



**G. C. E. (Advanced Level)**

**CHEMISTRY**

**Grade 12**

**Resource Book**

**Unit 4: Gaseous State of Matter**

**Unit 5: Energetics**

**Department of Science  
Faculty of Science and Technology  
National Institute of Education  
[www.nie.lk](http://www.nie.lk)**

**Chemistry**

Resource Book

Grade 12

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Faculty of Science and Technology  
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## **Message from the Director General**

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

**Dr. (Mrs.) T. A. R. J. Gunasekara**

Director General

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## **Message from the Director**

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers' Guide was introduced in place of the previous Teacher's Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers' Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

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# 1. Gaseous State of Matter

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- Calculations based on ideal gas equation

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#### 1.4.2 Equation of molecular kinetic theory

#### 1.4.3 Root mean square speed and mean speed

#### 1.4.4 Maxwell - Boltzmann distribution

### 1.5 Amendments to ideal gas equation to apply for real gases

#### 1.5.1 van der Waals equation




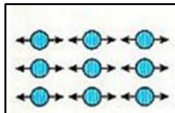
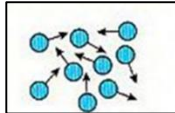
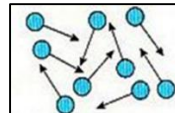
#### 1.5.2 Critical temperature and liquefaction of gases

## Introduction

Everything in the universe has a chemical identity. We know that the smallest particle of matter is an atom. “Study of matter and the changes that it undergoes” can simply be understood as the basic definition of chemistry. Usually matter is anything that occupies space and has mass and can be seen and touched (such as soil, water) as well as things we cannot see such as air. Based on the composition and properties, several categories such as substances, mixtures, elements as well as atoms and molecules can be identified. All substances, at least in principle, can exist in three states: solid, liquid and gas. In a solid, particles are held tightly and close together in an ordered structure with a definite shape having a small degree of motion. Particles in a liquid are close together but are not held so tightly in position and can move faster compared to that of solid. Gases differ largely from liquids and solids in the distances between the particles. In a gas, the particles are separated by distances, large compared with the size of the particles allowing them to behave freely. Therefore, the attractive forces between gas particles are very small or negligible and that allows us to consider gas particles individually and some hypotheses are easily predictable depending on the temperature and pressure changes.

### 1.1 Organization of particles in three principal states and their typical characteristics

Anything that occupies space and has a mass can be called “**matter**”. This could be things we can see and touch like trees or things we cannot see like the air we breathe. All matter can be classified broadly into three states **solid, liquid and gas**. Matter can be interconverted among these three states without changing the composition. For an example water in liquid state can be converted to gaseous state (steam) when heated and can be converted to a solid (ice) if cooled.

		
<b>Solid</b> (eg. nail) Fixed shape and volume	<b>Liquid</b> (eg. water) No Fixed shape but has fixed volume	<b>Gas</b> (eg. He balloons) No fixed shape and no fixed volume
		
<b>Solid</b> Strong interparticle (atoms, molecules or ions) forces. Particles vibrate but cannot move around.	<b>Liquid</b> Moderate interparticle (atoms, molecules or ions) forces. Particles can move around up to some extent.	<b>Gas</b> Weak interparticle (atoms, molecules or ions) forces. Particles can move around.

**Figure 1.1** Three states of matter

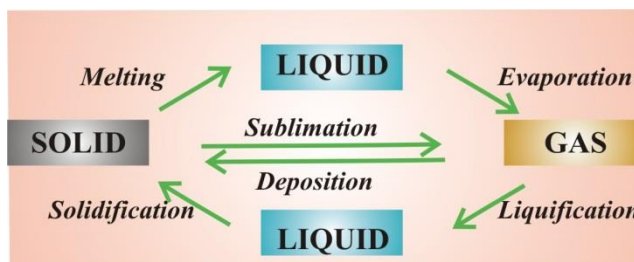
Three states of matter differ based on arrangement and movement of particles. The inter-particle distance is highest in gaseous state and lowest in solids. In liquid state, particles are relatively closer compared to gaseous state, yet not too close compared to the solid state. Therefore, a regular pattern of particles can be seen only in solid state, while both gaseous and liquid state particles show random arrangement. As a result, particles in gaseous state can move fast and freely compared to liquid state particles. However, movement of particles in solids is limited to vibrations. The arrangement and motions of particles in matter result in differences in macroscopic properties such as volume, shape, compressibility and density as indicated in the Table 1.1 below.

**Table 1.1** Qualitative comparison of properties of solids, liquids and gases

Property	Solids	Liquids	Gases
Shape	Definite	Take up shape of the container but do not spread throughout the entire volume of the container	Take up the shape of the container and occupy the entire volume of the container
Volume	Definite	Definite	Occupy the volume of the container
Density ( $\rho$ )/ g cm <sup>-3</sup> at 293 K	Have high values eg.: Iron (7.874 g cm <sup>-3</sup> )	Have moderately high values eg.: Water (0.997g cm <sup>-3</sup> )	Have low values eg.: Hydrogen (0.071g cm <sup>-3</sup> )
Compressibility	Extremely hard to compress	Extremely hard to compress	Can compress to a great extent

**Note:** Here we say that a liquid takes the shape of the container and we have to think why we get these shapes. Usually, particles of any object is being pulled by a variety of forces such as intermolecular forces, and that's why it has shape. Some given amount (volume) of water in a beaker is being shaped by surface tension resulting from intermolecular forces within the liquid creating a meniscus curve at the edge of the surface, by the force of the walls of the beaker pushing up on it, and by the gravity which is greater than the surface tension, pulling it down. So, it takes the shape of the beaker, with a flat surface on the top. This happens due to the satisfaction of all those different forces. However, in the case that the surface tension is stronger than gravity, the water's surface might not lie flat by taking the shape of the container. Assume that there is no gravity, and so surface tension is very much high. As each part of the surface wants to stay as close as possible to the rest of the surface it tries to minimize the forces within. So, the shape that best allows this is a sphere, because it is the shape that has the minimal surface area for a given volume.

Matter in one particular state can be converted to another state by heating or cooling. Increase of temperature makes particles move faster and inter-particle distance becomes greater leading to change in state. Accordingly, increase in temperature converts solid state materials to liquid and liquid state materials to gaseous state. The opposite happens with decreasing temperature. Figure 1.2 illustrates how matter can be interconverted among states.



**Figure 1.2** Interconversion of states of matter

### Example 1.1

In which state of matter are the particles mostly touching but arranged in a random way?

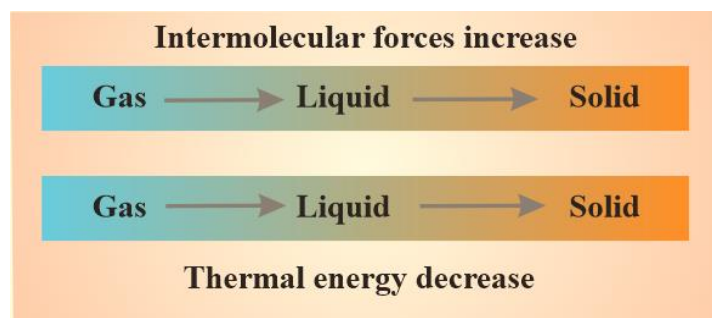
#### Answer

Liquid State

When we describe the properties of the three states of matter with the help of Table 1.1, motion and arrangement of particles are basically considered. Especially, thermal energy is the energy of a body arising from motion of its atoms or molecules and it is directly proportional to the temperature of the substance. Therefore, it measures the average kinetic energy of the particles of the matter and is thus responsible for movement of particles or the thermal motion.

As we already know, interparticle forces tend to keep the particles together but thermal energy of the particles tends to keep them apart. Therefore the existence of three states of matter can be regarded as a result of balance between interparticle forces and the thermal energy of the particles.

When inter molecular interactions are very weak, molecules do not tend to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquefy on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature, the gases can very easily be liquefied. These behaviours can be explained by Figure 1.3 where we can understand the reversible nature of intermolecular forces and the thermal energy acting on the three states of matter.



**Figure 1.3** Behaviour of three states of matter against intermolecular forces and thermal energy

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about the gaseous state and the laws which govern the behaviour of matter in this state.

## 1.2 Gaseous state

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure.

The gaseous state is characterized by the following physical properties as described in Table 1.1.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gas is due to the fact that the forces between their molecules are negligible. Their behaviour is governed by same general laws (will be discussed later), which were discovered as a result of experimental studies. These laws are usually relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and amount (moles or mass) are very important because relationships between these variables describe *state of the gas* (will be defined in unit 5). Interdependence of these variables leads to the formulation of gas laws.

### 1.2.1 Gas laws

The gas laws that we are going to discuss are the results of experiments carried out by several scientists on the physical properties of gases. In these experiments, relations among the variables of pressure, temperature, volume and amount of gases are considered and the results provide valuable information on the gaseous state of matter in turn helping the mankind in many ways.

**Ideal gas and ideal gas equation**

When it is assumed that intermolecular forces do not exist among the molecules of a gas, such a gas is called an **ideal gas**. That is molecules in an ideal gas do not exhibit attraction or repulsion among them. Furthermore, the volume of ideal gas particles is considered negligible when compared to the volume of the container.

The absolute temperature ( $T$ ), pressure ( $P$ ), volume ( $V$ ) and the amount ( $n$ , moles) of a gas are the factors that affect the behaviour of a gas.  $P$ ,  $T$ ,  $V$  and  $n$  are related by the expression;

$$PV = nRT$$

This is known as the **ideal gas equation** or **ideal gas law** where the gas constant  $R$  is same for every gases. Any gas which obeys the above relationship under any given temperature and pressure is referred to as an **ideal gas**.

The value of the constant  $R$  for one mole of an ideal gas can be calculated under the conditions of 0 °C and 1 atm as given below: (At 0 °C and 1 atm, the volume of one mole of ideal gas is 22.414 dm<sup>3</sup>)

$$R = \frac{PV}{nT} = \frac{101325 \text{ Pa} \times 22.414 \times 10^{-3} \text{ m}^3}{1 \text{ mol} \times 273.15 \text{ K}} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

We can see that the ideal gas equation is a relationship among four variables and it describes the state of any gas. Therefore, it is also called **equation of state**.

**Calculations based on ideal gas equation**

The ideal gas law allows us to determine any one of the quantities volume, pressure, temperature, or moles of the gas when the other three are given. If the amount of moles of the gas is known, we can also calculate its mass using its molar mass. Further it can also be used to determine the density of a gas. It is important to keep in mind that all the other quantities must be in units that match the value used for the ideal gas constant. Usually pressure can be expressed in several units such as atm, Pa, bar, torr, etc. Therefore, in solving these problems it may helpful to use pressure conversions as given in the Table 1.2.

**Table 1.2** Pressure units

Pressure unit	Pa	bar	atm	torr/mmHg
1 Pa	1 N m <sup>-2</sup>	10 <sup>-5</sup>	9.87 × 10 <sup>-6</sup>	7.5 × 10 <sup>-3</sup>
1 bar	100,000	1 bar	0.987	750.06
1 atm	101,325	1.01325	1 atm	760
1 torr/mmHg	133.32	1.3332 × 10 <sup>-3</sup>	1.3158 × 10 <sup>-3</sup>	1 torr/ 1 mmHg

**Example 1.2**

The volume of a gas cylinder is  $0.950 \text{ dm}^3$ . When filled, the cylinder contains liquid propane ( $\text{C}_3\text{H}_8$ ) stored under pressure. When the cylinder is empty, it contains some residual propane gas molecules at atmospheric pressure and temperature.

- Calculate the number of moles of propane gas remaining in a cylinder when it is empty if the surrounding atmospheric conditions are  $25.0 \text{ }^\circ\text{C}$  and  $750 \text{ torr}$  ( $1 \text{ torr} = 133.32 \text{ Pa}$ ) (when the internal pressure equals to the external pressure).
- Calculate the mass of propane remaining in the cylinder.
- Calculate the density of remaining propane gas in the cylinder.

**Answer**

- First summarize the given information;

Temperature,  $T = (25 + 273) \text{ K} = 298 \text{ K}$

Pressure,  $P = 750 \text{ torr} \times 133.32 \text{ Pa} / 1 \text{ torr} = 99990 \text{ Pa}$

Volume,  $V = 0.950 \text{ dm}^3 = 0.950 \times 10^{-3} \text{ m}^3$

Unknown is  $n$

Using  $PV = nRT$ ;

$$n = \frac{PV}{RT} = \frac{99990 \text{ Pa} \times 0.950 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 0.038 \text{ mol}$$

- Molar mass of propane ( $\text{C}_3\text{H}_8$ ) =  $44 \text{ g mol}^{-1}$

Mass of propane =  $0.038 \text{ mol} \times 44 \text{ g/mol} = 1.672 \text{ g}$

- Density of propane = mass/volume =  $1.672 \text{ g} / 0.950 \text{ dm}^3 = 1.76 \text{ g dm}^{-3}$

When we consider the above example, there are insights into the ideal gas equation that it can be expressed in different forms to estimate mass and density of a given gas with simple modifications as shown below.

$PV = nRT$  and we can write,

$$P = \frac{n}{V} RT$$

$$\therefore P = CRT,$$

where  $C$  is the concentration

We can also write  $PV = nRT$  as

$$PV = \frac{m}{M} RT,$$

where,  $m$  is the mass and  $M$  is the molar mass of the gas.

Also we can write the above as;

$$P = \frac{1}{M} \left( \frac{m}{v} \right) RT$$

$$\therefore P = \frac{d RT}{M}$$

where,  $d$  is the density and  $d = \frac{m}{v}$

Ideal gas law serves as the basis when deriving several other gas laws under specific conditions.

### 1.2.2 Boyle law (pressure – volume relationship)

That is the “*pressure of a fixed amount (mass) of gas at constant temperature inversely varies with (or proportional to) the volume of the gas*”. This is known as the **Boyle Law** (1627-1691) which was named after **Robert Boyle**, an Irish scientist in the seventeenth century who studied change in volume of a gas when pressure of a gas is varied under constant temperature conditions. Mathematical form of it, is given below.

$$P \propto \frac{1}{V} \text{ or } P = \frac{k}{V} ; k \text{ is a constant}$$

The ideal gas law can be used to derive Boyle law as follows.

$$PV = nRT$$

If the amount of the gas and temperature of the system are kept constant, then the product  $nT$  is a constant. Since  $R$  is also a constant, then the product,  $nRT = k$  (a constant)

$$PV = k$$

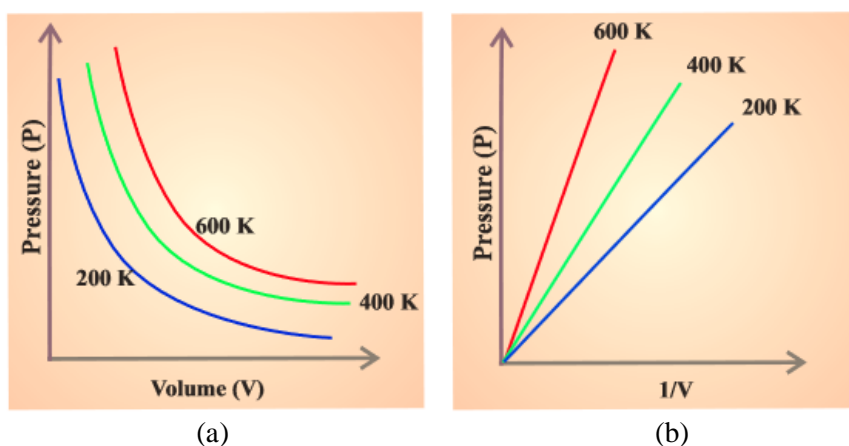
It means that “*at constant temperature, the product of pressure and volume of a fixed amount of gas is constant*”. This is another way of expressing Boyle law.

If a fixed amount of gas at constant temperature  $T$  occupying volume  $V_1$  at pressure  $P_1$  undergoes change, so that volume becomes  $V_2$  and pressure becomes  $P_2$ , then according to Boyle law:

$$P_1 V_1 = P_2 V_2$$

Figure 1.4 shows two conventional ways of graphical representation of Boyle law. Figure 1.4 (a) is the graph of  $PV = k$  at different temperatures for the comparison. The value of  $k$  for each curve is different because for a given mass of gas, it varies only with temperature. Note that at higher temperatures, curves shift upwards due to the expansion of volume. It should also be noted that volume of the gas doubles if pressure is halved at a constant temperature.





**Figure 1.4** Changes in pressure at different constant temperatures with respect to (a) volume ( $V$ ) changes and (b) with  $1/V$

Figure 1.4 (b) represents the graph of  $P$  vs  $1/V$ . It is a straight line passing through the origin. These plots obtained by the experiments carried out by Boyle, show in a quantitative manner that gases are highly compressible. That is because when a given mass of a gas is compressed, the same number of molecules will occupy a smaller space. This means that gases become denser at high pressures.

**Note:** We know that density ( $d$ ) of a given mass ( $m$ ) occupying volume ( $V$ ) is given by;  $d = m/V$ . Therefore at constant temperature we can write,  $d = \left(\frac{m}{k/P}\right) = \left(\frac{m}{k}\right) P = k' P$

### Example 1.3

Calculate the change in pressure of a gas when the volume is doubled at constant temperature for a known amount of a gas.

#### Answer

$$V_1 = V, V_2 = 2V, P_1 = P, P_2 = ?$$

$$\text{Applying Boyle law: } P_1 V_1 = P_2 V_2$$

$$P \times V = P_2 \times 2V$$

$$P_2 = P/2$$

$\therefore$  New pressure is half the initial pressure.

**Example 1.4**

A balloon is to be filled with a known amount of hydrogen gas at room temperature. At atmospheric pressure (100 kPa), the gas occupies 2.50 dm<sup>3</sup> volume. What would be the volume of the balloon when the pressure inside is 20 kPa at the same temperature.

**Answer**

$$P_1 = 100 \text{ kPa}, P_2 = 20 \text{ kPa}, V_1 = 2.5 \text{ dm}^3, V_2 = ?$$

Applying Boyle law:  $P_1V_1 = P_2V_2$

$$100 \text{ kPa} \times 2.5 \text{ dm}^3 = 20 \text{ kPa} \times V_2$$

$$\therefore V_2 = 12.5 \text{ dm}^3$$

The balloon is filled up to the volume of 12.5 dm<sup>3</sup>.

**1.2.3 Charles law (temperature – volume relationship)**

Investigations by the scientists **Jacques Charles** and **Joseph Gay-Lussac** have showed that for a fixed amount (mass) of a gas at constant pressure volume of a gas increases on heating and decreases on cooling. It was also found that for each degree change (rise or fall) in temperature, volume of a gas changes (increases or decreases) by a factor of 1/273.15 of the original volume of the gas at 0 °C.

Assume that volumes of the gas at 0 °C and at  $t$  °C are  $V_0$  and  $V_t$  respectively, then we can write,

$$V_t = V_0 + \left(\frac{t}{273.15}\right)V_0 = V_0 \left(1 + \frac{t}{273.15}\right) = V_0 \left(\frac{273.15 + t}{273.15}\right)$$

At this stage, a new scale of temperature is defined such that  $t$  °C on new scale is given by

$$T_t = 273.15 + t$$

and 0 °C will be given by

$$T_0 = 273.15$$

This new temperature scale is called the **Kelvin temperature scale (K)** or **absolute temperature scale**. -273.15 °C (0 K) is also defined as the thermodynamic zero, which is the lowest theoretically reachable temperature.

By applying this temperature scale, we can rewrite the relation  $V_t = V_0 \left(\frac{273.15 + t}{273.15}\right)$  as,

$$V_t = V_0 \left(\frac{T_t}{T_0}\right)$$

Hence,

$$\frac{V_t}{V_0} = \frac{T_t}{T_0}$$

For a general case when the change occurs from  $(V_1, T_1)$  to  $(V_2, T_2)$  at constant pressure

$$\frac{V_1}{V_2} = \frac{T_1}{T_2}$$

This can be rearranged as

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{V}{T} = \text{constant or } V = kT$$

Therefore, “the volume of a fixed amount of gas under constant pressure is directly proportional to the absolute temperature of the gas.” This is called **Charles law**.

Further, the ideal gas law can be used to study the effect of temperature on the volume of a gas if the pressure of the system is kept constant for a fixed amount of a gas. The ideal gas law can be rearranged as follows;

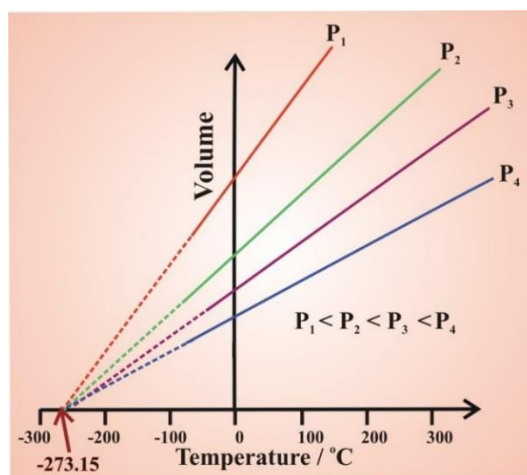
$$PV = nRT$$

$$V = nRT/P$$

When the pressure of a fixed mass of gas is constant,  $\frac{nR}{P}$  is constant.

$$\therefore V \propto T \text{ or } V = kT$$

According to Charles law for all gases, at any given pressure, graph of volume versus, temperature (in Celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at  $-273.15^\circ\text{C}$ . Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at  $-273.15^\circ\text{C}$  or 0 K as shown in Figure 1.5.



**Figure 1.5** Changes in volume of a gas with respect to temperature change at different constant pressures

**Example 1.5**

Calculate the change in temperature of a gas when the volume is tripled at constant pressure for a known amount of gas moles.

**Answer**

$$V_1 = V, V_2 = 3V, T_1 = T, T_2 = ?$$

$$V_1/V_2 = T_1/T_2$$

$$V/3V = T/T_2$$

$$T_2 = 3T$$

This can further be estimated directly, as the volume is directly proportional to Kelvin temperature T, the new temperature would be thrice the initial value, i.e 3T.

Let's consider the equation  $V_t = V_0 \left( \frac{273.15+t}{273.15} \right)$  and substitute  $t = -273.15$ , where we get the volume of the gas equal to zero meaning that the gas will not exist. Therefore, we can understand that all the gases get liquefied before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **absolute zero**.

**Example 1.6**

A balloon is filled with a known amount of hydrogen gas resulting a volume of 2.0 dm<sup>3</sup> at 23 °C. Calculate the change in volume of a gas when the temperature is increased to 27 °C at the same pressure.

**Answer**

$$T_1 = 23 + 273 = 296 \text{ K}, T_2 = 27 + 273 = 300 \text{ K}, V_1 = 2.0 \text{ dm}^3, V_2 = ?$$

Applying Charles law as the pressure and amount of gas constant,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{2.0 \text{ dm}^3}{296 \text{ K}} = \frac{V_2}{300 \text{ K}}$$

$$V_2 = 2.03 \text{ dm}^3$$

Therefore, the change in volume is 0.03 dm<sup>3</sup>

**1.2.4 Avogadro law (amount – volume relationship)**

Upon the developments of Boyle and Charles laws, in 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of those with the amount and volume of a gas and postulated a new hypothesis which is now known as Avogadro law. *It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles (Avogadro Law).*

$$\text{i.e. } V \propto n$$

$$\text{or we can write } V = k n$$

The number of molecules in one mole of a gas has been determined to be  $6.022 \times 10^{23}$  and also known as **Avogadro constant** (denoted as  $N_A$  or  $L$ ).

Avogadro law can be easily understood with the help of the ideal gas law as follows.

$$PV = nRT$$

$$V = \frac{RT}{P} \times n$$

$$V = \frac{RT}{P} \times \frac{N}{N_A} = \frac{RT}{PN_A} \times N$$

Here,  $N$  and  $N_A$  are the number of molecules of the gas and the Avogadro constant respectively. By applying the above relationships to equal volumes of gases P and Q at the same temperature and pressure,

$$V_P = \frac{RT}{PN_A} \times N_P$$

$$V_Q = \frac{RT}{PN_A} \times N_Q$$

At constant  $P$  and  $T$ , we can write (as  $R$  and  $N_A$  are constants)

$$V_P / V_Q = N_P / N_Q$$

Simply it says that for a gas at constant temperature and pressure equal volumes of gases have equal number of molecules. i.e.  $V \propto N$

It is useful to understand that the gas laws discussed above can also be used to obtain the ideal gas equation for a given volume  $V$  of a gas.

$$\text{Boyle Law : } V \propto \frac{1}{P} \text{ --- (1)}$$

$$\text{Charles Law : } V \propto T \text{ --- (2)}$$

Avogadro Law :  $V \propto n$  — — — — — (3)

The only equation that fulfills (1), (2) and (3) is,

$$V \propto \frac{nT}{P}$$

$$\frac{PV}{nT} = k$$

When  $k = R$

$$PV = nRT$$

### 1.2.5 Molar volume ( $V_m$ )

Since volume of a gas is directly proportional to the number of moles we can write,

$$V_m = \frac{V}{n}$$

As temperature and pressure are the same, one mole of any gas should occupy the same volume  $V_m$  and that can be calculated as,

$$V_m = \frac{RT}{P}$$

Therefore, at temperature and standard pressure molar volume ( $V_m$ ) of any gas should have the same value. There are two sets of conditions applied for the standard value.

- *In the first set of condition; the temperature is taken as 0 °C (273.15 K) and the standard pressure as 1 atm (101325 Pa). At this standard condition molar volume of an ideal gas or a combination of ideal gases is 22.414 dm<sup>3</sup> mol<sup>-1</sup>. Molar volume under these conditions is denoted as  $V_m^\ominus$ .*
- *In the second set of condition; the ambient temperature is taken as 25 °C (298.15 K) and the standard pressure as 1 atm (101325 Pa). In that case, the molar volume of a gas has the value 24.790 dm<sup>3</sup> mol<sup>-1</sup>.*

**Note:** From Avogadro law we can see that the molar mass ( $M$ ) of a gas is directly proportional to its density ( $d$ ).

$$V = k n = k (m/M),$$

therefore  $M = k (m/V) = k d$

#### Example 1.7

Show that the molar volumes of 1 mole of He and 1 mole of Ne gas at 298 K temperature and 1atm pressure are the same.

**Answer**

$$P_{He} = 1 \text{ atm} = 101325 \text{ Pa}, T_{He} = 298 \text{ K}, n_{He} = 1.00 \text{ mol}, V_{He} = ?$$

$$P_{He}V_{He} = n_{He}RT_{He}$$

$$V_{He} = n_{He}RT_{He} / P_{He}$$

$$V_{He} = (1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}) / 101325 \text{ Pa} = 24.4 \text{ dm}^3$$

$$P_{Ne} = 1 \text{ atm} = 101325 \text{ Pa}, T_{Ne} = 298 \text{ K}, n_{Ne} = 1.00 \text{ mol}, V_{Ne} = ?$$

$$P_{Ne}V_{Ne} = n_{Ne}RT_{Ne}$$

$$V_{Ne} = n_{Ne}RT_{Ne} / P_{Ne}$$

$$V_{Ne} = (1 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 298 \text{ K}) / 101325 \text{ Pa}$$

$$V_{Ne} = 24.4 \text{ dm}^3$$

i.e. at the same temperature and pressure, if number of moles are the same, then different gases will occupy the same volume.

**1.2.6 Combined gas law**

As all gases behave the same way with respect to pressure, volume, and temperature, if the amount is measured per mole, then the ideal gas expression itself can be written as a ratio useful in the events like when temperature, volume, and pressure of a fixed amount of gas vary from  $(T_1, V_1, P_1)$  to  $(T_2, V_2, P_2)$ . For such an instance we can write,

$$\text{for the initial condition; } nR = \frac{P_1V_1}{T_1}$$

$$\text{for the final condition; } nR = \frac{P_2V_2}{T_2}$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is called the combined gas law.

**Example 1.8**

At 25 °C and 760 mm Hg pressure, a given amount of a gas occupies a volume of 600 cm<sup>3</sup>. What will be its pressure at 10 °C when volume of the gas is 650 cm<sup>3</sup>.

**Answer**

( $T_1, V_1, P_1$ ) to ( $T_2, V_2, P_2$ ) we can write

$$P_1 = 760 \text{ mm Hg} = 1 \text{ atm} = 101325 \text{ Pa}, V_1 = 600 \text{ cm}^3 = 0.600 \text{ dm}^3, T_1 = 25 + 273 = 298 \text{ K}$$

$$V_2 = 650 \text{ cm}^3 = 0.650 \text{ dm}^3, T_2 = 10 + 273 = 283 \text{ K}, P_2 = ?$$

According to Combined gas law;  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$

$$\frac{760 \text{ mm Hg} \times 600 \text{ cm}^3}{298 \text{ K}} = \frac{P_2 \times 650 \text{ cm}^3}{283 \text{ K}}$$

$$P_2 = 666.2 \text{ mmHg} = 88823 \text{ Pa} = 88.823 \text{ kPa}$$

**1.3 Dalton law of partial pressure**

In most practical applications we encounter a mixture of gases rather than a single gas. The air we breathe has nitrogen and oxygen gases as major components and a variety of other gases in minute quantities. All of these gases contribute to the total atmospheric pressure.

Also, the pressure that a constituent gas of a mixture of gases would exert if it alone occupies the volume of the mixture at same temperature is defined as the **partial pressure** of that gas. A postulate introduced by Dalton says that *the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases*. This is known as “**Dalton law of partial pressures**”.

Accordingly, if partial pressures of individual gases in a mixture of gases A, B and C are  $P_A, P_B$  and  $P_C$  respectively, at constant temperature and constant volume the total pressure  $P_T$  of the mixture is given by the following equation.

$$P_T = P_A + P_B + P_C$$

The Dalton law of partial pressure can be derived using ideal gas equation as follows. Consider a mixture of gases A and B with  $n_A$  and  $n_B$  moles, respectively exerting the total pressure of  $P_T$ .

$$PV = nRT$$

For gas A,  $n_A = P_A V / RT$  ( $P_A$  is the partial pressure of gas A)

For gas B,  $n_B = P_B V / RT$  ( $P_B$  is the partial pressure of gas B)

For the mixture of gases,  $n_T = P_T V / RT$

and  $n_T = n_A + n_B$

Therefore,  $P_T V / RT = (P_A V / RT) + (P_B V / RT)$



Simplification gives ,  $P_T = P_A + P_B$

This is the **Dalton law of partial pressures**.

### 1.3.1 Partial pressure in terms of mole fraction

Suppose at the temperature  $T$ ,  $n_A$  moles of gas A and  $n_B$  moles of gas B, are enclosed in a container of volume  $V$ , then partial pressures exerted by gases A and B are  $P_A$  and  $P_B$  respectively while the total pressure is  $P_T$ .

Therefore, we can write,  $P_A = \frac{n_A RT}{V}$  and  $P_B = \frac{n_B RT}{V}$

According to Dalton law,  $P_T = P_A + P_B$

Substituting from the above,  $P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} = (n_A + n_B) \frac{RT}{V}$

Dividing the expressions for  $P_A$  and  $P_B$  separately by  $P_T$ , we get;

$$\frac{P_A}{P_T} = \frac{n_A RT/V}{(n_A + n_B) RT/V} = \frac{n_A}{(n_A + n_B)} = x_A \text{ this is the mole fraction of A}$$

Likewise,

$$\frac{P_B}{P_T} = \frac{n_B RT/V}{(n_A + n_B) RT/V} = \frac{n_B}{(n_A + n_B)} = x_B : \text{ this is the mole fraction of B}$$

Therefore, we can write,

$$P_A = x_A P_T \text{ and } P_B = x_B P_T$$

Partial pressure of the constituent gas is equal to the product of total pressure and mole fraction of the gas.

#### Example 1.9

- (i) A mixture of gases contains 0.8 mol of nitrogen gas ( $N_2$ ) and 0.2 mol of oxygen ( $O_2$ ). Calculate the partial pressures of the gases if the total pressure is 1.00 atm at a certain temperature.
- (ii) When the container is heated and kept at a constant temperature,  $N_2$  gas is reacted with  $O_2$  gas to produce  $NO_2$  gas. At equilibrium the container has 0.7 mol of  $N_2$  gas, 0.15 mol of  $O_2$  gas and 0.1 mol of  $NO_2$  gas. If the partial pressure of  $N_2$  gas is now 0.88 atm, calculate partial pressures of  $O_2$  gas and  $NO_2$  gas.

**Answer**

$$(i) \quad X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2}} = \frac{0.8 \text{ mol}}{0.8 \text{ mol} + 0.2 \text{ mol}} = 0.8$$

$$P_{N_2} = X_{N_2} P_T$$

$$P_{N_2} = 0.8 \times 1.00 \text{ atm}$$

$$P_{N_2} = 0.8 \text{ atm}$$

Similarly for  $O_2$ ,

$$P_{O_2} = 0.2 \text{ atm}$$

$$(ii) \quad X_{N_2} = \frac{n_{N_2}}{n_{N_2} + n_{O_2} + n_{NO_2}} \text{ therefore, } X_{N_2} = \frac{0.7 \text{ mol}}{0.7 \text{ mol} + 0.15 \text{ mol} + 0.1 \text{ mol}} = \frac{0.7}{0.95}$$

$$P_{N_2} = X_{N_2} P_T \text{ therefore, } P_T = P_{N_2} / X_{N_2} = \frac{0.88 \text{ atm}}{0.7/0.95} = 1.19 \text{ atm}$$

$$X_{O_2} = \frac{n_{O_2}}{n_{N_2} + n_{O_2} + n_{NO_2}} \text{ therefore, } X_{O_2} = \frac{0.15 \text{ mol}}{0.7 \text{ mol} + 0.15 \text{ mol} + 0.1 \text{ mol}} = \frac{0.15}{0.95}$$

$$P_{O_2} = X_{O_2} P_T \text{ therefore, } P_{O_2} = \frac{0.15}{0.95} \times 1.19 \text{ atm} = 0.19 \text{ atm}$$

$$X_{NO_2} = \frac{n_{NO_2}}{n_{N_2} + n_{O_2} + n_{NO_2}} \text{ therefore, } X_{NO_2} = \frac{0.10 \text{ mol}}{0.7 \text{ mol} + 0.15 \text{ mol} + 0.1 \text{ mol}} = \frac{0.10}{0.95}$$

$$P_{NO_2} = X_{NO_2} P_T \text{ therefore, } P_{NO_2} = \frac{0.10}{0.95} \times 1.19 \text{ atm} = 0.12 \text{ atm}$$

Therefore,

$$P_{N_2} = 0.88 \text{ atm, } P_{O_2} = 0.19 \text{ atm, } P_{NO_2} = 0.12 \text{ atm,}$$

$$P_T = 1.19 \text{ atm}$$

We apply our knowledge on Dalton law for a mixture of gases assuming that they have the same properties as pure gases, provided that all gases in the mixture are ideal gases thus do not react chemically with each other. However, in practical situations such as chemical reactions involving gases, the procedure used to collect may introduce another gas. For example, a technique often used to collect gases from a chemical reaction is the displacement of water from an inverted container. In this method, a gas is collected in the container by bubbling the gas through a tube into a gas jar filled with water which is placed upside-down in a water trough. So that the gas push all the liquid out from the bottle when it is collected. Here, we assume that the gas does not dissolve in water and does not react with water. However; we do not get the gas which is in the pure state. Instead, the collected gas is a mixture of the gas generated by the reaction and some water vapour formed from evaporation. The amount of water vapour contained in the gas is most readily measured by the pressure it exerts at that temperature, called the **saturated vapour pressure**. Therefore, to determine the pressure exerted by a gas collected in this

way at a specific temperature, it is necessary to subtract the vapour pressure of water from the total pressure of the mixture. Then from the partial pressure of the gas and its volume and temperature, the ideal gas law can be used to calculate the amount of the gas collected. This is illustrated in example 1.10

**Example 1.10**

Suppose we produce gaseous oxygen by heating  $\text{KClO}_3(\text{s})$  as shown in the following reaction:



1.50 dm<sup>3</sup> of O<sub>2</sub> gas is collected over water at 27.0 °C and 760 torr. Saturated vapour pressure of water at 27.0 °C is 26.7 torr.

Calculate the number of moles of O<sub>2</sub> gas produced.

**Answer**

According to Dalton law, we can write:

$$P_{\text{total}} = P_{\text{oxygen}} + P_{\text{water}}$$

$$\therefore P_{\text{oxygen}} = P_{\text{total}} - P_{\text{water}} = (760 - 26.7) \text{ torr} = 733.3 \text{ torr} = 97764 \text{ Pa}$$

Using the ideal gas equation:

$$PV = nRT \quad \text{and} \quad n = \frac{PV}{RT} = \frac{97764 \text{ Pa} \times 1.5 \times 10^{-3} \text{ m}^3}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} = 0.058 \text{ mol}$$

**1.4 Molecular kinetic theory of gases**

In the above sections we have gone through and understood the laws related to gaseous state based on experimental observations (Boyle law, Charles law, etc.). By conducting such experiments we can understand how the particular system behaves under different conditions. Though, such observations are made from experiments we then have to know or understand why a system behaves that way. For example, gas laws help us to predict that pressure increases when we compress gases but we need to know what happens in the molecular level when a gas is compressed. Therefore, a theoretical model is needed to explain such events or questions where the theory should help us to understand observations. The theory that attempts to explain the behaviour of gases at the molecular level is known as “**molecular kinetic theory**”.

**1.4.1 Assumptions of the molecular kinetic theory of an ideal gas**

- *Gases are composed of widely separated large number of small particles (molecules or atoms).*

Because the particles are widely separated, the actual volume of the particles is very small compared to the total volume occupied by the gas. Or in other words the actual volume of the molecules is negligible in comparison to the empty space

between them. This postulate correctly predicts that the volume occupied by a gas is much larger than that of a liquid or a solid, in which the particles are much closer together. Because gas particles are so widely separated, gases have relatively low densities compared to liquids and solids. This assumption explains high compressibility of gases.

- *Each particle in a gas is in random (all possible directions), straight-line motion and undergoes perfectly elastic collisions with another particle or with the walls of the container. Different particles have different speeds.*

Energy may be transferred from one particle to another, their individual energies may change, but there is no net loss or gain of energy. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- *The average kinetic energy of gas particles depends only on the absolute temperature.*

This tells us that the gas particle (molecule or atom) has its own mass and speed because the kinetic energy ( $KE$ ) for a given gas particle is given by the equation

$$KE = \frac{1}{2} m v^2$$

where  $m$  is the mass of a gas particle and  $v$  is the velocity (or speed). We can see that upon heating a gas at constant volume, the pressure increases. That is because, on heating the gas, kinetic energy of the particles increases and they strike the walls of the container more frequently thus exerting more pressure. As such the relation of kinetic energy of one mole of particle with the temperature is given by the following equation.

$$KE = \frac{3}{2} RT$$

Further, we can make following notes too.

- *Particles of a gas behave independently of one another.*

Because gas particles are widely separated, they move independently of one another unless they collide. That is, no forces of attraction or repulsion operate among gas particles. We can see that this postulate explains Dalton law of partial pressures. This postulate also explains why gases fill their containers entirely.

- *The pressure of a gas arises from the sum of the collisions of the particles with the walls of the container.*

This postulate explains Boyle law; at a given temperature, for the same amount of gas, the smaller the volume of the container and hence more collisions occur per unit area. The average distance traveled by a gas particle before a collision is less in a smaller volume. Therefore, more collisions occur in a given area producing greater pressure.

This assumption also predicts that pressure should be proportional to the number of moles of gas particles. The more gas particles, the greater the frequency of collisions with the walls, so the greater the pressure.

#### 1.4.2 Equation of molecular kinetic theory

The equation below is named as the equation of molecular kinetic theory.

$$PV = \frac{1}{3} mN\bar{c}^2$$

This equation now gives pressure, a macroscopic quality, in terms of molecular motion. The significance of the above relationship is that pressure is proportional to the mean-square speed of molecules in a given container at a given temperature. From the equation we can see that when molecular speed increases the pressure exerted on the container increases.  $\bar{c}^2$  is defined as the mean square speed of molecules.

#### 1.4.3 Root mean square speed and mean speed

It is worth knowing the definitions of molecular speeds in different forms as follows: When  $N$  number of molecules in a constant volume container at constant temperature travel with the different speeds of  $c_1, c_2, \dots, c_N$ , it can be written as shown below.

$$\text{Average speed, } \bar{C} = \frac{c_1 + c_2 + \dots + c_N}{N}$$

$$\text{Mean square speed } \bar{c}^2 = \frac{(c_1^2 + c_2^2 + c_3^2 + \dots + c_N^2)}{N}$$

$$\text{Root mean square speed} = \sqrt{\bar{c}^2}$$

Molecular kinetic equation can be used to derive equation to show temperature dependence of the mean square speed  $\bar{c}^2$ . Consider the equation for having  $N$  number of particles in volume  $V$ . We know that,  $P = \frac{mN\bar{c}^2}{3V}$  and we can write this as;  

$$PV = \frac{mN\bar{c}^2}{3}$$

Since,  $N = nN_A$ , where  $N_A$  is the Avogadro's constant and  $n$  is the number of moles;

$$PV = \frac{1}{3} mnN_A\bar{c}^2$$

Since,  $M = m N_A$ , then the above equation can be rearranged as, ( $M$  is the molar mass)

$$PV = \frac{1}{3} n M \bar{c}^2$$

Substitution of ideal gas law,  $PV = nRT$  in the above equation gives,

$$nRT = \frac{1}{3} M n \overline{c^2}$$

$$\overline{c^2} = \frac{3RT}{M}$$

And hence we can write root mean square speed as;

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}}$$

### Example 1.11

Calculate the root mean square speed of  $H_2$  and  $N_2$  gases at  $25^\circ C$ .

#### Answer

$$T = 25^\circ C = 298 K$$

$$M(H_2) = 2.0 \text{ g mol}^{-1} = 0.002 \text{ kg mol}^{-1}$$

$$M(N_2) = 28.0 \text{ g mol}^{-1} = 0.028 \text{ kg mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

For  $H_2$

$$\text{Substituting in } \sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.002 \text{ kg mol}^{-1}}} = 1927.8 \text{ m s}^{-1}$$

For  $N_2$

$$\text{Substituting in } \sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.028 \text{ kg mol}^{-1}}} = 515.2 \text{ m s}^{-1}$$

From the above example, we can see that heavier molecules move slowly at a given temperature implying that the molecules having higher mass do not have to move as rapidly as lighter molecules to have the same kinetic energy. This kinetic energy directly related to temperature and this can be proved based on the equation of molecular kinetic theory as follows.

$$\text{We have, } PV = \frac{mN\overline{c^2}}{3}$$

Multiply the above equation by 2 and also divide by 2, then we can rearrange the equation as;

$$PV = \frac{mN\overline{c^2}}{3} = \frac{2N}{3} \left( \frac{1}{2} m\overline{c^2} \right) = nRT$$

$$N \left( \frac{1}{2} m\overline{c^2} \right) = \frac{3}{2} nRT$$

$$\text{And also we can write } \left( \frac{1}{2} m\overline{c^2} \right) = \frac{3}{2} \left( \frac{Rn}{N} \right) T = \frac{3}{2} \left( \frac{R}{N_A} \right) T = \frac{3}{2} (k_B)T$$

$k_B$  is the Boltzmann constant.

We can then write these as  $\frac{1}{2} m\overline{c^2}$  is the kinetic energy (KE)

$$KE = \frac{3}{2} k_B T \text{ (per molecule)}$$

$$KE = \frac{3}{2} (k_B) T N_A$$

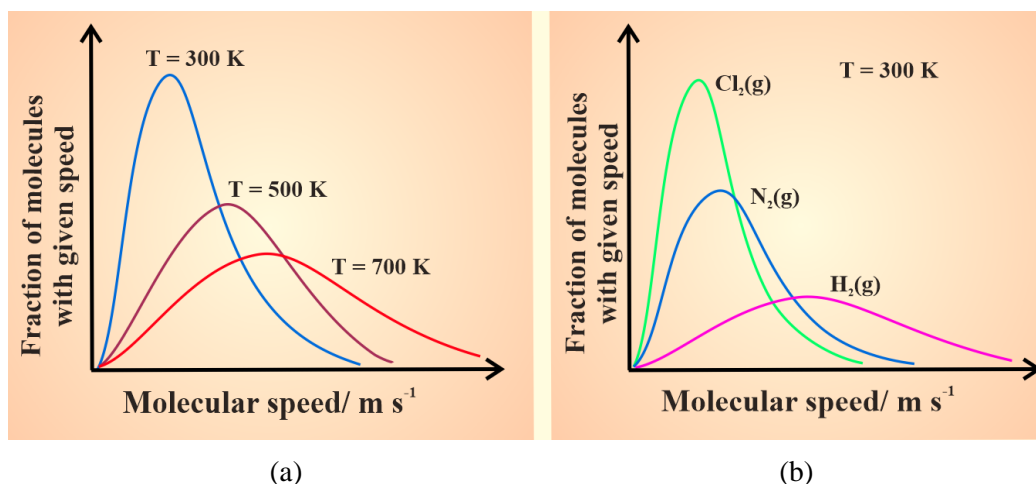
$$KE = \frac{3}{2} \left( \frac{R}{N_A} \right) T N_A$$

$$KE = \frac{3}{2} RT \text{ (per mole)}$$

This proves that the kinetic energy of a gas depends only on the Kelvin temperature.

#### 1.4.4 Maxwell- Boltzmann distribution

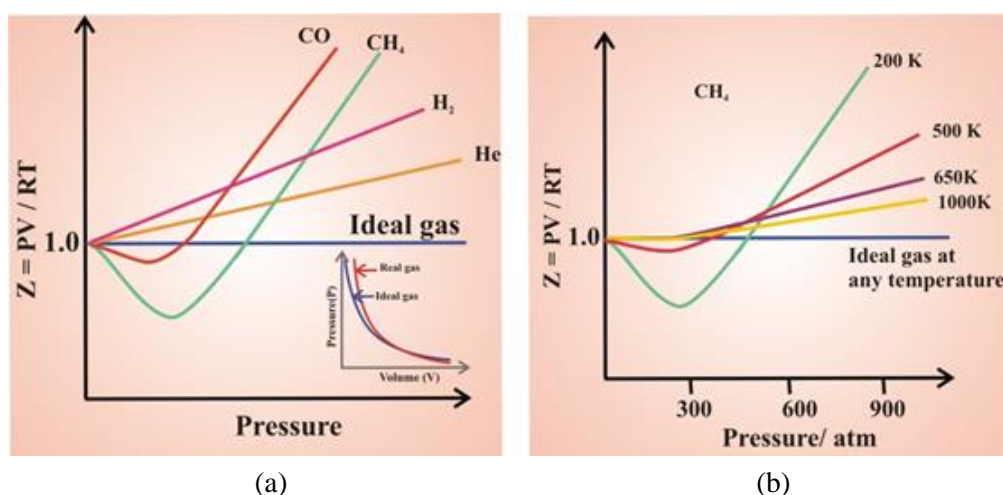
Although from the above example we have calculated speed of  $N_2$  molecule as  $515 \text{ m s}^{-1}$ , it does not mean that all the  $N_2$  molecules travel at this speed (as the molecules move in straight line directions, that the motion has vector properties, such that the molecular speeds are expressed in relation). There is a distribution of speeds from zero to values considerably above  $515 \text{ m s}^{-1}$ . This is because as individual molecules collide and exchange energy, their speeds vary. This speed distribution can be shown as a fraction of molecules travelling with particular speeds as shown in Figure 1.6 and such a distribution is called **Maxwell- Boltzmann distribution of speeds**.



**Figure 1.6** (a) Maxwell- Boltzmann speed distribution for nitrogen gas at different temperatures (b) Speed distribution of three gases at 300 K

### 1.5 Amendments to ideal gas equation to apply for real gases

For a one mole of an ideal gas we can write  $PV = RT$  or in other words  $\frac{PV}{RT} = 1$  at a given temperature. When we have a real gas it actually deviates from ideal behaviour to some extent. The quantity,  $Z = \frac{PV}{RT}$ , called **compressibility factor (coefficient)** is used as one of the measures of this deviation. For example, for a one mole of an ideal gas if we study or analyze the variation of  $Z$  with pressure at constant temperature,  $PV$  will be constant (Boyle law) and  $Z$  vs  $P$  graph at all pressures will be a straight line parallel to  $x$ -axis (pressure - axis). Figure 1.7(a) shows such a plot for several gases at 273 K and Figure 1.7(b) for a one gas at several temperatures.



**Figure 1.7** Variation of compressibility factor for several gases with the comparison of an ideal gas. (a) The variation of  $Z$  with pressure at a constant temperature. Inset in (a) shows the Boyle law plot for ideal gas and real gas. (b) is the variation of  $Z$  with pressure at different temperatures for  $\text{CH}_4$  gas.



From the plots shown in Figure 1.7 (a) it can be seen easily that at constant temperature  $\frac{PV}{RT}$  vs  $P$  ( $Z$  vs  $P$ ) plots for real gases is not a straight line parallel to the  $x$ -axis (pressure). There is a significant deviation from ideal behaviour. For different types of real gases, two types of curves are resulted. In the curves for hydrogen and helium, the value of  $Z$  increases as the pressure increases. The second type of plot is seen in the case of other gases like carbon monoxide (CO) and methane (CH<sub>4</sub>). In these plots first there is a negative deviation from ideal behavior, the  $Z$  value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that it starts increasing, crosses the line for ideal gas and increases continuously showing a positive deviation. With these observations it can be found that real gases do not follow ideal gas equation perfectly under all conditions.

This deviation from ideal behaviour can also be understood when pressure versus volume plot is considered which is drawn as an inset in the Figure 1.7(a). In that plot the pressure versus volume data of a real gas is compared with those calculated theoretically. We know that this is the plot of Boyle law (for an ideal gas) and if the real gas follows the same behaviour two plots should coincide. It is clearly apparent that at very high pressures the measured volume is more than the calculated volume and at low pressures, measured and calculated volumes approach close to each other indicating further that low pressure conditions favour the ideal behavior. Thus gases show ideal behavior when the volume occupied is large so that the volume of the molecules can be neglected in comparison to the volume of the container. In other words, the behaviour of the real gas becomes more ideal when pressure is very low and depends upon the nature of the gas and its temperature.

We can further interpret the above behaviour of real gases where  $Z$  is less than 1 ( $Z < 1$ ) as a combination of intermolecular interactions and repulsions caused by the significant sizes of the molecules when they become crowded at high pressures. At low pressures but still high for the ideal behaviour intermolecular attractions lower the molar volume and  $Z$  value is less than 1. At sufficiently high pressures, molecules tend to become crowded and the volume of the gas particles become large compared to the situation when it would be a point mass. At high temperature (Figure 1.7(b)) intermolecular attractions become less and  $PV$  factor increases making  $Z$  values greater than one ( $Z > 1$ ). However deviation from the ideal line is less indicating that the higher temperatures favour the ideality to some extent. Therefore, we can say very low pressures and high temperatures are the favourable conditions for the ideal behaviour of real gases.

If we compare this behaviour of real gases with ideal gases considering these variations in molar volume at a given temperature and pressure, then the relation of compressibility factor  $Z$  may be understood. Assume that one mole of a real gas has the volume  $V_{real}$  and that for the ideal gas as  $V_{ideal}$ . Therefore, we can write;

$$Z = \frac{PV_{real}}{RT}$$

If the gas shows ideal behaviour under the same conditions;

$$PV_{ideal} = RT \text{ (per one mole)}$$

Substituting this in the first equation we get;  $Z = \frac{PV_{real}}{PV_{ideal}}$

Therefore,  $Z = \frac{V_{real}}{V_{ideal}}$

Therefore, we can see that the compressibility factor  $Z$  is the ratio of actual molar volume of a gas to the molar volume of it if it behaves as an ideal gas at that temperature and pressure.

Based on this kinds of experiments, it has been found that real gases do not follow Boyle law, Charles law and Avogadro law perfectly under all conditions. Therefore we have to understand; why gases deviate from the ideal behaviour and the conditions under which gases deviate from ideal behaviour.

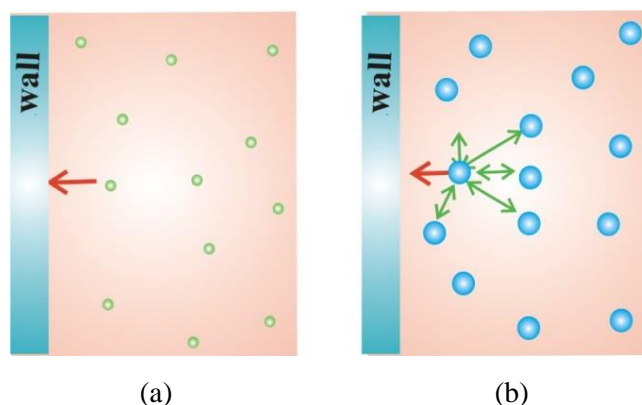
For the first one we can use the assumptions made in the molecular kinetic theory where it was assumed that; there is no force of attraction between the molecules of a gas and volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If there are no interactions among gas molecules, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. Once the gases are cooled and compressed the gas molecules will come close and then form liquids. If the volume of a gas molecule is negligible then the pressure versus volume graph of real gas and that of an ideal gas should coincide (see the inset of Figure 1.7 (a) and the behavior shown in the inset help us to understand the deviation of real gases from ideality). But it does not happen therefore, the real gases deviate from ideality.

### 1.5.1 van der Waals equation

At the beginning of this unit, an ideal gas law,  $PV = nRT$  known as **equation of state** was used to understand the behaviour of gases under different conditions with the measurable variables of  $P, V, T$  and  $n$ . From the above clarifications it can be understood that real gases show deviations from the ideal gas law due to the interactions among molecules and a significant volume of a gas molecule. Therefore, it is necessary to have another kind of equations of state to describe the behaviour of real gases as the measured pressures and volumes would not be the same as those for an ideal gas. Dutch physicist, **J. D. van der Waals** suggested the following which relates pressure and volume of a real gas to the pressure and volume of an ideal gas.

At high pressures molecules of gases are very close to each other and molecular interactions start to operate. Therefore, at high pressures, molecules cannot strike on the walls of the container with full force of impact as these are dragged back by other molecules due to the operation of these molecular attractive forces (a sketch on this behaviour is shown in Figure 1.8 comparing with an ideal gas). This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the real gas is lower than the pressure exerted by the ideal gas under similar conditions.



**Figure 1.8** Comparison of the impact on the wall due to the collision of (a) an ideal gas molecule and (b) a real gas molecule.

As shown in the above figure reduction of pressure of a real gas is due to the intermolecular attractions. As it was found that the number of collisions with the wall in a given time is proportional to the density of the gas, the correction factor to pressure is proportional to the square of the gas amount and inversely proportional to the square of the volume and then the correction factor can be written as  $\frac{a n^2}{V^2}$  where  $a$  is a constant related to magnitude of attractive forces and is independent of temperature and pressure.  $n$  and  $V$  are the number of moles of the gas and volume of the container respectively. Therefore, the pressure of the system under this condition is given by the following expression.

$$P_{ideal} = P_{real} + \frac{a n^2}{V^2}$$

At high pressure, repulsive forces are significant as molecules are almost in contact. Therefore, these repulsive forces cause the molecules to behave as small spheres to minimize the effect and hence results a significant volume occupied by the molecules. Now the ideal volume should be less than the measured volume because instead of moving in volume  $V$ , these are now restricted to an effective volume of

$$(V - nb)$$

$nb$  is approximately the total volume occupied by the molecules themselves and  $b$  is a constant (volume of one molecule). Having taken into account the corrections for pressure and volume, we can rewrite the equation  $PV = nRT$  as,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This is called **van-der Waals equation** and  $a$  and  $b$  are called **van-der Waals constants**. If we write this equation for one mole of a real gas it takes the following form.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

### 1.5.2 Critical temperature and liquefaction of gases

At the beginning of the chapter the importance of the extent of the intermolecular forces to maintain a particular physical state was discussed. Matter can be interconverted between physical states supplying heat or cooling as needed to change the intermolecular distance.

For example, we may think that liquefaction of a gas can be done just by cooling and compression. Though it is correct to some extent, we need more ideas about the behaviour of real gases in accordance with their phase changes.

*Note: This is one of the topics discussed in detail in unit 12 and a little description will be given here as it is important to have a basic idea about the conditions necessary for liquefaction of gases.*

For example, such kind of information on the pressure, temperature and volume relations are available for carbon dioxide where it has been found that carbon dioxide can behave as a gas, a liquid and a solid depending on the variations in pressure and temperature.

We know that high temperatures favour the ideal behaviour and a gas cannot be liquefied even at very high pressures. In the case of carbon dioxide, which exists as a gas at high temperatures starts to liquefy at 30.98 °C (304.2 K) when the pressure is below 73 atm. The temperature 30.98 °C is called **critical temperature ( $T_C$ )** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed and above this temperature it exists only as a gas. Therefore, we can define the critical temperature of a substance as the temperature at and above which the vapour of the substance cannot be liquefied, no matter how much pressure is applied. The **critical pressure** of a substance is the pressure required to liquefy a vapour at critical temperature.

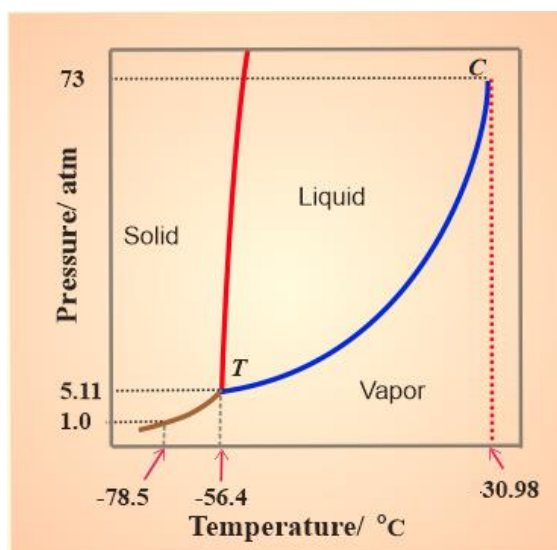
Figure 1.9 Phase diagram of CO<sub>2</sub>

Table 1.3 A summary of equations

Gas law	Equation	Parameters kept constant
Ideal gas law	$PV = nRT$	None
Boyle law	$P = k/V$	n and T
Charles law	$V = kT$	n and P
Avogadro law	If $V_A = V_B$ then $N_A = N_B$	P and T
Molecular kinetic equation	$PV = \frac{1}{3} mN\bar{c}^2$	
Average speed	$\bar{c} = \frac{c_1 + c_2 + \dots + c_N}{N}$	
Mean square speed	$\overline{c^2} = \frac{(c_1^2 + c_2^2 + c_3^2 \dots + c_N^2)}{N}$	
Mean square speed	$\overline{c^2} = \frac{3RT}{M}$	
Dalton law of partial pressures	$P_A = x_A P_T$ $P_T = P_A + P_B + P_C$	
Compressibility factor	$z = \frac{PV}{RT}$	for one mole of gas
van der Waals equation	$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$	

## 2. Energetics



### Content

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- Standard enthalpy change of solvation,  $\Delta H_{sol}^\ominus$

- Standard enthalpy change of hydration,  $\Delta H_{hyd}^\ominus$

- Standard enthalpy change of dissolution,  $\Delta H_{dissolution}^\ominus$

- Standard enthalpy change of sublimation,  $\Delta H_{sub}^\ominus$

- Standard enthalpy change of evaporation,  $\Delta H_{evap}^\ominus$

- Standard enthalpy change of fusion,  $\Delta H_{fus}^\ominus$

- Standard enthalpy change of atomization,  $\Delta H_{at}^\ominus$

- Standard enthalpy change of first ionization,  $\Delta H_{IE1}^\ominus$

- Standard enthalpy change of electron gain,  $\Delta H_{EG}^\ominus$

- Standard lattice enthalpy change of an ionic compound,  $\Delta H_L^\ominus$

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- 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.

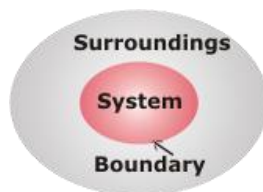


Figure 2.1 Schematic representation of a system, surroundings and boundary

### 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.

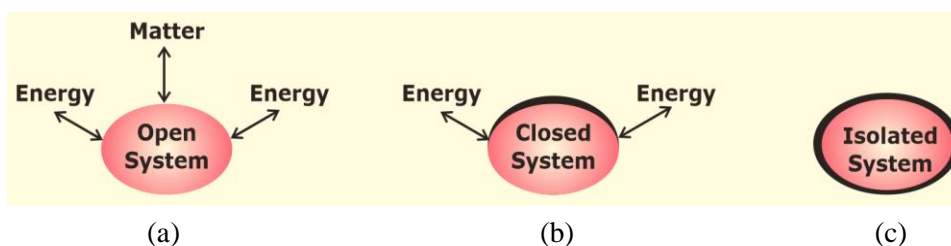


Figure 2.2 Schematic view of (a) open, (b) closed and (c) isolated systems

- **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  $m_1$  g,  $m_2$  g and  $m_3$  g are mixed in a system. Then the total mass of the system is equal to  $(m_1+m_2+m_3)$  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 ( $\text{mol}^{-1}$ ) or per gram ( $\text{g}^{-1}$ ) or per  $\text{cm}^3$  ( $\text{cm}^{-3}$ ) or per  $\text{cm}^2$  ( $\text{cm}^{-2}$ ), 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  $P^\ominus$  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  $P^\ominus$  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  $\ominus$  to the symbol of the quantity ( $\Delta H^\ominus$ ,  $\Delta G^\ominus$ ,  $\Delta S^\ominus$  etc.) It has to be noted that when solutions are involved, a concentration is  $1 \text{ mol dm}^{-3}$ .*

- **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,  $\Delta H$ , that we actually measure.

The **enthalpy change of reaction**,  $\Delta H$ , is the difference between the total enthalpies of the products and the total enthalpies of the reactants.

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

### 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

$$C = m c$$

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  $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$  and the heat capacity of  $100.0 \text{ g}$  of water is  $(100.0 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}) = 418.4 \text{ J }^\circ\text{C}^{-1}$ .

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

Knowing the specific heat, the mass of a substance and the change in the sample's temperature  $\Delta t$  (temperature in  $^\circ\text{C}$ ) or  $\Delta T$  (temperature in  $\text{K}$ ), the amount of heat ( $Q$ ) that has been absorbed or released in a particular process can be calculated by the equation;

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

where  $m$  is the mass of the sample and  $\Delta t$  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

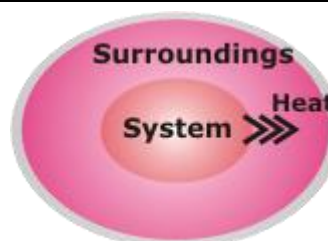
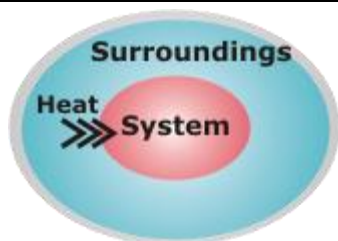
$\Delta H$  represents the heat given off or absorbed during a reaction. The enthalpy of reaction can be positive or negative, depending on the process. Enthalpy change is directly proportional to the amounts of substances in a system.

### 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:

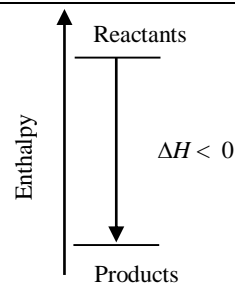
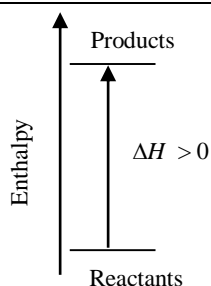
**Table 2.1** Comparison between endothermic and exothermic processes

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 $\frac{1}{2} \text{N}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) + 90 \text{ kJ} \rightarrow \text{NO}(\text{g})$	Reactant → Products + Energy(Heat) $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + 242 \text{ kJ}$



For an endothermic process (heat absorbed by the system from the surroundings),  $\Delta H$  is positive (that is,  $\Delta H > 0$ )

For an exothermic process (heat released by the system to the surroundings),  $\Delta H$  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,  $\Delta H^\ominus$ . 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.*

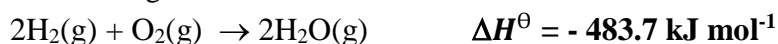
### 2.2.2 Thermochemical equations

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

- The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.
- The enthalpy change of a reaction has unit **kJ mol<sup>-1</sup>** 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.
- When a chemical reaction is reversed the value of  $\Delta H$  is reversed in sign with the magnitude remaining the same.
- Physical states of all species is important and must be specified in a thermochemical equation since  $\Delta H$  (or  $\Delta H^\ominus$ ) depends on states (phases) of reactants and products.
- If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number.
- The negative sign of  $\Delta H^\ominus$  indicates an exothermic reaction and a positive sign of  $\Delta H^\ominus$  indicates an endothermic reaction.

#### Example:

Consider the following reactions.



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

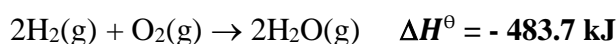
- 483.7 kJ given off per mole of the reaction\*
- 483.7 kJ given off per 2 moles of  $\text{H}_2(\text{g})$  consumed
- 483.7 kJ given off per mole of  $\text{O}_2(\text{g})$  consumed

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

$\Delta H^\theta$  tells how much the enthalpy change would be, if the number of moles reacting is the same as the stoichiometric coefficients.

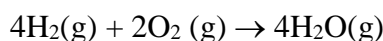
*\* Note: In this case, 483.7 kJ mol<sup>-1</sup> means that 483.7 kJ of heat is evolved when 2 moles of hydrogen gas were to react with 1 mole of oxygen gas to form 2 moles of gaseous water*

Sometimes the above reaction is written as;



*\* 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 ;  $\Delta H = \Delta H^\theta \times \text{mol} = - 483.7 \text{ kJ mol}^{-1} \times \text{mol} = - 483.7 \text{ kJ}$*

For example if we write the reaction as;



then we write  $\Delta H$  of the reaction as  $2 \times \Delta H^\theta = - 967.4 \text{ kJ}$

That means the original  $\Delta H^\theta$  value has to be multiplied by 2 or in other words the value of  $\Delta H$  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  $\Delta H^\theta$ , then it would equals to  $- 967.4 \text{ kJ mol}^{-1}$

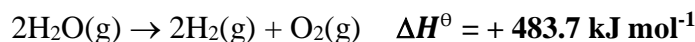
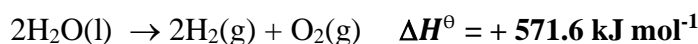
If we write the equations as;



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

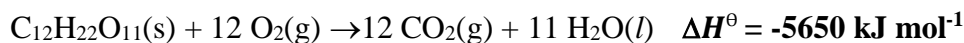
The above equations describe the combustion of hydrogen gas to water in a general sense. The first reaction can be considered the formation reaction of liquid water and the second reaction the formation of water vapour. The negative sign of  $\Delta H$  indicates that they are exothermic reactions.

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.

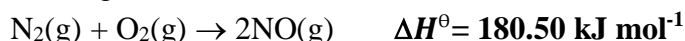


### 2.2.3 Enthalpy diagrams

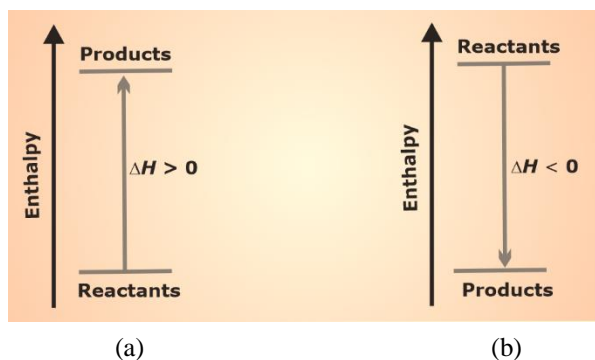
Consider the following reaction.



The negative sign of  $\Delta H^\theta$  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.



In the above reaction the products have a higher enthalpy than the reactants so  $\Delta H^\theta$  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).



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

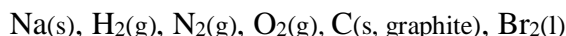
### 2.2.4 Enthalpy changes and standard enthalpy changes

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

The **standard enthalpy of formation,  $\Delta H_f^\theta$**  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  $\theta$  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*.

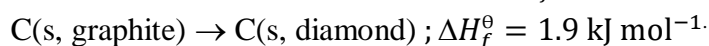


For example, listed below are the most stable forms of some elements/ compounds at 298.15 K, the temperature at which thermochemical data are commonly tabulated.



**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  $\Delta H_f^\ominus = 0$



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

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



Note that the difference between these two  $\Delta H_f^\ominus$  values is just the heat of vapourization (44 kJ mol<sup>-1</sup>) 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  $\Delta H_f^\ominus$  value applies, as illustrated in following examples in the text.

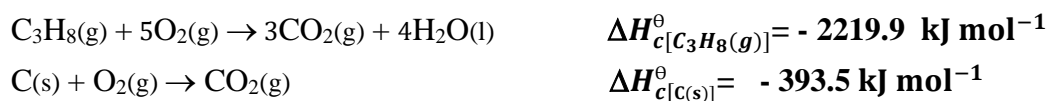
The standard enthalpy of formation of formaldehyde (HCHO) is -108 kJ mol<sup>-1</sup> at 298 K and the chemical equation below shows this event.



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

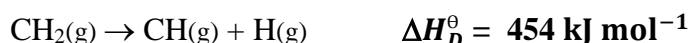
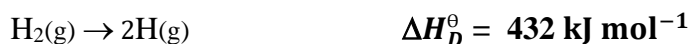
- **Standard enthalpy change of combustion,  $\Delta H_c^\ominus$**

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.



- **Standard enthalpy change of bond dissociation,  $\Delta H_D^\circ$**

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.



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

$$\begin{aligned} \text{Mean standard enthalpy change of} &= \frac{(428 + 441 + 454 + 344) \text{ kJ mol}^{-1}}{4} \\ \text{bond dissociation of CH}_4(\text{g}) &= 416.75 \text{ kJ mol}^{-1} \end{aligned}$$

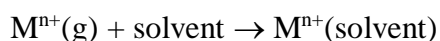
- **Standard enthalpy change of neutralization,  $\Delta H_{neu}^\circ$**

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



- **Standard enthalpy change of solvation,  $\Delta H_{sol}^\circ$**

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



- **Standard enthalpy change of hydration,  $\Delta H_{hyd}^\circ$**

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  $1.0 \text{ mol dm}^{-3}$ .



- **Standard enthalpy change of dissolution,  $\Delta H_{dissolution}^\circ$**

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  $1.0 \text{ mol dm}^{-3}$  (a saturated solution formed by a sparingly soluble salt).



- **Standard enthalpy change of sublimation,  $\Delta H_{sub}^{\ominus}$**

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.



- **Standard enthalpy change of evaporation,  $\Delta H_{evap}^{\ominus}$**

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.



- **Standard enthalpy change of fusion,  $\Delta H_{fus}^{\ominus}$**

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.



- **Standard enthalpy change of atomization,  $\Delta H_{at}^{\ominus}$**

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



- **Standard enthalpy change of first ionization,  $\Delta H_{IE1}^{\ominus}$**

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.



- **Standard enthalpy change of electron gain,  $\Delta H_{EG}^{\ominus}$**

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.



- **Standard lattice dissociation enthalpy change of an ionic compound,  $\Delta H_L^{\ominus}$**

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.



**2.2.5 Indirect determination of  $\Delta H$  ( $\Delta H^\ominus$ ): 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.

$\Delta H$  is an extensive property and is also a function of state. Consider the standard enthalpy change of formation of  $\text{NO}(\text{g})$  from its elements at  $25^\circ\text{C}$ .



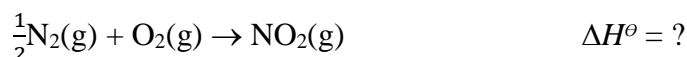
To express the enthalpy change in terms of one mole of  $\text{NO}(\text{g})$  we divide all coefficients and the value  $\Delta H^\ominus$  by two.



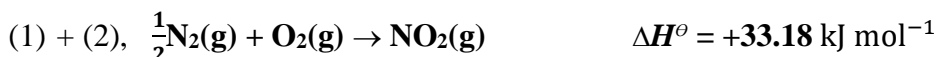
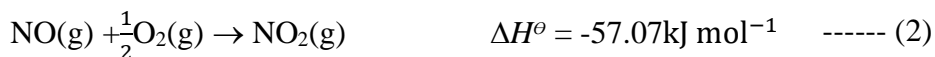
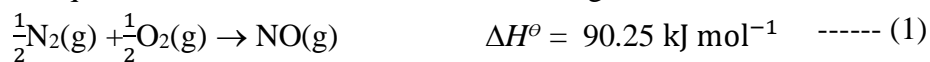
$\Delta H^\ominus$  changes sign when a process is reversed as the change in a function of state reverses sign. Thus, for the decomposition of one mole of  $\text{NO}(\text{g})$ , standard enthalpy change is  $-90.25 \text{ kJ mol}^{-1}$  which is the negative value of the enthalpy for the formation of one mole of  $\text{NO}(\text{g})$ .

**An example for Hess Law of constant heat summation:**

The standard enthalpy change for the formation of  $\text{NO}_2(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$  can be found as follows.



We can think of the reaction as proceeding in two steps: First we form  $\text{NO}(\text{g})$  from  $\text{N}_2(\text{g})$  and  $\text{O}_2(\text{g})$ , and then  $\text{NO}_2(\text{g})$  from  $\text{NO}(\text{g})$  and  $\text{O}_2(\text{g})$ . 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.

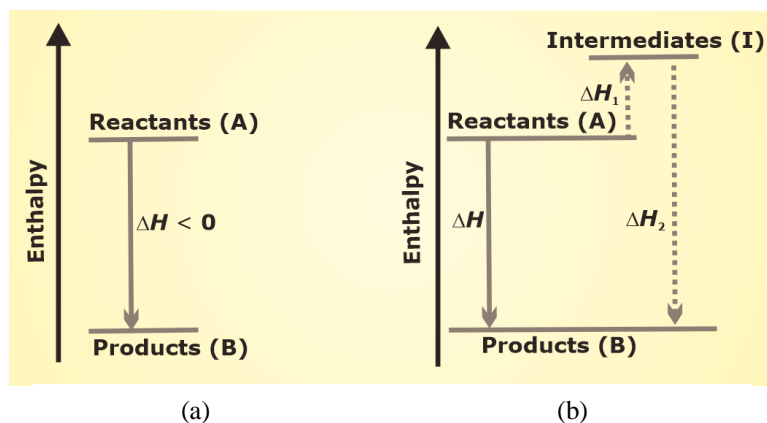


As of the above example the **Hess law** states the principle we used: i.e.

*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,  $\Delta H$  (or  $\Delta H^\ominus$  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.



**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.

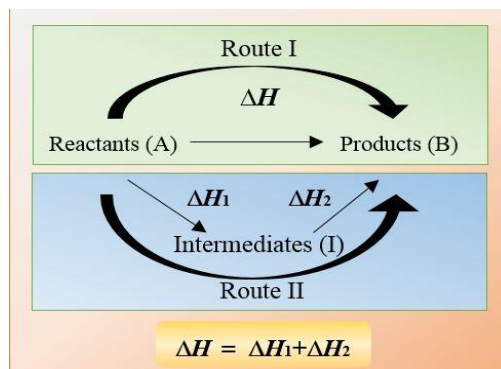


Figure 2.5 Thermochemical cycle

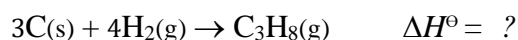
When we write the thermochemical cycle it is important to follow the instructions given below.

First write the chemical reaction in which the enthalpy change needs to find and write  $\Delta H$  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.

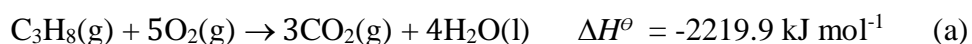
### Example:

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

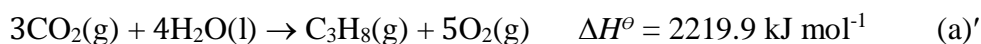


Now we have a question that how should we proceed? If we try to get graphite and hydrogen to react, but it will not go to completion. Furthermore, the product will not be limited to propane and several other hydrocarbons will form as well. The fact is that we cannot directly measure  $\Delta H^\theta$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

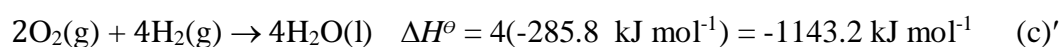
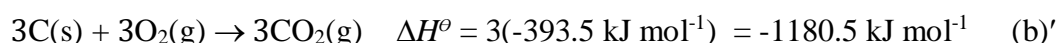
To determine an enthalpy change with Hess law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on one mole of the indicated reactant. Considering that the products of the combustion of carbon–hydrogen–oxygen compounds are  $\text{CO}_2\text{(g)}$  and  $\text{H}_2\text{O(l)}$  we can find the path to solve the problem as follows.



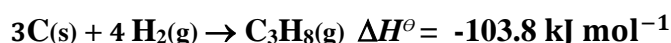
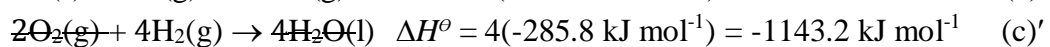
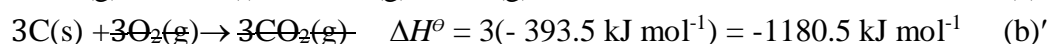
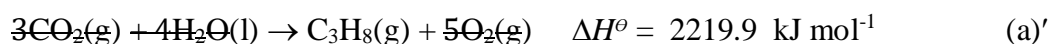
Reverse of the reaction (a).



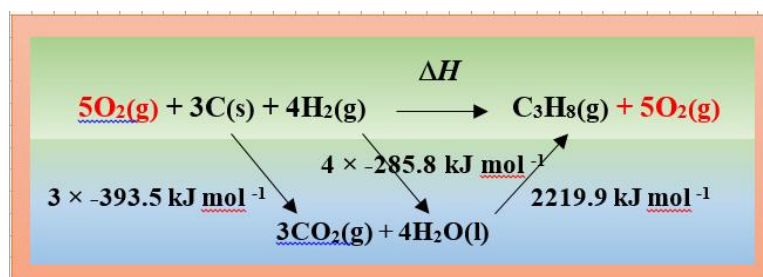
Considering the reactants of the reaction of interest, C(s) and H<sub>2</sub>(g), to get the proper number of moles of each, we must multiply equation (b) by three and equation (c) by four.



Here is the overall change we have described: 3 mol of C(s) and 4 mol of H<sub>2</sub>(g) have been consumed, and 1 mol of C<sub>3</sub>H<sub>8</sub>(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)')



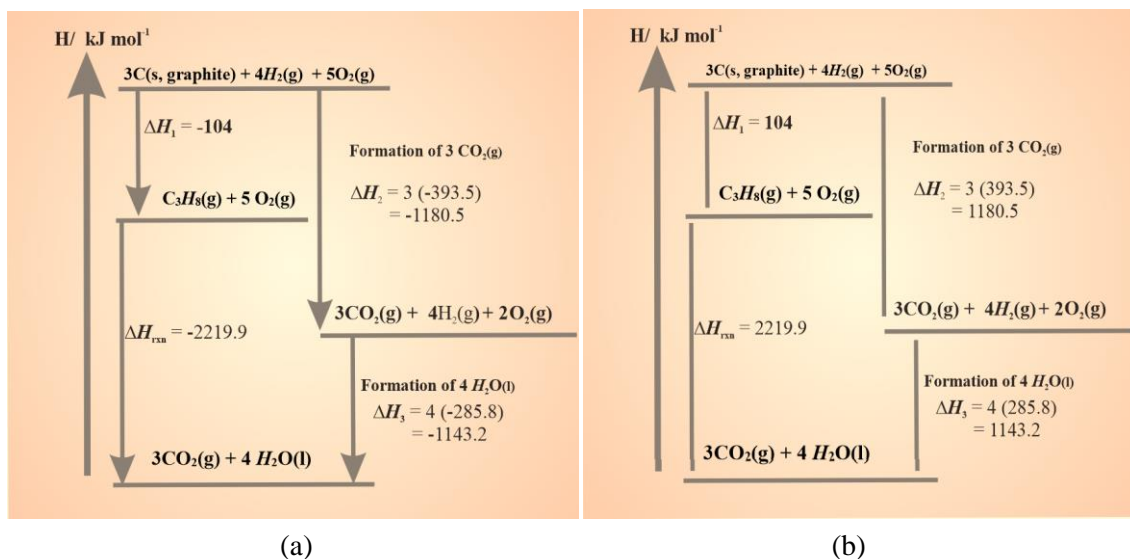
*Solving the above with a thermochemical cycle:*



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

*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,  $\Delta H$  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.



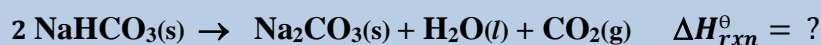
**Figure 2.6** Enthalpy diagram for  $3\text{C}(\text{s}) + 4\text{H}_2(\text{g}) \rightarrow \text{C}_3\text{H}_8(\text{g})$  reaction. (a) represents each process with the enthalpy values with respect to the direction of reaction. (b) shows the enthalpy-gap and we can decide the sign according to the 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  $\Delta H^\ominus$  or  $\Delta H_{rxn}^\ominus$ . One of the primary uses of standard enthalpies of formation is in calculating standard enthalpies of reaction.

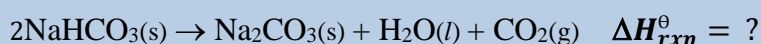
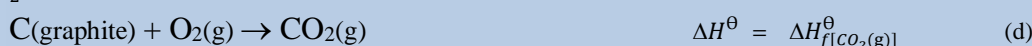
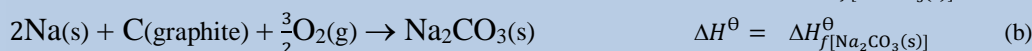
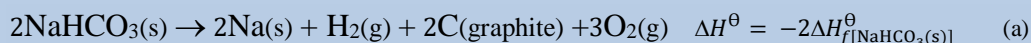
#### Example 2.1

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.



**Answer:**

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



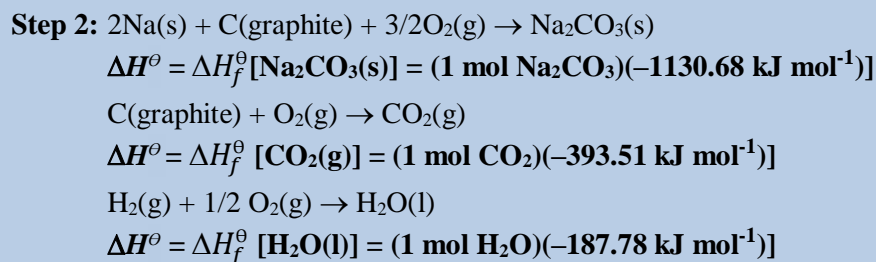
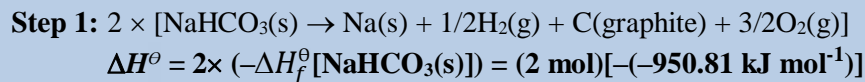


Equation (a) is the reverse of the equation representing the formation of two moles of  $\text{NaHCO}_3(\text{s})$  from its elements. This means that  $\Delta H^\theta$  for reaction (a) is the negative of twice  $\Delta H_{f[\text{NaHCO}_3(\text{s})]}^\theta$ . Equations (b), (c) and (d) represent the formation of one mole each of  $\text{Na}_2\text{CO}_3(\text{s})$ ,  $\text{H}_2\text{O}(\text{l})$  and  $\text{CO}_2(\text{g})$ . Thus, we can express the value of  $\Delta H^\theta$  for the reaction;

$$\begin{aligned}\Delta H_{rxn}^\theta &= \Delta H_{f[\text{Na}_2\text{CO}_3(\text{s})]}^\theta + \Delta H_{f[\text{H}_2\text{O}(\text{l})]}^\theta + \Delta H_{f[\text{CO}_2(\text{g})]}^\theta + (-2\Delta H_{f[\text{NaHCO}_3(\text{s})]}^\theta) \\ &= (-1130.68 \text{ kJ mol}^{-1}) + (-187.78 \text{ kJ mol}^{-1}) + (-393.51 \text{ kJ mol}^{-1}) + (1901.62 \text{ kJ mol}^{-1}) \\ &= \mathbf{189.65 \text{ kJ mol}^{-1}} \text{ (For 2 moles of NaHCO}_3(\text{s})) \\ &= \mathbf{94.825 \text{ kJ mol}^{-1}} \text{ (For 1 mole of NaHCO}_3(\text{s}))\end{aligned}$$

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  $\text{NaHCO}_3(\text{s})$  which is allowed to decompose into 2 mol  $\text{Na}(\text{s})$ , 2 mol  $\text{C}(\text{graphite})$ , and 3 mol of  $\text{O}_2(\text{g})$  as in equation (a) above. In the second step, recombine 2 mol  $\text{Na}(\text{s})$ , 2 mol  $\text{C}(\text{graphite})$ , 1 mol of  $\text{H}_2(\text{g})$  and 3 mol of  $\text{O}_2(\text{g})$  to form the products according to equations (b), (c) and (d) above.

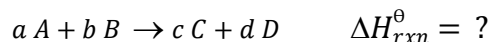


Because enthalpy is a state function and the change of any state function is independent of the path chosen, the enthalpy change for the overall reaction is the sum of the standard enthalpy changes of the individual steps as shown in the above equation according to Hess law. Therefore, the above procedure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

$$\Delta H_{rxn}^\theta = \sum v_p H_{f[\text{products}]}^\theta - \sum v_r H_{f[\text{reactants}]}^\theta$$

where  $v_p$  and  $v_r$  are the stoichiometric coefficients of products and reactants, respectively. The enthalpy change of the reaction ( $\Delta H_{rxn}^\ominus$ ) (sometimes written as  $\Delta H_r^\ominus$ ) is the sum of terms for the products minus the sum of terms for the reactants.

Simply for example, consider the hypothetical reaction



where  $a$ ,  $b$ ,  $c$  and  $d$  are stoichiometric coefficients. For this reaction  $\Delta H_{rxn}^\ominus$  is given by

$$\Delta H_{rxn}^\ominus = [c \Delta H_{f[C]}^\ominus + d \Delta H_{f[D]}^\ominus] - [a \Delta H_{f[A]}^\ominus + b \Delta H_{f[B]}^\ominus]$$

In order to use the above equation to calculate  $\Delta H_{rxn}^\ominus$ , we must know the  $\Delta H_f^\ominus$  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;

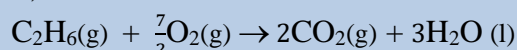
This method of measuring  $\Delta H_f^\ominus$  works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy,  $\Delta H_{rxn}^\ominus$  for the combustion of  $C_2H_6(g)$ . We must measure or know the  $\Delta H_f^\ominus$  values of  $C_2H_6(g)$ ,  $O_2(g)$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

#### Example 2.2

Calculate  $\Delta H_{rxn}^\ominus$  for the combustion of  $C_2H_6(g)$  using the direct method

#### Answer:

The reaction is;



$$\begin{aligned} \Delta H_{rxn}^\ominus &= [2\Delta H_{f[CO_2(g)]}^\ominus + 3\Delta H_{f[H_2O(l)]}^\ominus] - [\Delta H_{f[C_2H_6(g)]}^\ominus + \frac{7}{2}\Delta H_{f[O_2(g)]}^\ominus] \\ &= 2 \times -393.5 \text{ kJ mol}^{-1} + 3 \times -285.8 \text{ kJ mol}^{-1} - (-84.7 \text{ kJ mol}^{-1} + \frac{7}{2} \times 0.0 \text{ kJ mol}^{-1}) \\ &= \mathbf{-1559.7 \text{ kJ mol}^{-1}} \end{aligned}$$

### 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  $\Delta H_f^\ominus$  can be determined by an indirect approach of Hess law as described earlier.

**Example 2.3**

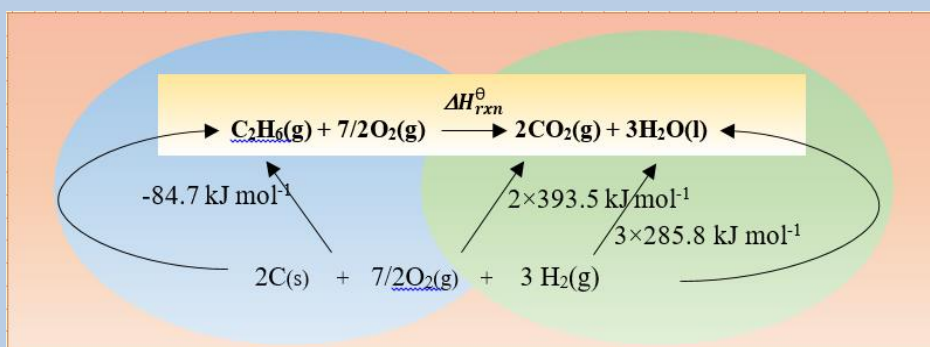
Calculate  $\Delta H_{rxn}^{\theta}$  for the combustion of  $C_2H_6(g)$  using the indirect method

**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.

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

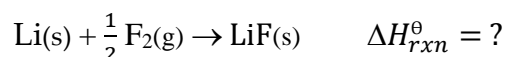
$$\Delta H^{\theta} = -1559.7 \text{ kJ mol}^{-1}$$

### 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.



The standard enthalpy change for this reaction is  $-594.1 \text{ kJ mol}^{-1}$  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



2. Atomization of  $\text{F}_2(\text{g})$  to  $\text{F}(\text{g})$



3. Ionization of gaseous Li atoms



4. Formation of  $\text{F}^-$  by capturing an electron



5. Combination between  $\text{Li}^+(\text{g})$  and  $\text{F}^-(\text{g})$



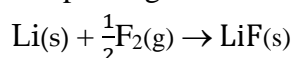
The lattice dissociation enthalpy of LiF is defined as



The value of  $\Delta H_5^{\circ}$  can be calculated by the following procedure. As the overall reaction has the standard enthalpy change,  $\Delta H_{rxn}^{\circ}$  of  $-594.1 \text{ kJ mol}^{-1}$ , we can write,

$$\Delta H_{rxn}^{\circ} = \Delta H_1^{\circ} + \Delta H_2^{\circ} + \Delta H_3^{\circ} + \Delta H_4^{\circ} + \Delta H_5^{\circ}$$

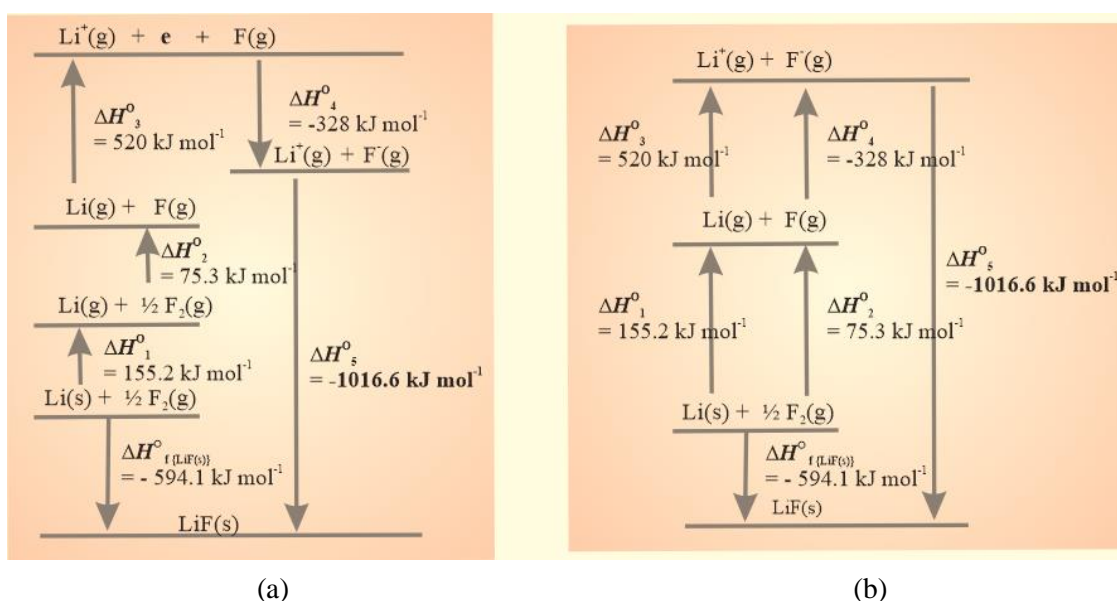
and by summing up reactions of 5 steps we get the overall reaction as ;



Therefore,  $-594.1 \text{ kJ mol}^{-1} = 155.2 \text{ kJ mol}^{-1} + 75.3 \text{ kJ mol}^{-1} + 520 \text{ kJ mol}^{-1} + (-328 \text{ kJ mol}^{-1}) + \Delta H_5^{\circ}$

$\Delta H_5^\ominus = -1016.6 \text{ kJ mol}^{-1}$  and hence the lattice dissociation enthalpy of LiF(s) is  $1016.6 \text{ kJ mol}^{-1}$

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  $\Delta H_5^\ominus$  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.



**Figure 2.7** Born-Haber cycle of the above system ( $\Delta H_5^\ominus = -1016.6 \text{ kJ mol}^{-1}$  and hence the lattice dissociation enthalpy of LiF(s) is  $1016.6 \text{ kJ mol}^{-1}$ ). 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,  $\Delta H$  or  $\Delta H^\ominus$ , by itself is not an adequate guide to spontaneity because while some spontaneous reactions are known to be exothermic ( $\Delta H^\ominus$  is -ve), many endothermic reactions ( $\Delta H^\ominus$  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 **J K<sup>-1</sup> mol<sup>-1</sup>**.

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<sub>2(g)</sub> 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  $\Delta S_{rxn}^\ominus$ . 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.

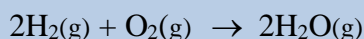
$$\Delta S_{rxn}^\ominus = \sum S^\ominus(\text{products}) - \sum S^\ominus(\text{reactants})$$

$\Delta S_{rxn}^\ominus$  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  $\Delta S_{rxn}^\ominus$  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  $\Delta S_{rxn}^{\ominus}$  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  $\Delta S_{rxn}^{\ominus}$  is negative.

**Example 2.4**

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



Predict the sign of the entropy change for this reaction and calculate  $\Delta S_{rxn}^{\ominus}$  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  $\Delta S_{rxn}^{\ominus}$  for this reaction should be negative.

Using standard molar entropy values to calculate the standard entropy;

$$\begin{aligned}\Delta S_{rxn}^{\ominus} &= S^{\ominus}(\text{products}) - S^{\ominus}(\text{reactants}) \\ &= (2 \text{ mol})(S^{\ominus}[\text{H}_2\text{O}(\text{g})]) - \{(2 \text{ mol})(S^{\ominus}[\text{H}_2(\text{g})]) + (1 \text{ mol})(S^{\ominus}[\text{O}_2(\text{g})])\} \\ &= (2)(188.8 \text{ J K}^{-1} \text{ mol}^{-1}) - \{(2)(130.7 \text{ J K}^{-1} \text{ mol}^{-1}) + (1)(205.1 \text{ J K}^{-1} \text{ mol}^{-1})\} \\ &= -88.9 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

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

For a reaction to occur spontaneously, both enthalpy,  $\Delta H_{rxn}^{\ominus}$  and entropy,  $\Delta S_{rxn}^{\ominus}$  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.

$\Delta H_{rxn}^{\ominus} -ve, \Delta S_{rxn}^{\ominus} + ve$	Spontaneous at all temperatures
$\Delta H_{rxn}^{\ominus} +ve, \Delta S_{rxn}^{\ominus} + ve$	Spontaneous at high temperatures
$\Delta H_{rxn}^{\ominus} -ve, \Delta S_{rxn}^{\ominus} - ve$	Spontaneous at low temperatures
$\Delta H_{rxn}^{\ominus} +ve, \Delta S_{rxn}^{\ominus} - ve$	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:

$$G = H - TS$$

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

$$\Delta G = \Delta H - T \Delta S$$

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

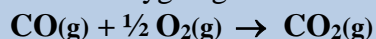
$$\Delta G_{rxn}^{\ominus} = \Delta H_{rxn}^{\ominus} - T \Delta S_{rxn}^{\ominus}$$

**Note:** Sometimes  $\Delta G_{rxn}^{\ominus}$  indicated as  $\Delta G_r^{\ominus}$ .

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

**Example 2.5**

Carbon monoxide and oxygen gas react to form carbon dioxide.



Calculate the standard free energy change for this reaction at 25°C from  $\Delta H_{rxn}^{\ominus}$  and  $\Delta S_{rxn}^{\ominus}$ .

( $\Delta H_f^{\ominus}[\text{CO}_2\text{(g)}] = -393.5 \text{ kJ mol}^{-1}$ ,  $\Delta H_f^{\ominus}[\text{CO(g)}] = -110.5 \text{ kJ mol}^{-1}$ ,  $S^{\ominus}[\text{CO}_2\text{(g)}] = 213.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^{\ominus}[\text{CO(g)}] = 197.7 \text{ J mol}^{-1} \text{ K}^{-1}$ ,  $S^{\ominus}[\text{O}_2\text{(g)}] = 205.1 \text{ J mol}^{-1} \text{ K}^{-1}$ )

**Answer:**

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

$$\begin{aligned} \Delta H_{rxn}^{\ominus} &= \Delta H_f^{\ominus}(\text{products}) - \Delta H_f^{\ominus}(\text{reactants}) \\ &= \Delta H_f^{\ominus}[\text{CO}_2\text{(g)}] - \Delta H_f^{\ominus}[\text{CO(g)}] - \frac{1}{2} \Delta H_f^{\ominus}[\text{O}_2\text{(g)}] \\ &= -393.5 \text{ kJ mol}^{-1} - (-110.5 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1} \\ &= -283.0 \text{ kJ mol}^{-1} \end{aligned}$$



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

$$\begin{aligned}\Delta S_{rxn}^{\theta} &= S^{\theta}(\text{products}) - S^{\theta}(\text{reactants}) \\ &= S^{\theta}[\text{CO}_2(\text{g})] - S^{\theta}[\text{CO}(\text{g})] - \frac{1}{2} S^{\theta}[\text{O}_2(\text{g})] \\ &= 213.7 \text{ J mol}^{-1} \text{ K}^{-1} - (197.7 \text{ J mol}^{-1} \text{ K}^{-1}) - (\frac{1}{2})(205.1 \text{ J mol}^{-1} \text{ K}^{-1}) \\ &= -86.6 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

**Note:**  $\Delta S_{rxn}^{\theta}$  is negative, as predicted by the stoichiometry: 1.5 moles of gas forms 1 mole of gas.

Calculate  $\Delta G_{rxn}^{\theta}$  using

$$\begin{aligned}\Delta G_{rxn}^{\theta} &= \Delta H_{rxn}^{\theta} - T \Delta S_{rxn}^{\theta} \\ &= -283.0 \text{ kJ mol}^{-1} - (298 \text{ K})(-86.6 \text{ J mol}^{-1} \text{ K}^{-1})(1 \text{ kJ}/1000 \text{ J}) \\ &= -257 \text{ kJ mol}^{-1}\end{aligned}$$

$\Delta G_{rxn}^{\theta}$  is negative. Therefore, the reaction occurs spontaneously.

Table 2.2 A summary

Relationships		Units
Enthalpy change of reaction	$\Delta H = \sum \nu_p H_{(\text{products})} - \nu_r \sum H_{(\text{reactants})}$	$\text{kJ mol}^{-1}$
Standard enthalpy change of a reaction	$\Delta H_{rxn}^{\theta} = \sum \nu_p H_f^{\theta}[\text{products}] - \sum \nu_r H_f^{\theta}[\text{reactants}]$ <p>(Where <math>\nu_p</math> and <math>\nu_r</math> are the stoichiometric coefficients of products and reactants)</p>	$\text{kJ mol}^{-1}$
Hess Law	<p>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.</p> <p>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, <math>\Delta H</math> (or <math>\Delta H^{\theta}</math>) if the process is carried out under standard conditions) has the same value or it is independent of the route.</p>	
Standard entropy change for a reaction	$\Delta S_{rxn}^{\theta} = \sum \nu_p S^{\theta}(\text{products}) - \sum \nu_r S^{\theta}(\text{reactants})$	$\text{J K}^{-1} \text{mol}^{-1}$
Standard change in free energy	$\Delta G_{rxn}^{\theta} = \Delta H_{rxn}^{\theta} - T \Delta S_{rxn}^{\theta}$	$\text{kJ mol}^{-1}$
Spontaneity of a reaction	Spontaneous at all temperatures	$\Delta H_{rxn}^{\theta}$ -ve $\Delta S_{rxn}^{\theta}$ +ve
	Spontaneous at high temperatures	$\Delta H_{rxn}^{\theta}$ +ve $\Delta S_{rxn}^{\theta}$ +ve
	Spontaneous at low temperatures	$\Delta H_{rxn}^{\theta}$ -ve $\Delta S_{rxn}^{\theta}$ -ve
	Not spontaneous at all temperatures (Reverse reaction is spontaneous)	$\Delta H_{rxn}^{\theta}$ +ve $\Delta S_{rxn}^{\theta}$ -ve
	Spontaneous	$\Delta G_{rxn}^{\theta} < 0$
	Not spontaneous	$\Delta G_{rxn}^{\theta} > 0$
	Equilibrium	$\Delta G_{rxn}^{\theta} = 0$

**Reference:**

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

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