) of substance reacting. Therefore, instead of the extent of reaction, we can use the actual amount of substance of any species reacting, divided by its stoichiometric coefficient in the simplest balanced chemical equation. Hence for the above reaction we get (for oxygen),

$$\Delta H = -\ 483.7\ \text{kJ mol}^{-1} \times \left(\frac{2\ \text{mol}}{1}\right) = -\ 967.4\ \text{kJ}$$

If we are giving only ΔH^θ, then it would equals to - 967.4 kJ mol^{-1}

If we write the equations as;

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \boldsymbol{\Delta H_f^0 = -285.8\ \text{kJ mol}^{-1}}$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \boldsymbol{\Delta H_f^0 = -241.85\ \text{kJ mol}^{-1}}$$

We can see that the enthalpy values are halves of the above values.

The above equations describe the combustion of hydrogen gas to water in a general sense. The first reaction can be considered the formation reaction of liquid water and the second reaction the formation of water vapour. The negative sign of ΔH indicates that they are exothermic reactions.

The reaction which is exothermic in the forward direction is endothermic in the reverse direction and vice-versa. This rule applies to both physical and chemical processes.

$$2H_2O(l) \rightarrow 2H_2(g) + O_2(g) \quad \Delta H^\ominus = +\ 571.6\ \text{kJ mol}^{-1}$$
$$2H_2O(g) \rightarrow 2H_2(g) + O_2(g) \quad \Delta H^\ominus = +\ 483.7\ \text{kJ mol}^{-1}$$

2.2.3 Enthalpy diagrams

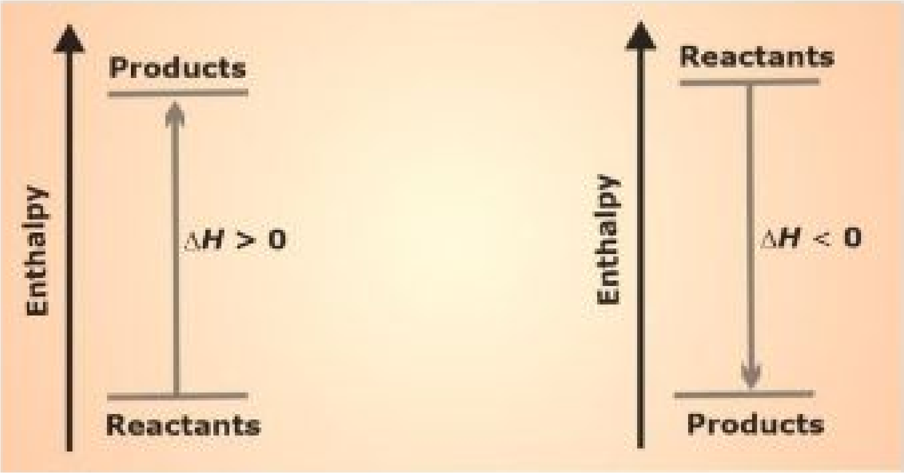
Consider the following reaction.

$$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l) \quad \Delta H^\ominus = -5650\ \text{kJ mol}^{-1}$$

The negative sign of $\Delta H^\ominus$ in the above equation means that the enthalpy of the products is lower than that of the reactants. This decrease in enthalpy appears as heat evolved to the surroundings. The combustion of sucrose is an exothermic reaction.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad \Delta H^\ominus = 180.50\ \text{kJ mol}^{-1}$$

In the above reaction the products have a higher enthalpy than the reactants so $\Delta H^\ominus$is positive. To produce this increase in enthalpy, heat is absorbed from the surroundings. The reaction is endothermic. An **enthalpy diagram** is a diagrammatic representation of enthalpy changes in a process. Figure 2.3 below shows how exothermic and endothermic reactions can be represented through such diagrams as are already shown in the Table 2.1).



(a) (b)

Figure 2.3 Enthalpy diagrams of (a) endothermic and (b) exothermic processes

2.2.4 Enthalpy changes and standard enthalpy changes

- **Standard enthalpy change of formation,** $\Delta H_f^\ominus$

The **standard enthalpy of formation,** $\Delta H_f^\ominus$ of a substance is the enthalpy change that occurs in the formation of one mole of the substance in the standard state from the reference forms of the elements in their standard states. The reference forms of the elements in all but a few cases are the most stable forms of the elements at one atm (101325 Pa) and the given temperature. The $\ominus$ symbol denotes that the enthalpy change is a standard enthalpy change, and the subscript "*f*" signifies that the reaction is one in which a substance is formed from its elements. Because the formation of the most stable form of an element from itself is no change at all that is *the standard enthalpy of a pure element in its reference form is 0.*

For example, listed below are the most stable forms of some elements/ compounds at 298.15 K, the temperature at which thermochemical data are commonly tabulated.

$Na(s), H_2(g), N_2(g), O_2(g), C(s, graphite), Br_2(l)$

Example :

One may concern the situation with carbon. In addition to graphite, carbon also exists naturally in the form of diamond. However, because there is a measurable enthalpy difference between them, they cannot both be assigned $\Delta H_f^\theta = 0$

$$C(s, \text{graphite}) \rightarrow C(s, \text{diamond}) \; ; \Delta H_f^\theta = 1.9 \text{ kJ mol}^{-1}$$

We choose as the reference form the more stable form, the one with the lower enthalpy. Thus, we assign $\Delta H^{\circ}_{f(graphite)} = 0$.

The physical state of the product of the formation reaction must be indicated explicitly if it is not the most stable one at 25 °C and 1 atm pressure

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \boldsymbol{\Delta H_f^\theta = -285.8 \text{ kJ mol}^{-1}}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \boldsymbol{\Delta H_f^\theta = -241.8 \text{ kJ mol}^{-1}}$$

Note that the difference between these two $\boldsymbol{\Delta H_f^\theta}$ values is just the heat of vapourization (44 kJ mol^{-1}) of water.

We often use standard enthalpies of formation in a variety of calculations and the first thing we must do is to write the chemical equation to which a ΔH_f^θ value applies, as illustrated in following examples in the text.

The standard enthalpy of formation of formaldehyde (HCHO) is -108 kJ mol^{-1} at 298 K and the chemical equation below shows this event.

$$H_2(g) + \frac{1}{2}O_2(g) + C(\text{graphite}) \rightarrow HCHO(g) \qquad \boldsymbol{\Delta H_f^\theta = -108 \text{ kJ mol}^{-1}}$$

Before going to discuss some examples it is worth defining standard enthalpies of some chemical reactions/events.

- **Standard enthalpy change of combustion, ΔH_c^θ**

It is the enthalpy change when one mole of an element or a compound in the standard state undergoes complete combustion with excess oxygen (or one may say air) in the standard state to give the products in the standard state.

$$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \qquad \boldsymbol{\Delta H^\theta_{c[C_3H_8(g)]} = -\ 2219.9 \text{ kJ mol}^{-1}}$$

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad \boldsymbol{\Delta H^\theta_{c[C(s)]} = -\ 393.5 \text{ kJ mol}^{-1}}$$

- **Standard enthalpy change of bond dissociation, ΔH°_{D}**

It is the enthalpy change when a gaseous compound in the standard state undergoes dissociation to gaseous atoms or components in the standard state by breaking a mole of bonds.

$H_2(g) \rightarrow 2H(g)$ $\quad \Delta H^{\theta}_{D} = 432 \text{ kJ mol}^{-1}$

$CH_4(g) \rightarrow CH_3(g) + H(g)$ $\quad \Delta H^{\theta}_{D} = 428 \text{ kJ mol}^{-1}$

$CH_3(g) \rightarrow CH_2(g) + H(g)$ $\quad \Delta H^{\theta}_{D} = 441 \text{ kJ mol}^{-1}$

$CH_2(g) \rightarrow CH(g) + H(g)$ $\quad \Delta H^{\theta}_{D} = 454 \text{ kJ mol}^{-1}$

$CH\,(g) \rightarrow C(g) + H(g)$ $\quad \Delta H^{\theta}_{D} = 344 \text{kJ mol}^{-1}$

Therefore the bond dissociation energy change of methane is the mean value of the above four enthalpy values.

Mean standard enthalpy change of bond dissociation of $CH_4(g)$ $= \frac{(428 + 441 + 454 + 344) \text{ kJ mol}^{-1}}{4}$

$= 416.75 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of neutralization, ΔH^{θ}_{neu}**

It is the enthalpy change when a mole of an aqueous H^+ ions and a mole of an aqueous OH^- ions in the standard state react to form a mole of liquid water.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\quad \Delta H^{\theta}_{neu} = -57 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of solvation, ΔH^{θ}_{sol}**

It is the enthalpy change when a mole of gaseous ions in the standard state changes into a solution to form 1.0 mol dm^{-3}.

$M^{n+}(g) + \text{solvent} \rightarrow M^{n+}(\text{solvent})$

- **Standard enthalpy change of hydration, ΔH^{θ}_{hyd}**

It is the enthalpy change when a mole of gaseous ions in the standard state changes into a solution with water with the concentration of 1.0 mol dm^{-3}.

$Na^+(g) + \text{water} \rightarrow Na^+(aq)$ $\quad \Delta H^{\theta}_{hyd} = -406 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of dissolution, $\Delta H^{\theta}_{dissolution}$**

It is the enthalpy change when a mole of a substance in the standard state dissolved in a solvent to form a solution with the concentration of 1.0 mol dm^{-3} (a saturated solution formed by a sparingly soluble salt).

$NaCl(s) + \text{water} \rightarrow NaCl(aq)$ $\quad \Delta H^{\theta}_{dissolution} = 1 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of sublimation, ΔH^{θ}_{sub}**

It is the enthalpy change when a mole of a solid element or a mole of a solid compound in the standard state converts completely into a gas at its standard state.

$Ca(s) \rightarrow Ca(g)$ $\quad$ $\Delta H^{\theta}_{sub} =$ **193 kJ mol^{-1}**

- **Standard enthalpy change of evaporization, ΔH^{θ}_{evap}**

It is the enthalpy change when a mole of a liquid compound or an element in the standard state converts into a mole of gaseous compound or element at its standard state.

$Br_2(l) \rightarrow Br_2(g)$ $\quad$ $\Delta H^{\theta}_{evap} =$ **30.91 kJ mol^{-1}**

- **Standard enthalpy change of fusion, ΔH^{θ}_{fus}**

It is the enthalpy change when a mole of a solid compound or an element in the standard state converts into a mole of liquid compound or element at its standard state.

$Al(s) \rightarrow Al(l)$ $\quad$ $\Delta H^{\theta}_{fus} =$ **10.7 kJ mol^{-1}**

- **Standard enthalpy change of atomization, ΔH^{θ}_{at}**

It is the enthalpy change when an element in the standard state converts into a one mole of gaseous atoms at the standard state.

$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ $\quad$ $\Delta H^{\theta}_{at} =$ **121 kJ mol^{-1}**

- **Standard enthalpy change of first ionization, ΔH^{θ}_{IE1}**

It is the enthalpy change when a mole of a gaseous mono-positive ions at standard state are formed by removing an electron from each atom that is most weakly bonded to the nucleus from a mole of gaseous atoms of an element in standard state.

$Na(g) \rightarrow Na^{+}(g) + e$ $\quad$ $\Delta H^{\theta}_{IE1} =$ **496 kJ mol^{-1}**

- **Standard enthalpy change of electron gain, ΔH^{θ}_{EG}**

It is the enthalpy change when a mole of gaseous mono-negative ions are formed by gaining electrons to a mole of gaseous atom at the standard state.

$Cl(g) + e \rightarrow Cl^{-}(g)$ $\quad$ $\Delta H^{\theta}_{EG} =$ **-349 kJ mol^{-1}**

- **Standard lattice dissociation enthalpy change of an ionic compound, ΔH^{θ}_{L}**

It is the enthalpy change when one mole of a solid ionic compound is converted to its gaseous positive and negative ions at the standard state.

$NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$ $\quad$ $\Delta H^{\theta}_{L} =$ **+788 kJ mol^{-1}**

2.2.5 Indirect determination of ΔH ($\Delta H^{\ominus}$): Hess Law

One of the reasons that the enthalpy concept is so useful is that a large number of heat of reaction can be calculated from a small number of measurements. The following features of enthalpy change make this possible.

ΔH is an extensive property and is also a function of state. Consider the standard enthalpy change of formation of $NO_{(g)}$ from its elements at 25 °C.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^{\ominus} = 180.50 \text{ kJ mol}^{-1}$$

To express the enthalpy change in terms of one mole of $NO_{(g)}$ we divide all coefficients and the value $\Delta H^{\ominus}$ by two.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H^{\ominus} = 90.25 \text{ kJ mol}^{-1}$$

$\Delta H^{\ominus}$ changes sign when a process is reversed as the change in a function of state reverses sign. Thus, for the decomposition of one mole of $NO_{(g)}$, standard enthalpy change is **-90.25 kJ mol^{-1}** which is the negative value of the enthalpy for the formation of one mole of $NO_{(g)}$.

$$NO(g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \qquad \Delta H^{\ominus} = -90.25 \text{ kJ mol}^{-1}$$

An example for Hess Law of constant heat summation:

The standard enthalpy change for the formation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$ can be found as follows.

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = ?$$

We can think of the reaction as proceeding in two steps: First we form $NO_{(g)}$ from $N_{2(g)}$ and $O_{2(g)}$, and then $NO_{2(g)}$ from $NO_{(g)}$ and $O_{2(g)}$.When the thermochemical equations for these two steps are added together with their individual and distinctive $\Delta H^{\ominus}$ values, we get the overall equation and $\Delta H^{\ominus}$ value that we are seeking.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H^{\ominus} = 90.25 \text{ kJ mol}^{-1} \quad \text{------ (1)}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = -57.07 \text{kJ mol}^{-1} \quad \text{------ (2)}$$

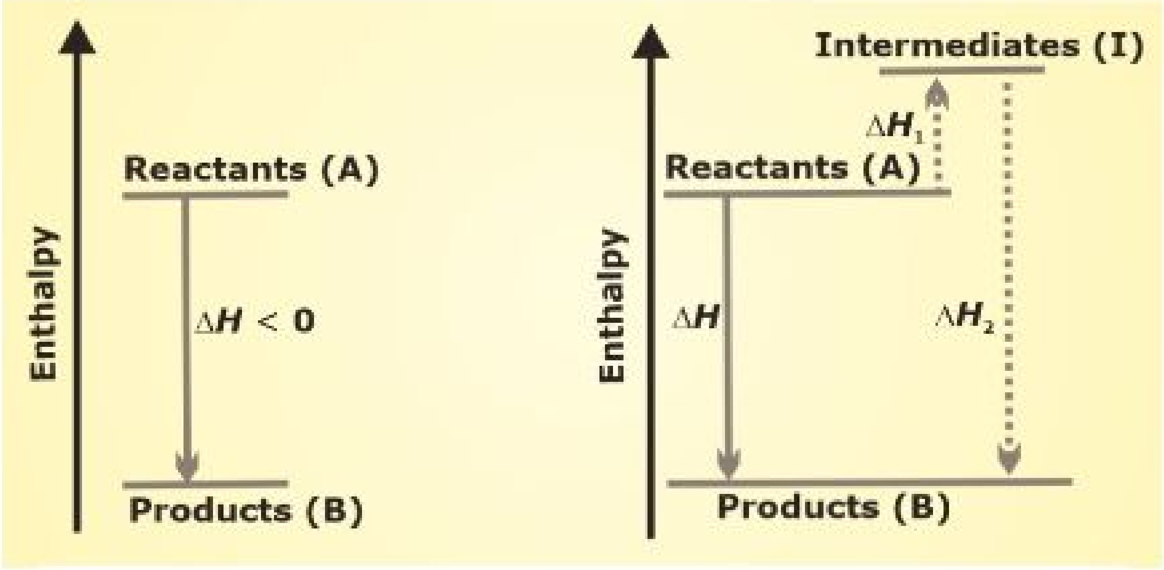
$$(1) + (2), \quad \tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = +33.18 \text{ kJ mol}^{-1}$$

As of the above example the **Hess law** states the principle we used: i.e.

> *If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.*

In other words, Hess law is simply a consequence of the state function property of enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH^o if the process is carried out under standard states) has the same value or it is independent of the route.

This concept can also be illustrated by an enthalpy diagram and a thermochemical cycle as described in Figure 2.4 and 2.5 respectively.



(a) (b)

Figure 2.4 Enthalpy changes for an exothermic reaction using two different ways of getting from reactants A to products B. (a) direct conversion and (b) two-step process involving some intermediates

Figure 2.4 describes the statement of Hess Law, that is, if you convert reactants A into products B, the overall enthalpy change will be exactly the same whether you do it in one step or two steps or many steps. In either case, the overall enthalpy change must be the same, because it is governed by the relative positions of the reactants and products on the enthalpy diagram.

Calculations can also be done by setting them out as enthalpy diagrams as above, but there is a much simpler way of doing it which needs a cycle to understand the process as below where the conversion of reactant A to product B is considered in two routes.

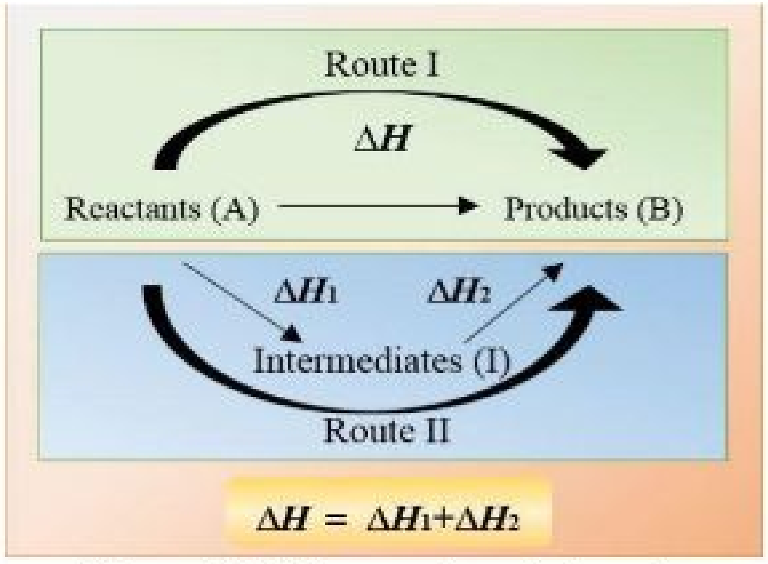


Figure 2.5 Thermochemical cycle

When we write the thermochemical cycle it is important to follow the instructions given below.

First write the chemical reaction in which the enthalpy change needs to find and write ΔH over the top of the arrow. Then include the other reactions with thermodynamic information to the same diagram to make a thermochemical cycle (Hess law cycle), and write the known enthalpy changes over the arrows for each of the other reactions. Find two routes around the diagram, always going with the flow of the various arrows. There must be no arrows going in the opposite direction.

In addition, it is necessary to multiply the known enthalpy values by a number of moles involved in a particular reaction. For example, standard enthalpy changes of combustion starts with one mole of the substance (carbon) burning and the enthalpy value should be multiplied by the number of carbon atoms involved in the reaction (see the example given below). Remember that this should also be included when the problem is solved with the equations.

Example:
Suppose we want the standard enthalpy change for the following reaction.

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \qquad \Delta H^\ominus = \ ?$$

Now we have a question that how should we proceed? If we try to get graphite and hydrogen to react, but it will not go to completion. Furthermore, the product will not be limited to propane and several other hydrocarbons will form as well. The fact is that we cannot directly measure ΔH^θ for reaction above. Instead, we must resort to an indirect calculation from ΔH^θ values that can be established by experiment. Here is where Hess law is of greatest value. It permits us to calculate ΔH^θ values that we cannot measure directly.

To determine an enthalpy change with Hess law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on one mole of the indicated reactant. Considering that the products of the combustion of carbon–hydrogen–oxygen compounds are $CO_2(g)$ and $H_2O(l)$ we can find the path to solve the problem as follows.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l) \quad \Delta H^{\theta} = -2219.9 \text{ kJ mol}^{-1} \quad (a)$

$C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H^{\theta} = -393.5 \text{ kJ mol}^{-1} \quad (b)$

$\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l) \quad \Delta H^{\theta} = -285.8 \text{ kJ mol}^{-1} \quad (c)$

Reverse of the reaction (a).

$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g) \quad \Delta H^{\theta} = 2219.9 \text{ kJ mol}^{-1} \quad (a)'$

Considering the reactants of the reaction of interest, $C(s)$ and $H_2(g)$, to get the proper number of moles of each, we must multiply equation (b) by three and equation (c) by four.

$3C(s) + 3O_2(g) \rightarrow 3CO_2(g) \quad \Delta H^{\theta} = 3(-393.5 \text{ kJ mol}^{-1}) = -1180.5 \text{ kJ mol}^{-1} \quad (b)'$

$2O_2(g) + 4H_2(g) \rightarrow 4H_2O(l) \quad \Delta H^{\theta} = 4(-285.8 \text{ kJ mol}^{-1}) = -1143.2 \text{ kJ mol}^{-1} \quad (c)'$

Here is the overall change we have described: 3 mol of $C(s)$ and 4 mol of $H_2(g)$ have been consumed, and 1 mol of $C_3H_8(g)$ has been produced. This is exactly what is required. We can now combine the three modified equations by summing them up (i.e. (a)′ + (b)′ + (c)′)

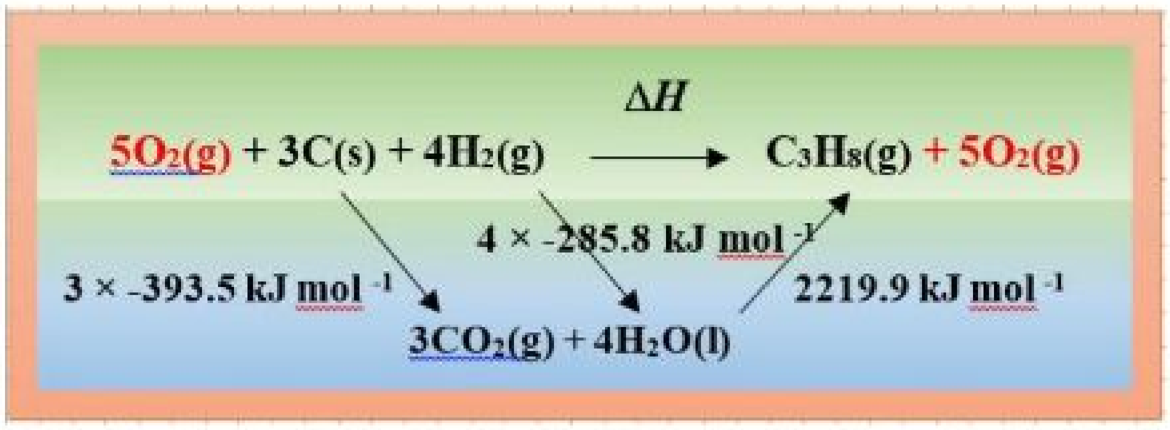
$\cancel{3CO_2(g)} + \cancel{4H_2O}(l) \rightarrow C_3H_8(g) + \cancel{5O_2(g)} \quad \Delta H^{\theta} = 2219.9 \text{ kJ mol}^{-1} \quad (a)'$

$3C(s) + \cancel{3O_2(g)} \rightarrow \cancel{3CO_2(g)} \quad \Delta H^{\theta} = 3(-393.5 \text{ kJ mol}^{-1}) = -1180.5 \text{ kJ mol}^{-1} \quad (b)'$

$\cancel{2O_2(g)} + 4H_2(g) \rightarrow \cancel{4H_2O(l)} \quad \Delta H^{\theta} = 4(-285.8 \text{ kJ mol}^{-1}) = -1143.2 \text{ kJ mol}^{-1} \quad (c)'$

$$\mathbf{3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \quad \Delta H^{\theta} = -103.8 \text{ kJ mol}^{-1}}$$

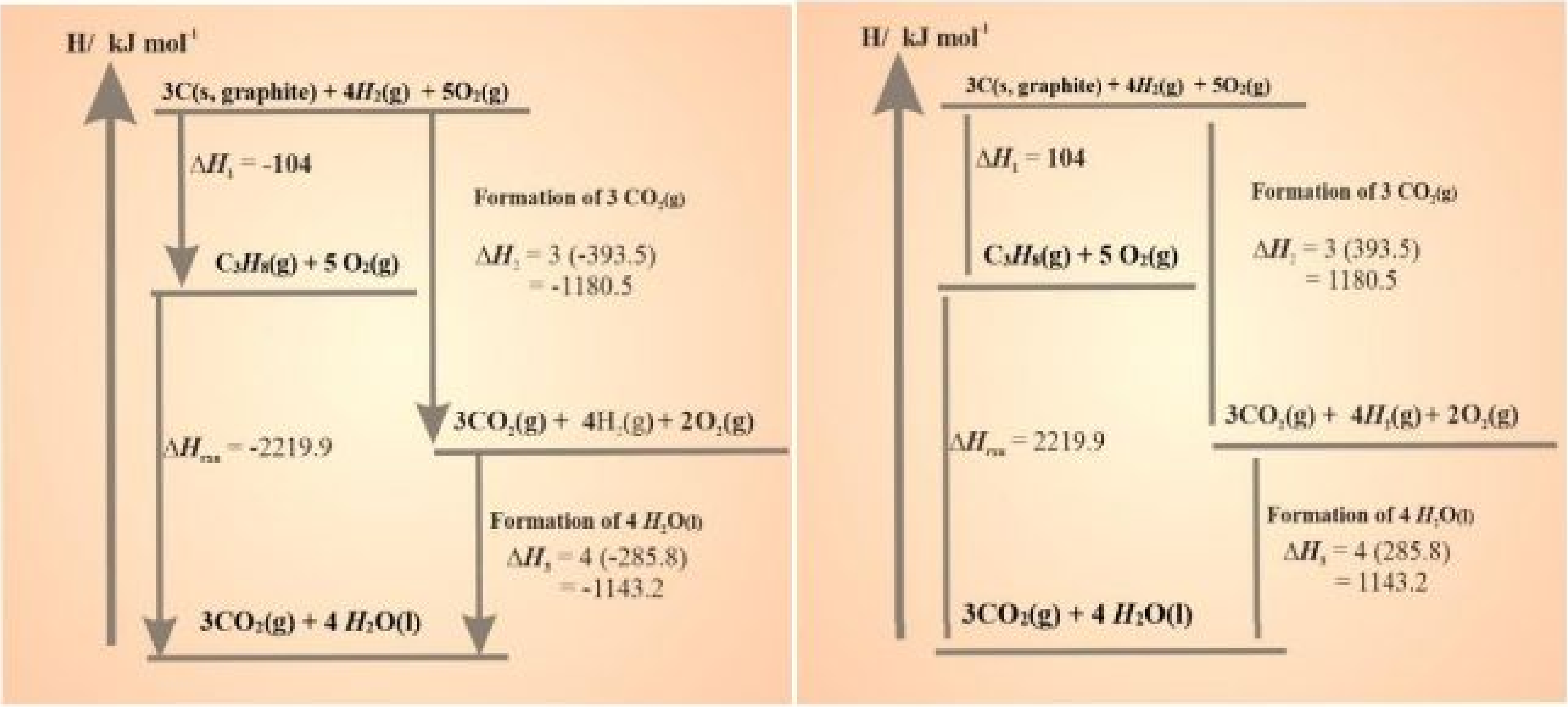
Solving the above with a thermochemical cycle:



$$\Delta H = 3(-393.5 \text{ kJ mol}^{-1}) + 4(-285.8 \text{ kJ mol}^{-1}) + 2219.9 \text{ kJ mol}^{-1} = \mathbf{-103.8 \text{ kJ mol}^{-1}}$$

Representation and solving of the above with an enthalpy diagram:

In the enthalpy diagrams we have drawn, we have not written any numerical values on the enthalpy axis. This is because we cannot determine absolute values of enthalpy, H. However, enthalpy is a function of state, so changes in enthalpy, ΔH have unique values. We can deal just with these changes. Nevertheless, as with many other properties, it is still useful to have a starting point, a zero value.



(a) (b)

Figure 2.6 Enthalpy diagram for $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ reaction. (a) represents each process with the enthalpy values with respect to the direction of reaction. (b) shows the enthalpy-gap and we can decide the sign according to the direction of the reactions wanted.

Standard enthalpies of reaction

We have learned that if the reactants and products of a reaction are in their standard states, the enthalpy change is the standard enthalpy change, which we can denote as ΔH^{θ} or ΔH^{θ}_{rxn}. One of the primary uses of standard enthalpies of formation is in calculating standard enthalpies of reaction.

Example 2.1

Calculate the standard enthalpy of reaction for the decomposition of sodium bicarbonate, a side reaction that occurs when baking soda is used in baking by using Hess law.

$$\mathbf{2\,NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\mathit{l}) + CO_2(g)} \quad \Delta H^{0}_{rxn} = ?$$

Answer:

From Hess law, we see that the following four equations yield the above equation when added together.

$2NaHCO_3(s) \rightarrow 2Na(s) + H_2(g) + 2C(graphite) + 3O_2(g)$ $\Delta H^{0} = -2\Delta H^{0}_{f[NaHCO_3(s)]}$ (a)

$2Na(s) + C(graphite) + \frac{3}{2}O_2(g) \rightarrow Na_2CO_3(s)$ $\Delta H^{\theta} = \Delta H^{\theta}_{f[Na_2CO_3(s)]}$ (b)

$\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)$ $\Delta H^{\theta} = \Delta H^{\theta}_{f[H_2O(l)]}$ (c)

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^{\theta} = \Delta H^{\theta}_{f[CO_2(g)]}$ (d)

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\mathit{l}) + CO_2(g) \quad \Delta H^{\theta}_{rxn} = ?$$

Equation (a) is the reverse of the equation representing the formation of two moles of $NaHCO_3(s)$ from its elements. This means that ΔH^θ for reaction (a) is the negative of twice $\Delta H^{\theta}_{f[NaHCO_3(s)]}$. Equations (b), (c) and (d) represent the formation of one mole each of $Na_2CO_3(s)$, $H_2O(l)$ and $CO_2(g)$. Thus, we can express the value of ΔH^θ for the reaction;

$$\Delta H^{\theta}_{rxn} = \Delta H^{\theta}_{f[Na_2CO_3(s)]} + \Delta H^{\theta}_{f[H_2O(l)]} + \Delta H^{\theta}_{f[CO_2(g)]} + (-2\Delta H^{\theta}_{f[NaHCO_3(s)]})$$

$= (-1130.68 \text{ kJ mol}^{-1}) + (-187.78 \text{ kJ mol}^{-1}) + (-393.51 \text{ kJ mol}^{-1}) + (1901.62 \text{ kJ mol}^{-1})$

= **189.65 kJ mol^{-1}** (For **2 moles** of $NaHCO_3(s)$)

= **94.825 kJ mol^{-1}** (For **1 mole** of $NaHCO_3(s)$)

We can use the enthalpy diagram to visualize the Hess law procedure and to show how the state function property of enthalpy enables us to arrive at the equation above.

Imagine the decomposition of sodium bicarbonate taking place in two steps. In the first step, suppose a vessel contains 2 mol of $NaHCO_3(s)$ which is allowed to decompose into 2 mol Na(s), 2 mol C(graphite), and 3 mol of $O_2(g)$ as in equation (a) above. In the second step, recombine 2 mol Na(s), 2 mol C(graphite), 1 mol of $H_2(g)$ and 3 mol of $O_2(g)$ to form the products according to equations (b), (c) and (d) above.

Step 1: $2 \times [NaHCO_3(s) \rightarrow Na(s) + 1/2H_2(g) + C(graphite) + 3/2O_2(g)]$

$\boldsymbol{\Delta H^\theta = 2\times (-\Delta H^{\theta}_{f}[NaHCO_3(s)]) = (2\ mol)[-(-950.81\ kJ\ mol^{-1})]}$

Step 2: $2Na(s) + C(graphite) + 3/2O_2(g) \rightarrow Na_2CO_3(s)$

$\boldsymbol{\Delta H^\theta = \Delta H^{\theta}_{f}[Na_2CO_3(s)] = (1\ mol\ Na_2CO_3)(-1130.68\ kJ\ mol^{-1})]}$

$C(graphite) + O_2(g) \rightarrow CO_2(g)$

$\boldsymbol{\Delta H^\theta = \Delta H^{\theta}_{f}\ [CO_2(g)] = (1\ mol\ CO_2)(-393.51\ kJ\ mol^{-1})]}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\boldsymbol{\Delta H^\theta = \Delta H^{\theta}_{f}\ [H_2O(l)] = (1\ mol\ H_2O)(-187.78\ kJ\ mol^{-1})]}$

Because enthalpy is a state function and the change of any state function is independent of the path chosen, the enthalpy change for the overall reaction is the sum of the standard enthalpy changes of the individual steps as shown in the above equation according to Hess law. Therefore, the above procedure is a specific application of the following more general relationship for a standard enthalpy of reaction.

$$\boxed{\Delta H^{\theta}_{rxn} = \sum \nu_p\, H^{\theta}_{f[\text{products}]} - \sum \nu_r\, H^{\theta}_{f[\text{reactants}]}}$$

where ν_p and ν_r are the stoichiometric coefficients of products and reactants, respectively. The enthalpy change of the reaction (ΔH^{θ}_{rxn}) (sometimes written as ΔH^{θ}_{r}) is the sum of terms for the products minus the sum of terms for the reactants.

Simply for example, consider the hypothetical reaction

$$a\,A + b\,B \rightarrow c\,C + d\,D \qquad \Delta H^{\theta}_{rxn} = \ ?$$

where a, b, c and d are stoichiometric coefficients. For this reaction ΔH°_{rxn} is given by

$$\Delta H^{0}_{rxn} = \left[\, c\,\Delta H^{0}_{f[\mathrm{C}]} + d\,\Delta H^{0}_{f[\mathrm{D}]} \right] - \left[\, a\,\Delta H^{0}_{f[\mathrm{A}]} + b\,\Delta H^{0}_{f[\mathrm{B}]} \right]$$

In order to use the above equation to calculate ΔH^{θ}_{rxn}, we must know the ΔH^{θ}_{f} values of the compounds that take part in the reaction. To determine these values we can apply the direct method or the indirect method.

The Direct Method;

This method of measuring ΔH^{θ}_{f} works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy, ΔH^{θ}_{rxn} for the combustion of $C_2H_6(g)$. We must measure or know the ΔH^{θ}_{f} values of $C_2H_6(g)$, $O_2(g)$, $CO_2(g)$ and $H_2O(l)$ in their standard states.

Example 2.2

Calculate ΔH^{θ}_{rxn} for the combustion of $C_2H_6(g)$ using the direct method

Answer:

The reaction is;

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O\,(l)$$

$$\Delta H^{\theta}_{rxn} = [2\Delta H^{\theta}_{f[CO_2(g)]} + 3\Delta H^{\theta}_{f[H_2O(l)]}] - [\,\Delta H^{\theta}_{f[C_2H_6(g)]} + \tfrac{7}{2}\Delta H^{\theta}_{f[O2(g)]}]$$

$$= 2\times -393.5\ \mathrm{kJ\ mol^{-1}} + 3 \times -285.8\ \mathrm{kJ\ mol^{-1}} - (-84.7\ \mathrm{kJ\ mol^{-1}} + \tfrac{7}{2}\times 0.0\ \mathrm{kJ\ mol^{-1}})$$

$$= \mathbf{-1559.7\ kJ\ mol^{-1}}$$

The Indirect Method;

In many cases or reactions, compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases ΔH^{θ}_{f} can be determined by an indirect approach of Hess law as described earlier.

Example 2.3

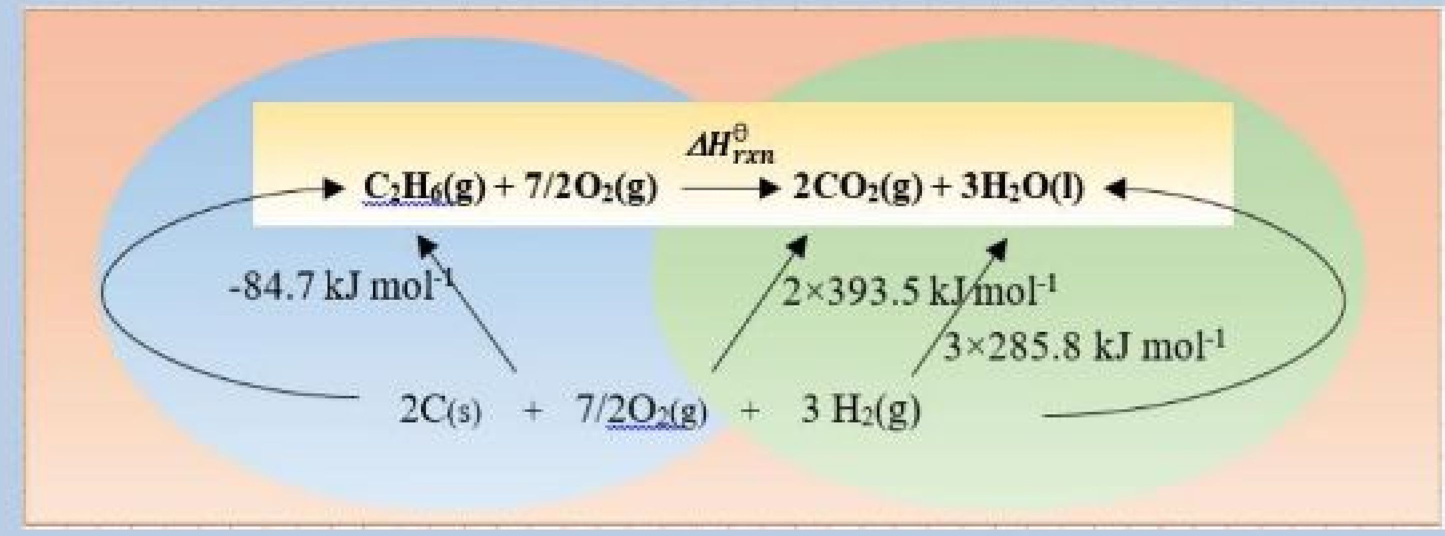
Calculate ΔH^{0}_{rxn} for the combustion of $C_2H_6(g)$ using the indirect method

Answer:

This is use of simple Hess Law cycles that you are likely to come across.

In the cycle below, this reaction has been written horizontally, and the enthalpy of formation values are added to complete the cycle.

Hess law cycle for the reaction of C_2H_6 with O_2.



And now for the calculation we can write down all the enthalpy changes which make up the two routes, and equate.

$$-84.7\ \text{kJ mol}^{-1} + \Delta H^{\ominus} = 2 \times -393.5\ \text{kJ mol}^{-1} + 3 \times -285.8\ \text{kJ mol}^{-1}$$

$$\Delta H^{\ominus} = \mathbf{-1559.7\ kJ\ mol^{-1}}$$

2.3 Lattice enthalpy or enthalpy of formation of an ionic compound: Born-Haber cycle

We can predict which elements are likely to form stable ionic compounds based on ionization energy and electron gain enthalpy. Ionization energy and electron gain enthalpy are defined for processes occurring in the gas phase, but at 100 kPa (1 atm) and 25 °C all ionic compounds are solids. The solid state is a very different environment because each cation in a solid is surrounded by a specific number of anions, and vice versa. Thus the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion. A quantitative measure of the stability of any ionic solid is its **lattice (dissociation) enthalpy,** defined as *the enthalpy change when one mole of a solid ionic compound is completely separated into its gaseous ions.*

Lattice (dissociation) enthalpy cannot be measured directly. However, if we know the structure and composition of an ionic compound, we can calculate the compound's lattice enthalpy by using **Coulomb law,** which states that *the potential energy (E) between two ions is directly proportional to the product of their charges and inversely proportional to the distance of separation between them (will not discuss here).*

We can also determine lattice enthalpy indirectly, by assuming that the formation of an ionic compound takes place in a series of steps. This procedure, known as the **Born-Haber cycle,** *relates lattice enthalpies of ionic compounds to ionization energies, electron gain energies and other atomic and molecular properties.* Basically, it is based on Hess law. The Born-Haber cycle defines the various steps that precede the formation of an ionic solid. We will illustrate its use to find the lattice (dissociation) enthalpy of lithium fluoride. Consider the reaction between lithium and fluorine.

$$\mathrm{Li(s)} + \frac{1}{2}\mathrm{F_2(g)} \rightarrow \mathrm{LiF(s)} \qquad \Delta H^{0}_{rxn} = ?$$

The standard enthalpy change for this reaction is -594.1 kJ $\mathrm{mol^{-1}}$ which is the standard enthalpy of formation of LiF. Considering the formation of LiF from its elements through five separate steps as described below. This pathway facilitates to analyze the energy (enthalpy) changes in ionic compound formation, with the help of Hess law.

1. Sublimation step to convert solid lithium to lithium vapour

$$\mathrm{Li(s)} \rightarrow \mathrm{Li(g)} \qquad \boldsymbol{\Delta H^{\theta}_{sub} = \Delta H^{\theta}_{1} = 155.2\ \mathrm{kJ\ mol^{-1}}}$$

2. Atomization of $F_2(g)$ to F(g)

$$\frac{1}{2}\mathrm{F_2(g)} \rightarrow \mathrm{F(g)} \qquad \boldsymbol{\Delta H^{0}_{at} = \Delta H^{\theta}_{2} = 75.3\ \mathrm{kJ\ mol^{-1}}}$$

3. Ionization of gaseous Li atoms

$$\mathrm{Li(g)} \rightarrow \mathrm{Li^{+}(g)} + \mathrm{e} \qquad \boldsymbol{\Delta H^{\theta}_{IE1} = \Delta H^{\theta}_{3} = 520\ \mathrm{kJ\ mol^{-1}}}$$

4. Formation of F^- by capturing an electron

$$\mathrm{F(g)} + \mathrm{e} \rightarrow \mathrm{F^{-}(g)} \qquad \boldsymbol{\Delta H^{\theta}_{EG} = \Delta H^{\theta}_{4} = -328\ \mathrm{kJ\ mol^{-1}}}$$

5. Combination between $Li^+(g)$ and $F^-(g)$

$$\mathrm{Li^{+}(g)} + \mathrm{F^{-}(g)} \rightarrow \mathrm{LiF(s)} \qquad \boldsymbol{\Delta H^{0}_{5} = x\ \mathrm{kJ\ mol^{-1}}}$$

The lattice dissociation enthalpy of LiF is defined as

$$\mathrm{LiF(s)} \rightarrow \mathrm{Li^{+}(g)} + \mathrm{F^{-}(g)} \qquad \boldsymbol{\Delta H^{\theta}_{L} = -\Delta H^{\theta}_{5} = -x\ \mathrm{kJ\ mol^{-1}}}$$

The value of ΔH^{θ}_{5} can be calculated by the following procedure. As the overall reaction has the standard enthalpy change, ΔH°_{rxn} of -594.1 kJ $\mathrm{mol^{-1}}$, we can write,

$$\Delta H^{0}_{rxn} = \Delta H^{\theta}_{1} + \Delta H^{\theta}_{2} + \Delta H^{\theta}_{3} + \Delta H^{\theta}_{4} + \Delta H^{\theta}_{5}$$

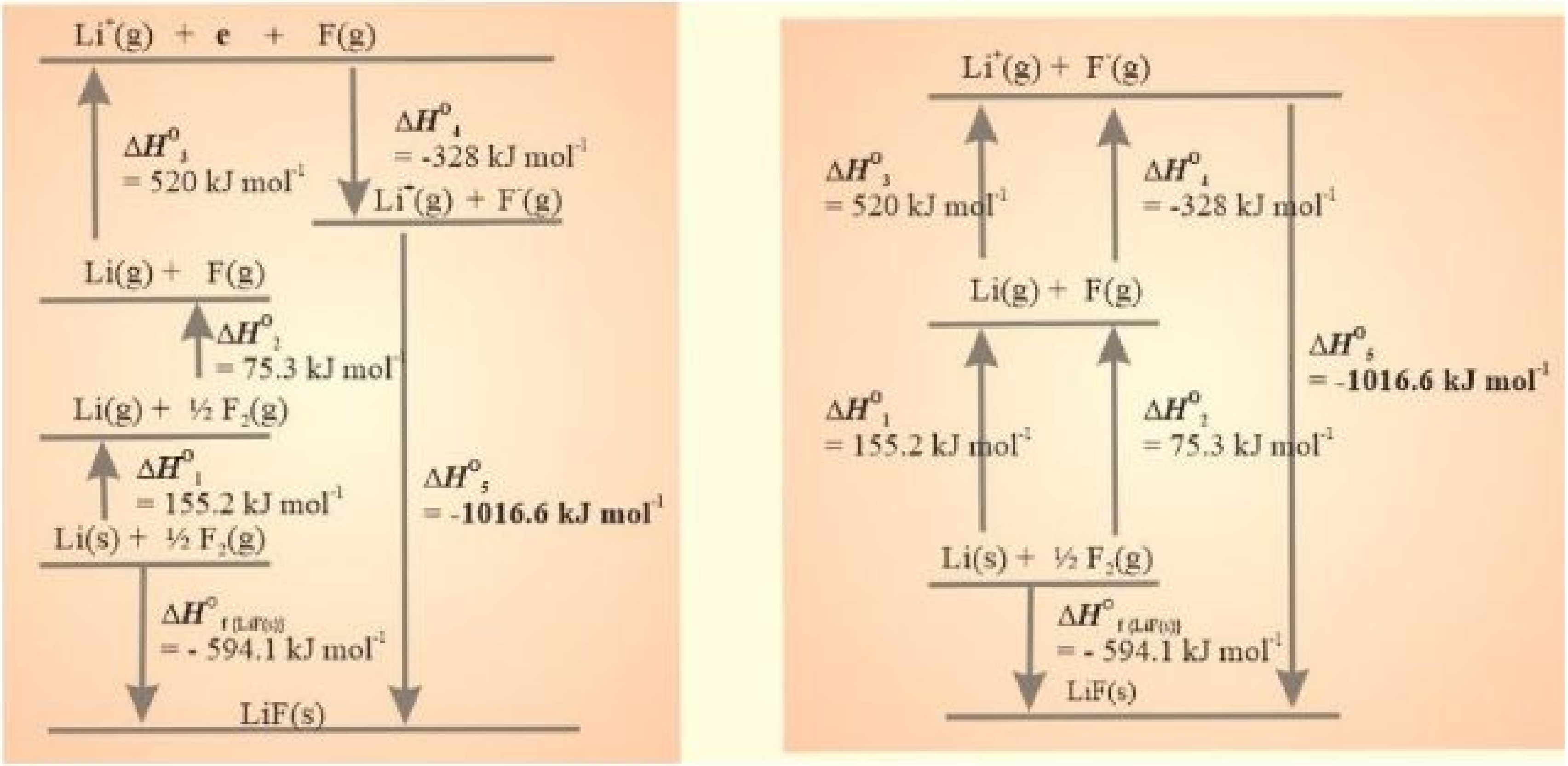
and by summing up reactions of 5 steps we get the overall reaction as ;

$$\mathrm{Li(s)} + \frac{1}{2}\mathrm{F_2(g)} \rightarrow \mathrm{LiF(s)}$$

Therefore, -594.1 kJ $\mathrm{mol^{-1}}$ = 155.2 kJ $\mathrm{mol^{-1}}$+75.3 kJ $\mathrm{mol^{-1}}$+520 kJ $\mathrm{mol^{-1}}$+(-328 kJ $\mathrm{mol^{-1}}$) + ΔH^{θ}_{5}

ΔH_5^θ = -1016.6 $\mathbf{kJ\,mol^{-1}}$ and hence the lattice dissociation enthalpy of LiF(s) is $\mathbf{1016.6\ kJ\,mol^{-1}}$

The Figure 2.7 below summarizes the Born-Haber cycle for LiF. Steps 1, 2 and 3 all require the input of energy. On the other hand, steps 4 and 5 release energy. Because ΔH_5^θ is a large negative quantity, the lattice dissociation enthalpy of LiF is a large positive quantity, which accounts for the stability of solid LiF. The greater the lattice dissociation enthalpy means that the more stable the ionic compound which exists. Keep in mind that lattice dissociation enthalpy is *always* a positive quantity because the separation of ions in a solid into ions in the gas phase is an endothermic process.



(a) (b)

Figure 2.7 Born-Haber cycle of the above system (ΔH_5^θ = -1016.6 kJ mol^{-1} and hence the lattice dissociation enthalpy of LiF(s) is 1016.6 kJ mol^{-1}). In (a) each process is shown separately while (b) show respective processes together.

2.4 Spontaneity of chemical reactions

Spontaneous processes; An important part of experimental chemistry deals with spontaneous reactions, that is, reactions that take place without having to continually supply energy from outside the system. Or we can describe that as once a spontaneous reaction starts it will go to completion until either the reactants are consumed or it enters a state of equilibrium if the products are not removed. It is also important to remember that the term spontaneous does not necessarily mean a fast reaction rate. Time is not a part of the thermodynamic definition of a spontaneous process. A spontaneous process may or may not happen immediately, or at all.

For example, the conversion of diamond to graphite is a spontaneous process at 25 °C and a pressure of 100 kPa, even though this process is so slow that it cannot be observed in a human life time.

One goal of thermodynamics is to predict whether a reaction will take place when a given set of reactants is brought together. Thermodynamics only tells us whether or not the reaction will occur, but it tells us nothing about how fast.

The release of heat by a reaction was once thought to be an indication that the reaction was spontaneous. The sign of the enthalpy change, ΔH or ΔH^{θ} , by itself is not an adequate guide to spontaneity because while some spontaneous reactions are known to be exothermic (ΔH^{θ} is -ve), many endothermic reactions (ΔH^{θ} is +ve) are known to be spontaneous as well.

In addition to the heat absorbed or released in a spontaneous process, another factor called entropy must be considered. **Entropy** is a *measure of the disorder or randomness of a system.* The entropy *(S)* is a state function that increases in value as the disorder or randomness of the system increases. Entropy has the units **$\mathbf{J\,K^{-1}\,mol^{-1}}$.**

A number of factors contribute to the entropy of a substance, such as the physical state, temperature, molecular size, intermolecular forces, and mixing. Here at this stage it is simply described with physical state and temperature.

Gases tend to have the highest entropies because the motion of gas particles is highly random. Liquids tend to have higher entropies than solids, which are much more restricted in their motions. At room temperature, one mole of $CO_{2(g)}$ has a much higher entropy than one mole of liquid water, which has a higher entropy than one mole of solid copper metal. The entropy of a substance increases with temperature because the translational and rotational motions of the molecules increase with temperature. Water at 50 °C is higher in entropy than water at 25 °C.

Standard entropy change of a chemical reaction

The standard entropy change of a reaction is denoted by the symbol ΔS°_{rxn}. It can be calculated from standard molar entropy (entropy content of one mole of substance under a standard state) values where each standard molar entropy value is multiplied by the stoichiometric coefficient in the balanced chemical equation.

$$\boxed{\Delta S^{\theta}_{rxn} = \Sigma S^{\theta}(\text{products}) - \Sigma S^{\theta}\ (\text{reactants})}$$

ΔS^{θ}_{rxn} is the entropy change when pure (unmixed) reactants in their standard states are converted to pure (unmixed) products in their standard states. The sign of ΔS^{0}_{rxn} can often be estimated by taking into account the stoichiometry of a reaction and the physical states of reactants and products. If the total number of moles of gas increases when going from reactants to products, we can predict that the sign of ΔS^{θ}_{rxn} is positive. The entropy of products is higher than that of reactants. Conversely, if the number of moles of gaseous products is less than the number of moles of gaseous reactants then the sign of ΔS^{θ}_{rxn} is negative.

Example 2.4

Hydrogen and oxygen react to form water vapor in a spontaneous reaction.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Predict the sign of the entropy change for this reaction and calculate ΔS^{θ}_{rxn} at 25 °C.

Answer:

When hydrogen and oxygen gas react to form water vapour, three moles of gas are converted into two moles of gas, for every mole of reaction. The total number of moles of gas decreases, so ΔS^{θ}_{rxn} for this reaction should be negative.

Using standard molar entropy values to calculate the standard entropy;

$$\begin{aligned}\Delta S^{0}_{rxn} &= S^{0}\,(products) - S^{0}\,(reactants)\\ &= (2\text{ mol})(S^{\theta}\,[H_2O_{(g)}]) - \{(2\text{ mol})(S^{\theta}\,[H_{2(g)}]) + (1\text{ mol})(S^{\theta}\,[O_{2(g)}])\}\\ &= (2)(188.8\text{ J K}^{-1}\text{ mol}^{-1}) - \{(2)(130.7\text{ J K}^{-1}\text{ mol}^{-1}) + (1)(205.1\text{ J K}^{-1}\text{ mol}^{-1})\}\\ &= -88.9\text{ J K}^{-1}\text{mol}^{-1}\end{aligned}$$

The entropy change for this reaction is negative, as predicted based on the reaction stoichiometry.

For a reaction to occur spontaneously, both enthalpy, ΔH°_{rxn} and entropy, ΔS°_{rxn} should be considered. As we know, for a reaction we can simply say that the decrease in enthalpy and increase in entropy favour the reaction and hence the reaction occurs spontaneously. In addition following combinations can also be considered under some conditions of temperature.

ΔH^{θ}_{rxn} −ve, $\Delta S^{\theta}_{rxn} + ve$	Spontaneous at all temperatures
ΔH^{0}_{rxn} +ve, $\Delta S^{0}_{rxn} + ve$	Spontaneous at high temperatures
ΔH^{0}_{rxn} −ve, $\Delta S^{0}_{rxn} - ve$	Spontaneous at low temperatures
ΔH^{θ}_{rxn} +ve, $\Delta S^{\theta}_{rxn} - ve$	Not spontaneous at all temperatures (Reverse reaction is spontaneous)

Gibbs free energy *(G)* and spontaneity of a reaction

As we have seen, the spontaneity of a reaction is determined by both the entropy and enthalpy change of the system. The **Gibbs free energy (*G*)**, or simply free energy, is a state function that combines enthalpy and entropy, where T is the absolute temperature. G is defined as follows:

$$\boxed{G = H - T\,S}$$

For a reaction occurring at constant temperature, the change in free energy is,

$$\boxed{\Delta G = \Delta H - T\,\Delta S}$$

For a reaction occurring at constant temperature and at standard state the change in free energy is,

$$\boxed{\Delta G^{\theta}_{rxn} = \Delta H^{\theta}_{rxn} - T\,\Delta S^{\theta}_{rxn}}$$

***Note:** Sometimes ΔG^{θ}_{rxn} indicated as ΔG^{θ}_{r}.*

- A reaction that is at **equilibrium** has $\Delta G^{\theta}_{rxn} = 0$. There will be no net change in either the forward or reverse direction. For a spontaneous reaction at constant temperature and pressure, $\Delta G^{\theta}_{rxn} < 0$, and for non-spontaneous reaction $\Delta G^{\theta}_{rxn} > 0$.

Example 2.5

Carbon monoxide and oxygen gas react to form carbon dioxide.

$$CO(g) + \tfrac{1}{2}\,O_2(g) \rightarrow CO_2(g)$$

Calculate the standard free energy change for this reaction at 25°C from ΔH^{θ}_{rxn} and ΔS^{θ}_{rxn}.

($\Delta H^{\theta}_{f}[CO_2(g)] = -393.5$ kJ mol^{-1}, $\Delta H^{\theta}_{f}[CO(g)] = -110.5$ kJ mol^{-1}, $S^{0}[CO_2(g)] = 213.7$ J mol^{-1} K^{-1}, $S^{0}[CO(g)] = 197.7$ J mol^{-1} K^{-1}, $S^{0}[O_2(g)] = 205.1$ J mol^{-1} K^{-1})

Answer:

Using the standard heats of formation calculate first the enthalpy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta H^{\theta}_{rxn} &= \Delta H^{0}_{f}(\text{products}) - \Delta H^{0}_{f}(\text{reactants})\\ &= \Delta H^{0}_{f}[CO_2(g)] - \Delta H^{0}_{f}[CO(g)] - \tfrac{1}{2}\,\Delta H^{0}_{f}[O_2(g)]\\ &= -393.5\ \text{kJ mol}^{-1} - (-110.5\ \text{kJ mol}^{-1}) - 0\ \text{kJ mol}^{-1}\\ &= -283.0\ \text{kJ mol}^{-1}\end{aligned}$$

Using standard entropy values calculate the entropy change for this reaction under standard state conditions.

$$\begin{aligned}\Delta S^{\theta}_{rxn} &= S^{\theta}\,\text{(products)} - S^{\theta}\,\text{(reactants)}\\ &= S^{\theta}\,[\mathrm{CO_2(g)}] - S^{\theta}\,[\mathrm{CO(g)}] - \tfrac{1}{2}S^{\theta}\,[\mathrm{O_2(g)}]\\ &= 213.7\ \mathrm{J\ mol^{-1}\ K^{-1}} - (197.7\ \mathrm{J\ mol^{-1}\ K^{-1}}) - (\tfrac{1}{2})(205.1\ \mathrm{J\ mol^{-1}\ K^{-1}})\\ &= -86.6\ \mathrm{J\ mol^{-1}\ K^{-1}}\end{aligned}$$

***Note:** ΔS^{θ}_{rxn} is negative, as predicted by the stoichiometry: 1.5 moles of gas forms 1 mole of gas.*

Calculate ΔG^{θ}_{rxn} using

$$\begin{aligned}\Delta G^{\theta}_{rxn} &= \Delta H^{\theta}_{rxn} - T\,\Delta S^{\theta}_{rxn}\\ &= -283.0\ \mathrm{kJ\ mol^{-1}} - (298\ \mathrm{K})(-86.6\ \mathrm{J\ mol^{-1}\ K^{-1}})(1\ \mathrm{kJ}/1000\ \mathrm{J})\\ &= -257\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

ΔG^{θ}_{rxn} is negative. Therefore, the reaction occurs spontaneously.

Table 2.2 A summary

Relationships		**Units**
Enthalpy change of reaction	$\Delta H = \Sigma\, \nu_p H_{(\text{products})} - \nu_r \Sigma\, H_{(\text{reactants})}$	kJ mol^{-1}
Standard enthalpy change of a reaction	$\Delta H^{\theta}_{rxn} = \sum \nu_p H^{\theta}_{f[\text{products}]} - \sum \nu_r H^{\theta}_{f[\text{reactants}]}$ (Where ν_p *and* ν_r are the stoichiometric coefficients of products and reactants)	kJ mol^{-1}
Hess Law	If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of enthalpy changes for the individual steps. In other words, Hess law is simply a consequence of the state function property enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH^{θ}) if the process is carried out under standard conditions) has the same value or it is independent of the route.	
Standard entropy change for a reaction	$\Delta S^{\theta}_{rxn} = \Sigma\, \nu_p S^{\theta}$ (products) $-\Sigma\, \nu_r S^{\theta}$ (reactants)	J K^{-1} mol^{-1}
Standard change in free energy	$\Delta G^{0}_{rxn} = \Delta H^{0}_{rxn} - T\,\Delta S^{0}_{rxn}$	kJ mol^{-1}
Spontaneity of a reaction	Spontaneous at all temperatures	ΔH^{θ}_{rxn} -ve $\Delta S^{\theta}_{rxn} + ve$
	Spontaneous at high temperatures	ΔH^{θ}_{rxn} +ve $\Delta S^{\theta}_{rxn} + ve$
	Spontaneous at low temperatures	ΔH^{0}_{rxn} -ve $\Delta S^{\theta}_{rxn} - ve$
	Not spontaneous at all temperatures (Reverse reaction is spontaneous)	ΔH^{θ}_{rxn} +ve $\Delta S^{\theta}_{rxn} - ve$
	Spontaneous	$\Delta G^{\theta}_{rxn} < 0$
	Not spontaneous	$\Delta G^{0}_{rxn} > 0$
	Equilibrium	$\Delta G^{0}_{rxn} = 0$

Reference:

Atkins, P. and Paula, J. (2000) *Atkins' Physical Chemistry.* Oxford, New York: Oxford University Press.

Chang, R. (2010) *Chemistry 10th Edition.* New York: McGraw Hill.