1. DEFINITIONS AND BASIC CONCEPTS
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- Chemistry is the science of matter and the changes it can undergo.
- Physical chemistry is the branch of chemistry concerned with the physical principles that underlie chemistry.
- Thermodynamics is a branch of physics and it intertwine and overlap with physical chemistry.
- Thermodynamics is concerned with heat, work, temperature and energy.
- Thermodynamics development came as a result of the works of the French physicist Sadi Carnot in 1824 who was seeking improvement of steam engines which were already developed earlier in the nineteenth century.
- In 1858 the word “thermo-dynamic” developed to be “thermo-dynamics” by William Thomson in his paper titled "An Account of Carnot's Theory of the Motive Power of Heat”.
- The first definition of thermodynamics was given by the Scottish physicist Lord Kelvin in 1854. His definition was: "Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency”.

1.1 The states of matter and the physical state

- The term “state” has many different meanings in chemistry, and it is important to keep them all in mind.
- “The states of matter” is the term by which we distinguish between the well-known solid, liquid and gaseous state of matter while the physical state or just the state which is the term we use to specify the condition of a certain sample of matter.

First: The states of matter

✓ We distinguish the three states of matter by noting the behavior of a substance enclosed in a container:
  ➢ A gas is a fluid form of matter that fills the container it occupies.
  ➢ A liquid is a fluid form of matter that possesses a well-defined surface and (in a gravitational field) fills the lower part of the container it occupies.
  ➢ A solid retains its shape regardless of the shape of the container it occupies.

✓ One of the roles of physical chemistry is to establish the link between the properties of bulk matter and the behavior of the particles, i.e. atoms, ions, or molecules, of which it is composed.

✓ A physical chemist formulates a model, a simplified description, of each physical state and then shows how the state’s properties can be understood in terms of this model.

✓ The existence of different states of matter is a first illustration of this procedure, as the properties of the three states suggest that they are composed of particles with different degrees of freedom of movement.
  ➢ A gas is composed of widely separated particles in continuous rapid, disordered motion. A particle travels several (often many) diameters before colliding with another particle. For most of the time the particles are so far apart that they interact with each other only very weakly.
➢ **A liquid** consists of particles that are in contact but are able to move past each other in a restricted manner. The particles are in a continuous state of motion but travel only a fraction of a diameter before bumping into a neighbor. The overriding image is one of movement, but with molecules jostling one another.

➢ **A solid** consists of particles that are in contact and only rarely able to move past one another. Although the particles oscillate at an average location, they are essentially trapped in their initial positions, and typically lie in ordered arrays.

✓ The essential difference between the three states of matter is the freedom of the particles to move past one another:

✓ If the average separation of the particles is large, there is hardly any restriction on their motion and the substance is a **gas**.

✓ If the particles interact so strongly with one another that they are locked together rigidly, then the substance is a **solid**.

✓ If the particles have an intermediate mobility between these extremes, then the substance is a **liquid**.

✓ We can understand the melting of a solid and the vaporization of a liquid in terms of the progressive increase in the liberty of the particles as a sample is heated and the particles become able to move more freely.

**Second: The Physical state**

✓ by **physical state** (or just “state”) we shall mean a specific condition of a substance that is described in terms of:

➢ the state of the substance (gas, liquid, or solid)

➢ the volume which the substance occupies

➢ the pressure exerted on the substance

➢ the temperature of the substance

➢ the amount of the substance

✓ The precise meanings of these terms are described by the following examples:

➢ 1 kg of hydrogen gas in a container of volume 10 dm$^3$ at a specified pressure and temperature is in a particular state.

➢ The same mass of hydrogen gas in a container of volume 5 dm$^3$ at the same pressure and temperature is in a different state.

➢ Two samples of a certain substance are in the same state if they are in the same state of matter (both present as gas, liquid, or solid) and if they have the same mass, volume, pressure, and temperature.

• The above discussion is just enough to understand that term “**state**” has different meanings.

### 1.2 Mass

• The **mass**, $m$, of a sample is a measure of the quantity of matter it contains. Thus, if the mass of an object is doubled the object will contain twice as much matter as before doubling.

Be sure to distinguish mass and weight. Mass is a measure of the quantity of matter and is independent of location. Weight is the force exerted by an object and depends on the pull of gravity. An astronaut has a different weight on the Earth and the Moon, but the same mass.

• The SI unit of mass is “kilogram” and is denoted as “kg”.

4
1.3 Length
- The **length** of an object is the distance between two specific points of an object.
- Length may carry sub-names such as height, width, depth, etc.
- The SI unit of length is “meter” and is denoted as “m”.

1.4 Volume
- The **volume** of an object is the amount of three-dimensional space it occupies. Thus, we write “Volume = 100 cm$^3$” if the sample occupies 100 cm$^3$ of space.
- The SI units of volume is “cubic meter” denoted as “m$^3$”.

1.5 Time
- The **time** is the indefinite continued progress existence and events that occur in an irreversible succession from the past through the present to the future.
- The SI units of time is “second” and is denoted as “s”.

1.6 Speed
- The **speed** of an object is the magnitude of the rate of change of its position (the rate of change of its position = velocity).
- It is conceived as how much distance is travelled within a specified time.

\[
\text{speed} = \frac{\text{distance}}{\text{time}}
\]

- If an object changes its position by 400 m in 5 s its speed is:

\[
\text{speed} = \frac{400 \text{ m}}{5 \text{ s}}
\]

\[
\text{speed} = 80 \text{ m s}^{-1}
\]

- The SI units of speed is “\(\text{\frac{meter}{second}}\)” and is denoted as “\(\frac{m}{s}\)”.

1.7 Acceleration
- The **acceleration** of an object is the rate of change of speed or velocity of an object with respect to time.
- It is conceived as how much velocity is changed within a specified time.

\[
\text{acceleration} = \frac{\text{speed or velocity}}{\text{time}}
\]

- If an object is moving with a speed that equals to 80 m/s, and if its speed starts to increase by 1/s, we say that the acceleration of this object is

\[
\text{acceleration} = \frac{80 \text{ m}}{1 \text{ s}}
\]

\[
\text{acceleration} = 80 \text{ m s}^{-2}
\]

- The SI units of acceleration is “\(\text{\frac{meter}{second^2}}\)” and is denoted as “\(\frac{m}{s^2}\)”.
- As described by Newton’s Second Law, acceleration of an object cannot occur without an acting force.
1.8 Force
- One of the most basic concepts of physical science is that of force, $F$.
- The Newton’s second law of motion states that a body of mass “$m$” travels in a straight line at constant speed until a force applied on it. Then it undergoes an acceleration “$a$”. The magnitude of this force is:

$$F = m \times a$$

- The SI unit of force is $\text{kg} \times \text{m} \times \text{s}^{-2}$ and is denoted as “kg m s$^{-2}$”.
- The SI unit of force “kg m s$^{-2}$” is named after Newton, and denoted as “N”:

$$1 \text{ N} = 1 \text{ kg m s}^{-2}$$

1.9 Pressure
- Pressure, $P$, is the force applied on unit area. So, it’s the force, $F$, divided by the area $A$, on which the force is exerted:

$$P = \frac{F}{A}$$

- If the force and the area are measured using the SI units, the SI unit of pressure will be “kg m$^{-1}$ s$^{-2}$” which is called the pascal (Pa):

$$\text{Units of P} = \frac{N}{\text{m}^2} = \frac{\text{kg m}}{\text{s}^2 \text{m}^2} = \text{kg m}^{-1} \text{s}^{-2} = \text{Pa}$$

- The following table lists the other units commonly used for pressure. One of the most important in modern physical chemistry is the bar, where 1 bar = $10^5$ Pa exactly; the bar is not an SI unit, but it is an accepted and widely used abbreviation for $10^5$ Pa.

<table>
<thead>
<tr>
<th>Unit</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>pascal, Pa</td>
<td>$1 \text{ Pa} = 1 \text{ N m}^{-2}$</td>
</tr>
<tr>
<td>bar</td>
<td>$1 \text{ bar} = 10^5 \text{ Pa}$</td>
</tr>
<tr>
<td>atmosphere, atm</td>
<td>$1 \text{ atm} = 101.325 \text{ kPa} = 1.01325 \text{ bar}$</td>
</tr>
<tr>
<td>torr, Torr†</td>
<td>$760 \text{ Torr} = 1 \text{ atm}$</td>
</tr>
<tr>
<td></td>
<td>$1 \text{ Torr} = 133.32 \text{ Pa}$</td>
</tr>
</tbody>
</table>

- The atmospheric pressure that we normally experience is close to 1 bar; meteorological information on weather maps is commonly reported in millibars ($1 \text{ mbar} = 10^{-3} \text{ bar} = 10^2 \text{ Pa}$).
- **Standard pressure**, which is used to report the values of pressure-sensitive properties systematically in a standard way (as we explain in later chapters), is denoted “P” and defined as exactly 1 bar.
Example 1.1
A scientist was exploring the effect of atmospheric pressure on the rate of growth of a
lichen and measured a pressure $P$ of 1.115 bar. What is the pressure in atmospheres?

Solution

\[
1.01325 \text{ bar} = 1 \text{ atm} \\
1.115 \text{ bar} = 1.115 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ Par}} = 1.100 \text{ atm}
\]

Practice exercise
The air pressure of many cars’ tires is maintained at 35 Psi. How much is it in torr and
in Pa? (1 Psi = 0.068 atm).
(Answer: 1808.8 torr, 241153.5 Pa)

Example 1.2
The pressure in the eye of a hurricane was recorded as 723 Torr. What is the pressure
in kilopascals?

Solution

\[
133.32 \text{ Pa} = 1 \text{ torr} \\
723 \text{ Torr} = 723 \text{ Torr} \times \frac{133.32 \text{ Pa}}{1 \text{ torr}} = 96.39 \text{ kPa}
\]

Practice exercise
A gas pressure is 35.47 kPa, what is pressure in mmHg?
(Answer: $7.2 \times 10^5$ mmHg)

- When you stand on a piece of tile on the floor, you generate a pressure on the tile
  as a result of the gravitational force acting on your mass and pulling you towards
  the center of the Earth. However, the pressure is low because the downward force
  of your body is spread over the area equal to that of the soles of your shoes.
- Generally, as the area you stand on and is in contact with the surface of Earth is
  smaller as the pressure you exert is much greater.
- The figure below two blocks of matter having the same mass, exerting the same
  force on the surface on which they are standing, but the block on the right exerts a
  stronger pressure because it exerts the same force over a smaller area than the
  block on the left.

- If you accidentally stand on a nail sticking out of a wood it will penetrates through
  the soles of your feet hearting you severely and most likely you will be rushed to
  hospital. The area of the end of the nail is extremely small and the force of your
  body is very large, this makes the pressure you applied on the nail so huge and
  this is why it hurts you a lot.
• On the contrary a person who makes exiting shows by standing on nails will not be hurt because the force of his/her body is distributed on a very large area making the pressure they exert small enough to keep them safe.

• Pressure can arise in ways other than from the gravitational pull of the Earth on an object. Example: the impact of gas molecules on a surface gives rise to a force and hence to a pressure. If an object is immersed in the gas, it experiences a pressure over its entire surface because molecules collide with it from all directions. In this way, the atmosphere exerts a pressure on all the objects in it. We are incessantly battered by molecules of gas in the atmosphere, and experience this battering as the atmospheric pressure.

• The pressure is greatest at sea level because the density of air, and hence the number of colliding molecules, is greatest there.

• The atmospheric pressure is very considerable: it is the same as would be exerted by loading 1 kg of lead (or any other material) on to a surface of area 1 cm².

• We go through our lives under this heavy burden pressing on every square centimeter of our bodies.

• Some deep-sea creatures are built to withstand even greater pressures: at 1000 m below sea level the pressure is 100 times greater than at the surface. Creatures and submarines that operate at these depths must withstand the equivalent of 100 kg of lead loaded on to each square centimeter of their surfaces.

• The pressure of the air in our lungs helps us withstand the relatively low but still substantial pressures that we experience close to sea level.

• When a gas is confined to a cylinder fitted with a movable piston, the position of the piston adjusts until the pressure of the gas inside the cylinder is equal to that exerted by the atmosphere. When the pressures on either side of the piston are the same, we say that the two regions on either side are in mechanical equilibrium. It shows a system is in mechanical equilibrium with its surroundings. Because the
wall separating them is a movable wall and the external pressure is equal to the pressure of the gas in the system.

- The pressure of the confined gas arises from the impact of the particles: they batter the inside surface of the piston and counter the battering of the molecules in the atmosphere that is pressing on the outside surface of the piston.
- Provided the piston is weightless (that is, provided we can neglect any gravitational pull on it), the gas is in mechanical equilibrium with the atmosphere whatever the orientation of the piston and cylinder, because the external battering is the same in all directions.
- The pressure of the atmosphere at sea level is about $10^5$ Pa (100 kPa). This fact lets us imagine the magnitude of 1 Pa, for we have just seen that 1 kg of lead resting on 1 cm$^2$ on the surface of the Earth exerts about the same pressure as the atmosphere; so $\frac{1}{10^5}$ of that mass, or 10 mg (1 mg = $10^{-3}$ g), will exert about 1 Pa, we see that the pascal is rather a small unit of pressure.

1.10 Work
- When an object is moved through a distance “d” against an opposing force “F”, we say that work “w” is done. The magnitude of the work is the product of the distance moved and the magnitude of the opposing force:

$$\text{work} = \text{force} \times \text{distance}$$

$$w = F \times d$$

This equation applies when the force along the distance its acting on is constant if the force varies along the path, then we use it for each segment of the path and then add together the resulting values.
- The SI unit of work “kg m$^2$ s$^{-2}$” is named after Joule who helped to establish the concept of energy, and denoted as “J”:

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2}$$
• To raise a body of mass 1.0 kg on the surface of the Earth through a vertical distance (against the direction of the force) of 1.0 m requires us to do the following amount of work:

\[
\text{Work} = (9.8 \text{ kg m s}^{-2}) \times (1.0 \text{ m}) = 9.8 \text{ kg m}^2 \text{s}^{-2} \\
\text{Work} = (9.8 \text{ N}) \times (1.0 \text{ m}) = 9.8 \text{ N m}
\]

• Because 1 kg m \(^2\) s\(^{-2}\) (or 1 N m) is called 1 joule (1 J), 9.8 J is needed to raise a mass of 1.0 kg through 1.0 m on the surface of the Earth.

• **Types of work**

Because there are different types of work, there are different ways of calculating it. For example:

- **Electric work, \(w_{\text{electric}}\):**
  
  It is calculated by:

  \[
  w_{\text{electric}} = -nFE
  \]

  where \(n\) is the number of moles of electrons passed, \(F\) is Faraday's constant, and \(E\) is the electric potential.

  It is clear that using the SI units for \(n\), \(F\), and \(E\) produces \(w\) in J unit.

- **PV work, \(w_{\text{pv}}\):**
  
  PV work is the work done on or by the gas as a result of a certain change in its volume (\(V\)) against a certain pressure (\(P\)).

**Why is PV work important?**

In thermodynamics, the expansion and the compression of gases are the processes that mostly attracted the attention of scientists due to their magnificent role in manufacturing steam, and in general heat engines. Therefore, work accompanying gases' expansions and compressions, is the most important type of work in thermodynamics.

The figure below shows a gas in a cylinder with a piston of area "A". The piston is pressed down from its initial height "\(h_i\)" to its final height "\(h_f\)" causing a decrease in the volume equals to \(\Delta V\).

![Diagram of a gas in a cylinder with a piston](image)

This compression is due to a work done on the system. This type of work is calculated by the following well-known equation:
\[
P = \frac{F}{A}
\]
\[
F = P \times A
\]
\[
w_{PV} = F \times \Delta h
\]
\[
w_{PV} = P \times A \times \Delta h
\]
\[
w_{PV} = P \times \Delta V
\]

Then, to convey the convention that gives the work done on the system a positive sign and the work done by the system a negative sign, we introduce the negative sign (\(-\)). This makes the work equation written as:

\[
w_{PV} = -P_{ext} \times \Delta V
\]

It is clear that using the \(\text{Pa}\) unit for \(P\) and \(\text{m}^3\) unit for \(V\) produces work in \(\text{J}\) unit.

**Example 1.3**
The pressure above the piston of a cylinder piston is 15.0 atm. How much work has been done if the piston is pushed to change the volume from 0.15 L to 0.48 L? Express your answer in joules.

**Solution**

\[
w = -P \Delta V
\]

\[
w = -15 \text{ atm} \times \frac{101325 \text{ Pa}}{1 \text{ atm}} \times (0.48 \text{ L} - 0.15 \text{ L}) \times \frac{10^{-3} \text{ m}^3}{1 \text{ L}} = -501.4 \text{ J}
\]

**Practice exercise**

A 0.54 mole of a gas at 30 \(^\circ\)C is compressed inside a cylinder to occupy 8.0 L. The external pressure is 1.3 atm. How much work would the gas do to expand until its final pressure equalizes the external pressure?

**1.11 Energy**

- Energy “E” is a property that will occur in just about every page in this text.
- Everyone uses the term “energy” in everyday language, but in science it has a precise meaning, a meaning that we shall draw on throughout the text.
- Energy is a name of one of the most important property of matter in our life.
- Energy does not appear to us except in a certain shape.
- Usually, we do not use the word "SHAPE", we rather use the word "FORM".
- Forms that energy appears in are different. Examples of its forms are:
  1) The kinetic energy
  2) The potential energy
  3) The nuclear energy
  4) The solar energy
  5) The internal energy
  6) The thermal energy
  And so many other.
- Energy is the capacity to do work:
  ✓ A fully wound spring can do more work than a half-wound spring (that is, it can raise a weight through a greater height, or move a greater weight through a given height.
✓ A hot object, when attached to some kind of heat engine (a device for converting heat into work) can do more work than the same object when it is cool, and therefore a hot object has a higher energy than the same cool object.

- Although the "Calorie", abbreviated "cal", is a very common energy unit, and probably is the most common unit we use in our daily life, it is not the SI unit of energy.
- The SI unit of energy is the same as that of work “kg m² s⁻²” or “J”:
  \[ 1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} \]

A Joule is quite a small unit, and in chemistry we often deal with energies of the order of kilojoules (1 kJ = 10³ J).
- Each calorie equals 4.184 Joule:
  \[ 1 \text{ cal} = 4.184 \text{ J} \]

---

**Example 1.4**

If your body mass is 67 kg and you walk 5 km in 1 hr then you will burn 245 cal. How much energy you burn in the unit of Joules.

**Solution**

\[ 245 \text{ cal} = 245 \text{ cal} \times \frac{4.184 \text{ J}}{1 \text{ cal}} = 1025.08 \text{ J} \]

**Practice exercise**

If your body mass is 78 kg and you walk 1.5 km you will burn 490 J. How much energy you burn in the unit of calorie.

---

- There are two contributions to the total energy of a particle.
  **FIRST: THE KINETIC ENERGY**
  ✓ The kinetic energy, \( E_k \), is the energy of a body due to its motion. For a body of mass “m” moving at a speed “v”,
  \[ E_k = \frac{1}{2}mv \]
  ✓ If two objects of different masses are moving at the same speed then the heavier object will have a higher kinetic energy.
  ✓ Doubling the speed of any object increases its kinetic energy by a factor of 4.
  ✓ A ball of mass 1 kg travelling at 1 m s⁻¹ has a kinetic energy of 0.5 J.

**SECOND: THE POTENTIAL ENERGY**

✓ The potential energy, \( E_p \), of a body is the energy it possesses due to its position.
✓ The precise dependence on position depends on the type of force acting on the body.
✓ For a body of mass \( m \) on the surface of the Earth, the potential energy depends on its height, \( h \), above the surface as
  \[ E_p = mgh \]

where \( g \) is a constant known as the **acceleration of free fall**, which is close to 9.81 m s⁻² at sea level.
✓ Thus, doubling the height, doubles the potential energy.
✓ This expression “\( E_p = mgh \)” is based on the convention of taking the potential energy to be zero at sea level.
✓ A ball of mass 1.0 kg at 1.0 m above the surface of the Earth has a potential energy of 9.8 J.
✓ Another type of potential energy is the **Coulombic potential energy** of one electric charge \( Q_1 \) (in coulombs, C) at a distance \( r \) (in meters, m) from another electric charge \( Q_2 \):

\[
E_p = \frac{Q_1 Q_2}{4\pi \varepsilon_0 r}
\]

\( \varepsilon_0 = \text{vacuum permittivity constant} = 8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1} \).

- The **total energy**, \( E \), of a body is the sum of its kinetic and potential energies:

\[
E = E_k + E_p
\]

- Provided no external forces are acting on the body, the total energy of the body is constant. This remark is elevated to a central statement of classical physics known as the **law of the conservation of energy**.
- Potential and kinetic energy may be freely interchanged: for instance, (a falling ball loses potential energy but gains kinetic energy as it accelerates), but their total remains constant provided the body is isolated from external influences.

**Thermal energy**
- "Thermal energy" is usually defined as the kind of energy contained by the system as a result of its molecular kinetic energy or as a result of the value of the system temperature. This as to say: "if we supply the system with thermal energy its temperature increases".
- However, it is well known that the **thermal energy contained in the system** can be increased or decreased without changing its temperature.
- This simply means that the previous definition of "thermal energy" is loose and is not a well definition of "thermal energy".
- The reason behind that is that we will never be able to specify which part of the system energy is the thermal energy.

**Heat**
- Heat is not a type of energy that is contained or possessed by the system.
- Yes, we usually think and say that the system absorbs or releases heat; we also say that the degree of hotness (temperature) of the system increases or decrease. However, we never think and never say that the "heat" of the system increases or decrease.
- We can realize the meaning of the degree of hotness (temperature), when it is high the system is hot and vice versa but we don’t say that the system has a high or low heat. It seems that when it comes to heat we find ourselves as lost in a dessert,
- About temperature, we said above: "If two systems having two different degrees of hotness become in contact with each other, energy will flow from the one with higher degree of hotness to the other with the lower degree of hotness". This flow of energy is **HEAT**.
- Heat is the energy in flow from a system to another system due to a difference in the temperatures of the two systems.
✓ Once heat flow ended the energy entered the system cannot be called heat because it will be stored as a kinetic energy, potential energy or any other kind of energy possessed by the system.
✓ Heat is not a property of the system. Heat is the energy that is in a state of transition from a system to another due to difference in their temperatures.

1.12 Temperature
- *Temperature* is simply a measure of the degree of hotness or coldness of the body.
- *Temperature* is an arbitrary measure of the kind of energy possessed by matter and is responsible for its hotness or coldness.
- *Temperature*, in science, is the property of an object that determines in which direction energy will flow when it is in contact with another object.
- If two systems having two different degrees of hotness become in contact with each other, energy will flow from the one with higher degree of hotness to the other with the lower degree of hotness.
- The following figure shows that energy flows from the object of higher temperature to the object of lower temperature. It also shows that when the two bodies have the same temperature, there is no net flow of energy between them and we say that the two bodies are in thermal equilibrium.

![Temperature Diagram]

- It appears from the figure that temperatures of objects act as a signpost showing the direction in which energy, as heat, will flow through a thermally conducting wall:
  (a) heat always flows from high temperature to low temperature.
  (b) When the two objects have the same temperature, although there is still energy transfer in both directions, there is no net flow of energy.
- Although temperature and heat have a close relation they are entirely two different concepts. A lot of us confuse temperature with heat. Heat is a mode of transfer of energy; temperature is a property that determines the direction of flow of energy as heat.
- Measuring temperature or the degree of hotness has a history:
  ✓ In the remote past as in our present daily life, when human touches a glass of water he can determine the degree of its hotness and expresses his determination by saying: it is *extremely hot, very hot, hot, fairly hot, fairly cold, cold, very cold, extremely cold* etc. This means that our hands are
thermometers. But they are not accurate thermometer. This technique which is merely the human skin does not give the temperature as numerical values.

✓ Hands stayed the predominant as the only available thermometer devise humans have. No significant change or development happened except almost 300 years ago when, in 1724, a Dutch-German-Polish scientist "Fahrenheit" proposed a scale which is still being used in a few countries like USA and UK.
✓ In 1742, the Swedish scientist "Celsius" proposed another scale which is the on used now in most of the countries over the globe.

- Although the unit for temperature that is used in all countries is either the Celsius unit or the Fahrenheit unit, the SI unit for temperature is Kelvin (K).

- Temperature in science is measured on either the Celsius scale or the Kelvin scale.
  ✓ **On the Celsius scale**, the temperature is expressed in degrees Celsius “°C”, and the freezing point of water at 1 atm corresponds to 0°C and the boiling point of water at 1 atm corresponds to 100°C. This scale is in widespread everyday use. Temperatures on the Celsius scale are denoted by the letter “t”.
  ✓ **On the Kelvin scale**, the temperature is expressed in Kelvin “K”, (note that the degree sign is not used for this unit), and the freezing point of water at 1 atm corresponds to 273.15 K and the boiling point of water at 1 atm corresponds to 373.15 K. This scale is not in widespread everyday use. Temperatures on the Kelvin scale are denoted by the letter “T”.
  ✓ The Celsius and Kelvin scales are related as follows:

\[
T \text{ (in kelvin)} = t \text{ (in degrees Celsius)} + 273.15
\]

<table>
<thead>
<tr>
<th>Example 1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>A gas having a temperature of 21 °C, what is its temperature in K unit?</td>
</tr>
<tr>
<td><strong>Solution</strong></td>
</tr>
<tr>
<td>Temperature in K = ( (\text{Temperature in °C} + 273.15 \ °C) \times \frac{1}{1 \ °C} )</td>
</tr>
<tr>
<td>Temperature in K = ( (21 \ °C + 273.15 \ °C) \times \frac{1}{1 \ °C} ) = 294 K</td>
</tr>
<tr>
<td><strong>Practice exercise</strong></td>
</tr>
<tr>
<td>A gas having a temperature of 315 K, what is its temperature in °C unit?</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Example 1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Express the body temperature, 37°C, in kelvins.</td>
</tr>
<tr>
<td><strong>Solution</strong></td>
</tr>
<tr>
<td>( T \text{ (in kelvin)} = t \text{ (in degrees Celsius)} + 273.15 )</td>
</tr>
<tr>
<td>( T \text{ (in kelvin)} = 37 \ °C + 273.15 = 310.15 \ K )</td>
</tr>
<tr>
<td><strong>Practice exercise</strong></td>
</tr>
<tr>
<td>A gas having a temperature of 50 °C, what is its temperature in K unit?</td>
</tr>
</tbody>
</table>

- **Temperature and kinetic energy**
  ✓ Increase or decrease in the temperature of the system depends solely on the kinetic energy of the particles of the system.
  ✓ If kinetic energy increases temperature increases and vice versa.
  ✓ No matter how much energy the system gains or losses, its temperature remains unchanged as long as its particles’ kinetic energy is unchanged.
  ✓ If two systems having two different degrees of hotness become in contact with each other, energy will flow from the one with higher degree of hotness to the other with the lower degree of hotness.
If the heat flowed into the system did not increase the kinetic energy of its particles then its temperature will remain as before this flow.

**Temperature of matter cannot be changed unless its kinetic energy is changed**

- This very important fact is the most decisive findings of the molecular kinetic theory which will be discussed immediately.

### 1.13 The kinetic molecular model of gases

The present formulation of this theory is, in fact, a result of the contributions of many scientists who will be listed shortly. However, the basis of this theory started in 1738 by the Swiss mathematician and physicist Daniel Bernoulli who asserted that gases consists of great numbers of molecules moving in all directions and their pressures is a result of their collisions and the heat we feel is due to the kinetic energy of their motion. Below is a list of the names of the scientists whose contributions were enormously responsible for the current model of this theory:

<table>
<thead>
<tr>
<th>Name</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mikhail Lomonosov</td>
<td>1747</td>
</tr>
<tr>
<td>George-Louis Le Sage</td>
<td>1780</td>
</tr>
<tr>
<td>John Herapath</td>
<td>1821</td>
</tr>
<tr>
<td>John James Waterson</td>
<td>1845</td>
</tr>
<tr>
<td>James Prescott Joule</td>
<td>1848</td>
</tr>
<tr>
<td>August Kroning</td>
<td>1856</td>
</tr>
<tr>
<td>Rudolf Clausius</td>
<td>1857</td>
</tr>
<tr>
<td>James Clerk Maxwell</td>
<td>1859</td>
</tr>
<tr>
<td>Ludwig Boltzmann</td>
<td>1871</td>
</tr>
<tr>
<td>Albert Einstien</td>
<td>1905</td>
</tr>
<tr>
<td>Marian Smoluchowski</td>
<td>1906</td>
</tr>
</tbody>
</table>

- The **kinetic model of gases** consists of the following five assumptions:
  1) A gas consists of molecules in ceaseless random motion.
  2) The gas molecules collisions with each other and with the walls of its container are elastic, i.e. do not affect their speeds or kinetic energies.
  3) The size of the molecules is negligible in the sense that their diameters are much smaller than the average distance travelled between collisions and therefore they occupy a negligible fraction of the volume of their container.
  4) The molecules do not interact, except during collisions.
  5) The kinetic energy of the molecules is proportional to their temperature.

- In the figure below, the point-like shows that molecules move randomly with a wide range of speeds and in random directions, both of which change when they collide with the walls or with other molecules.
• The third assumption that the volume of each molecule is zero (negligible) assumes that the unoccupied volume of the container in the presence or absence of the molecules is the same.

• The fourth assumption that the molecules do not interact unless they are in contact implies that the potential energy of the molecules (their energy due to their position) is independent of their separation and may be set equal to zero. Therefore, the total energy of a sample of gas is the sum of the kinetic energies (the energy due to motion) of all the molecules. This means that the faster the molecules travel (and hence the greater their kinetic energy), the greater the total energy of the gas.

• The speed of gaseous molecules: On the basis of this model, the speeds of molecules are not the same at any certain instant, also the speed of any molecule is not constant but undergoes changes in a continuous manner due to the continuous. Therefore, the speed of any molecule is expressed as the square root of the mean value of the squares of the speeds, \( c \), of the molecules. This expression of the speed is called “the root-mean-square speed” and abbreviated as “rms speed” of the molecules. The rms speed is denoted by “\( c \)” and is given by the following equation:

\[
c = \sqrt{\frac{3RT}{M}}
\]

Where \( M \) is the molar mass.

• The important conclusions to draw from this equation are:
  1) rms speed “\( c \)” is directly proportional to the square root of the absolute temperature.
  2) rms speed “\( c \)” is inversely proportional to the square root of the molar mass.
  3) rms speed “\( c \)” is the same for gases with equal molar masses as long as \( T \) is the same.

Example 1.7
Calculate the rms speed “\( c \)” of uniatomic oxygen (O) and diatomic oxygen (O\(_2\)) and triatomic oxygen (O\(_3\)) gases at room temperature.

Solution

\[
T \text{ (in kelvin)} = t \text{ (in degrees Celsius)} + 273.15
\]

\[
T = 25 \, ^\circ \text{C} + 273.15 = 298.15 \, \text{K}
\]

\[
M_{\text{O}} = 16 \text{ g/mol} = 0.016 \text{ kg/mol}
\]

\[
M_{\text{O}_2} = 32 \text{ g/mol} = 0.032 \text{ kg/mol}
\]

\[
M_{\text{O}_3} = 48 \text{ g/mol} = 0.048 \text{ kg/mol}
\]

\[
c = \sqrt{\frac{3RT}{M}} = c_{\text{O}} = \sqrt{\frac{3 \times 8.314 \frac{\text{J mol}^{-1} \text{K}^{-1}}{\text{mol}} \times 298.15 \, \text{K}}{0.016 \text{ kg mol}^{-1}}} = 681.75 \text{ m/s}
\]

\[
c = \sqrt{\frac{3RT}{M}} = c_{\text{O}_2} = \sqrt{\frac{3 \times 8.314 \frac{\text{J mol}^{-1} \text{K}^{-1}}{\text{mol}} \times 298.15 \, \text{K}}{0.032 \text{ kg mol}^{-1}}} = 482.07 \text{ m/s}
\]

\[
c = \sqrt{\frac{3RT}{M}} = c_{\text{O}_3} = \sqrt{\frac{3 \times 8.314 \frac{\text{J mol}^{-1} \text{K}^{-1}}{\text{mol}} \times 298.15 \, \text{K}}{0.048 \text{ kg mol}^{-1}}} = 393.61 \text{ m/s}
\]
Practice exercise
Calculate the rms speed “c” of diatomic oxygen gas (O\textsubscript{2}) and ammonia gas (NH\textsubscript{3}) at 50 °C and at 100 °C.
(Answer: c\textsubscript{O\textsubscript{2},50°C} = 501.87 m/s, c\textsubscript{O\textsubscript{2},100°C} = 539.30 m/s, c\textsubscript{NH\textsubscript{3},50°C} = 688.56 m/s, c\textsubscript{NH\textsubscript{3},100°C} = 739.92 m/s)

- **The kinetic energy of gaseous molecules:**
  ✓ The kinetic energy of any object is defined by the following equation:

  \[
  \text{Kinetic energy} = \frac{\text{mass} \times \text{speed}^2}{2}
  \]

  ✓ The kinetic energy of a certain mass, m, of a gas is:

  \[
  \text{Kinetic energy} = \frac{m \times c^2}{2}
  \]

  ✓ From the equation “\(c = \sqrt{\frac{3RT}{M}}\)”, we conclude that “\(c^2 = \frac{3RT}{M}\)”, therefore,

  \[
  \text{Kinetic energy} = \frac{m \times c^2}{2} = \frac{m \times \frac{3RT}{M}}{2} = \frac{m \times \frac{3RT}{M}}{2} = \frac{n \times 3RT}{2}
  \]

  \[
  \text{Kinetic energy} = \frac{3}{2} \times n \times R \times T
  \]

  \[
  \text{Kinetic energy} = \frac{3}{2} \times n \text{ (mol)} \times R \left(\frac{J}{\text{mol}K}\right) \times T \text{ (K)}
  \]

  \[
  \text{Kinetic energy} = \left(\frac{3}{2} \times nRT\right)J
  \]

  ✓ Because \(n = \frac{N}{N_A}\) where N is the number of molecules and \(N_A\) is Avogadro’s number, the equation “\(\text{Kinetic energy} = \frac{3}{2} \times nRT\)” can rewritten as:

  \[
  \text{Kinetic energy} = \frac{3}{2} \times \frac{N}{N_A} \times RT = \frac{3}{2} \times \frac{R}{N_A} \times N \times T = \frac{3}{2} \times k \times N \times T
  \]

  k is a constant called Boltzmann’ constant:

  \[
  k = \frac{R}{N_A} = \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1}}{6.022 \times 10^{23} \text{ molecule}^{-1}} = 1.3806 \times 10^{-23} \text{ J mol}^{-1} \text{ K}^{-1}
  \]

  Therefore,

  \[
  \text{Kinetic energy} = \frac{3}{2} \times k \left(\frac{J}{\text{molecule} K}\right) \times N \text{ (molecule)} \times T \text{ (K)}
  \]

  \[
  \text{Kinetic energy} = \left(\frac{3}{2} \times n \times R \times T\right)J = \left(\frac{3}{2} \times k \times N \times T\right)J
  \]

✓ The important conclusions to draw from this equation are:
1) The kinetic energy of any gas is directly proportional to its absolute temperature.

2) The kinetic energy of any gas is directly proportional to its number of moles or molecules.

3) The kinetic energy of the same number of moles or molecules of different gases is same as long as T is the same. This simply means that kinetic energy does not depend on the type of the gas. On the other hand, we should remember that the speed of the gaseous molecules does depend on the type of the gas.

4) The kinetic energy of \( n \) moles of a gas, \( ke_n \), is given by the equation

\[
ke_n = (\frac{3}{2} \times n \times R \times T) \text{ J}
\]

5) The kinetic energy of only one moles of a gas, \( KE_{\text{one mole}} \), is given by the equation

\[
KE_{\text{one mole}} = (\frac{3}{2} \times R \times T) \text{ J/mol}
\]

6) The kinetic energy of \( N \) molecules of a gas, \( ke_N \), is given by the equation

\[
ke_N = (\frac{3}{2} \times N \times k \times T) \text{ J}
\]

7) The kinetic energy of only one molecule of a gas, \( KE_{\text{one molecule}} \), is called the molar kinetic energy and is given by the equation

\[
KE_{\text{one molecule}} = (\frac{3}{2} \times k \times T) \text{ J/molecule}
\]

8) The values of \( ke_n \) and \( ke_N \) are equal:

\[
(\frac{3}{2} \times n \times R \times T) \text{ J} = (\frac{3}{2} \times N \times k \times T) \text{ J}
\]

### 1.14 The system, the surroundings, the boundaries and the universe

✓ The figure below shows the system, its surroundings and the boundaries that keep them separated from each other. The universe is all of them together.

- **The system** is a precisely defined macroscopic region of the universe. It is often described as a physical system that is studied using the principles of thermodynamics.
• **The surroundings** are all space outside the thermodynamic system. It is also known as the environment or the reservoir.

• **The boundaries** of the system act to separate the system from its surroundings. Boundaries may be notional or real, but which by convention delimit a finite volume. Boundaries are also called walls.
  ✓ Boundaries may be made of wood, glass, steel, or any other material.
  ✓ Any exchange of energy, such as heat or work, between the system and its surroundings occurs through the boundaries.
  ✓ Depending on the nature of the boundaries, matter and energy could or could not be exchanged.
  ✓ There are two distinct types of boundaries:
    - **The first** is called the *diathermic boundaries or walls*. These of boundaries or walls allows heat to flow through. The process happens inside a container with this kind of walls is called "diathermic (diathermal) process".
    - **The second** is called the *adiabatic boundaries or walls*. These of boundaries or walls does not allow heat to flow through. The process which happens inside a container with this kind of walls is called "adiabatic process".

• **The universe** is commonly defined as the totality of everything that exists including planets, stars, galaxies, the content of intergalactic space, and all matter and energy. This definition is also used to define other terms like the "cosmos", the "world", and the "nature". In thermodynamics, the system, its surroundings and boundaries comprise the universe. If the system is a place or a container that is isolated from anything else outside it, then the container and the system inside it is by themselves a universe.

• **Types of systems**
  Let’s look and carefully inspect the following figure.

The figure shows that there are three types of systems:

1) **The open system**
   An open system is a system which continuously interacts with its surroundings. The interaction can take the form of energy or matter transfers into or out of the system boundaries. An example of an open system is a flask that is not stoppered and to which various substances can be added. A biological cell is an open system because nutrients and waste can pass through the cell wall. We are open systems; don’t we ingest, respire, perspire, and excrete?

2) **The closed system**
   A closed system is a system in which matter cannot be transferred in or out of its boundaries. The system will always contain the same amount of matter, but heat and work can be exchanged across the boundaries of the system. An example of a closed system is a stoppered bottle through which energy can be
exchanged between the surroundings and the contents of the bottle but matter cannot.

3) **The isolated system**

An isolated system is a system which does not interact with its surroundings in any way. Matter and energy remains constant within the system, and no energy or matter transfer takes place across the boundaries. An example of an isolated system is a sealed flask that is thermally, mechanically, and electrically insulated from its surroundings.

### 1.15 Specific heat capacity, heat capacity and quantity of heat

- **Specific heat capacity (C<sub>s</sub>)**

  Specific heat, also called specific heat capacity, C<sub>s</sub>, is the amount of energy brought to a substance to increase the temperature of only 1 g of the substance by only 1 °C (or 1 Kelvin). Here ∆T = 1 °C.

  ✓ It is very important to remember here that:

  First: the mass is specified as exactly one gram no more no less.

  Second: the change in temperature is limited to only 1 °C no more no less.

  ✓ Values of specific heat capacity of some substances are listed below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>C&lt;sub&gt;s&lt;/sub&gt; / J g&lt;sup&gt;-1&lt;/sup&gt; °C&lt;sup&gt;-1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au(s)</td>
<td>0.129</td>
</tr>
<tr>
<td>Hg(s)</td>
<td>0.139</td>
</tr>
<tr>
<td>Cu(s)</td>
<td>0.385</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.444</td>
</tr>
<tr>
<td>C(diamond)</td>
<td>0.502</td>
</tr>
<tr>
<td>C(graphite)</td>
<td>0.720</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0.900</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;OH(L)</td>
<td>2.460</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O(L)</td>
<td>4.184</td>
</tr>
</tbody>
</table>

- **Heat capacity (C)**

  Heat capacity, C, is the amount of energy brought to a substance to increase the temperature of any mass of the substance (m gram) by only 1 °C (or 1 Kelvin). Here ∆T = 1 °C.

  It is very important to remember here that:

  ✓ First: the mass is not specified as only one gram but any mass other than that.

  ✓ Second: the change in temperature is again limited to only 1 °C no more no less.

  \[
  C = m \times C_s
  \]

- **Quantity of heat (q)**

  Quantity of heat, q, is the amount of energy brought to a substance to increase the temperature of any mass of the substance (m g) by any number of number of Celsius degrees (or Kelvin). Here ∆T = any value other than 1 °C.

  \[
  q = C \times \Delta T = m \times C_s \times \Delta T
  \]

  It is very important to remember here that:
✓ **First** the mass is not specified as only one gram but any mass other than that. 
✓ **Second**: the change in temperature is 1 °C but any degrees other than 1 °C.

**Example 1.8**
Calculate the amount of heat needed to increase the temperature of 250 g of water from 20 °C to 56 °C. \( C_{s,\text{water}} = 4.184 \text{ J g}^{-1} \text{ °C}^{-1} \)

**Solution**
\[
q = m \times C_s \times (T_2 - T_1) \\
q = 250 \text{ g} \times 4.184 \frac{\text{J}}{\text{g} \cdot \text{°C}} \times (56 - 20) \text{ °C} = 37656 \text{ J}
\]

**Practice exercise**
If 1.5 kg of cupper at 75 °C released 28875 J of heat, calculate its final temperature. \( C_{s,\text{copper}} = 0.385 \text{ J g}^{-1} \text{ °C}^{-1} \).
(Answer: 25 °C)

**Example 1.9**
The initial temperature of 150 g of ethanol was 22°C. What will be its final temperature if it absorbs 3257.4 J of heat? \( C_{s,\text{ethanol}} = 2.44 \text{ J g}^{-1} \text{ °C}^{-1} \).

**Solution**
\[
q = m \times c \times (T_2 - T_1) \\
3257.4 \text{ J} = 150 \text{ g} \times 2.44 \frac{\text{J}}{\text{g} \cdot \text{°C}} \times (T_2 - 22) \\
T_2 = 30.9 \text{ °C}
\]

**Practice exercise**
The temperature of a 1.0 \times 10^4 \text{ g} of a substance increased by 60.0 °C after it absorbed 2.5 \times 10^3 \text{ joules of heat. Calculate the specific heat capacity (}C_s\text{) of this substance.**}
(Answer: \( C_s = 4.17 \times 10^{-3} \text{ J g}^{-1} \text{ °C}^{-1} \))

1.16 **Heat capacity at constant volume and heat capacity at constant pressure**

- The kinetic energy of the ideal gas depends only on its amount and on its absolute temperature (see section 1.14).
- Kinetic energy of 1 mole of the ideal gas is the molar kinetic energy (KE\text{one mole}):
\[
\text{KE}_{\text{one mole}} = \left( \frac{3}{2} \times R \times T \right) \frac{\text{J}}{\text{mol}} = \frac{3}{2} \times 8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times T \\
\text{KE}_{\text{one mole}} = 12.471 \frac{\text{J}}{\text{mol} \cdot \text{K}} \times T \ (\text{K})
\]

- If the initial temperature is \( T_i \) and the final temperature, \( T_f \), is \( T_i + 1 \). Therefore,
\[
\text{KE}_{\text{one mol,initial}} = 12.471 \frac{1}{\text{K}} \times T_i \\
\text{KE}_{\text{one mol,final}} = 12.471 \frac{1}{\text{K}} \times (T_i + 1 \text{ K}) \\
\text{KE}_{\text{final}} = \{12.471 \frac{1}{\text{K}} \times T\} + 12.471 \text{ J} \\
\text{KE}_{\text{one mol,final}} = \text{KE}_{\text{one mol,initial}} + 12.471 \text{ J}
\]

- This simple final equation states that increasing the temperature of one mole of an ideal gas by only one degree Celsius requires an increase in its kinetic energy by a finite amount that exactly equals 12.471 J.
The question now is: "How can we increase the kinetic energy of one mole of an ideal gas by 12.471 J?"

The answer simply is: "We can increase the kinetic energy of one mole of an ideal gas by 12.471 J simply by transferring 12.471 J of energy by heating and allowing this quantity of energy to transform to kinetic energy."

When supplying the system with this quantity of heat we have to do it either at constant volume or at constant pressure.

First: supplying heat at constant volume ($q_v$)

$V_2 = V_1$
$\Delta V = V_2 - V_1 = 0$
$w = -P\Delta V$
$w = 0$

This simply means that absorbance of heat by a gas at constant volume will cause no work to be done by the gas or on the gas. Consequently, if heat is absorbed at constant volume it will transform completely to kinetic energy. This means that kinetic energy will increase by exactly the same amount of heat absorbed.

This quantity of heat is called the molar heat capacity of an ideal gas at constant volume, and is denoted as $C_{m,v}$ therefore:

$$C_{v,m} = 1.5 \times R$$

$$C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$$

If the amount of the ideal gas is not one mole but "n" mole, its heat capacity at constant volume ($C_v$) is:

$$C_v = n \times C_{m,v}$$

$$C_v = n \times 1.5 \times R$$

$$C_p = n \times 12.471 \text{ J K}^{-1}$$

Second: supplying heat at constant volume ($q_p$):

$V_2 \neq V_1$
$\Delta V = V_2 - V_1 \neq 0$
$w = -P\Delta V$
$w \neq 0$

This simply means that absorbance of heat by a gas at constant pressure will cause work to be done by the gas. Consequently, if heat is absorbed at constant pressure it will not transform completely to kinetic energy. i.e. Some of it will be
consumed do work and kinetic energy will increase by less than the amount of heat absorbed.

**Increasing the temperature of one mole of an ideal gas by only one degree can be achieved by increasing its kinetic energy by 12.471 J, which cannot be done by supplying it with 12.471 J of heat while keeping its pressure unchanged but by supplying it with 12.471 J of heat plus an additional amount of heat equals the amount of work to be done due to change in volume required to keep pressure constant.**

This amount of heat is called the **molar heat capacity of an ideal gas at constant pressure**, and is denoted as $C_{p,m}$. Therefore:

\[
C_{p,m} = 1.5 \times R + w \\
w = n \times R \times \Delta T \\
n = 1 \text{ mol} \\
\Delta T = 1 \text{ K} = 1 \text{ °C} \\
w = R \\
C_{p,m} = 1.5 \times R + R \\
C_{p,m} = 2.5 \times R \\
C_{p,m} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}
\]

If the amount of the ideal gas is not one mole but $n$ mole, its heat capacity at constant pressure ($C_p$) is:

\[
C_p = n \times C_{m,p} \\
C_p = n \times 2.5 \times R \\
C_p = n \times 20.785 \text{ J K}^{-1}
\]

**Third: The difference between $C_p$ and $C_v$**

The difference between the heat capacity at constant pressure and at constant volume is as follows:

\[
C_p - C_v = (n \times C_{m,p}) - (n \times C_{m,v}) \\
C_p - C_v = n (2.5 \times R - 1.5 \times R) \\
C_p - C_v = n \times R \\
C_p - C_v = n \times 8.314 \text{ J K}^{-1}
\]

If the gas amount is one mole:

\[
C_{m,p} - C_{m,v} = R \\
C_{p,m} - C_{v,m} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}
\]

**Fourth: The ratio of $C_p$ to $C_v$**

The ratio ($\gamma$) of the heat capacity at constant pressure to that at constant volume is:

\[
\gamma = \frac{C_p}{C_v} = \frac{n \times C_{p,m}}{n \times C_{v,m}}
\]
\[ \gamma = \frac{c_{p,m}}{c_{v,m}} = \frac{20.785}{12.471} \]
\[ \gamma = 1.67 \]

It is clear from the above discussion that if the quantity of the gas is not one mole, the following equations must be applied:

\[ q_v = C_{m,v} \times n \times (T_2 - T_1) \]
\[ q_p = C_{m,p} \times n \times (T_2 - T_1) \]

**Example 1.10**
Calculate, in kJ, the quantity of heat released at constant pressure (\(q_p\)) from 56 g of O\(_2\)(g) if its temperature decreased from 298 K to 278 K at constant pressure. (\(C_{m,v} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}\)).

**Solution**
\[ C_{p,m} = C_{v,m} + R \]
\[ C_{p,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ n = \frac{m}{M} = \frac{56 \text{ g}}{16 \text{ mol}} = 3.5 \text{ mol} \]
\[ q_p = C_{p,m} \times n \times (T_2 - T_1) \]
\[ q_p = 20.785 \text{ J K}^{-1} \text{ mol}^{-1} \times 3.5 \text{ mol} \times (298 - 281) \text{ K} \]
\[ q_p = 1236.71 \text{ J} = 12.37 \text{ kJ} \]

**Practice exercise**
Calculate, in kJ, the quantity of heat absorbed at constant volume (\(q_v\)) from 56 g of O\(_2\)(g) if its temperature increased from 278 K to 298 K at constant volume. (\(C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}\)).

(Answer: \(q_v = 436.485 \text{ J}\))

### 1.17 Intensive and extensive properties

- **Intensive property**
  An intensive property is a physical property of a system that does not depend on the system size or the amount of material in the system, it is scale variant. For example, density is an intensive property of a substance because its value does not depend on the amount of the substance.

- **Extensive property**
  An extensive property is a physical property of a system that is additive for independent, noninteracting subsystems. It is directly proportional to the amount of material in the system. For example, mass is an extensive property of a substance because its value depends on the amount of that substance.

- If the quantity of matter is kept constant, then any of its properties becomes an intensive property. For example, the gas kinetic energy, \(k_e\), is an extensive property because its value depends on its number of moles; however, its molar kinetic energy is an intensive property because it is the kinetic energy of an amount fixed as one mole.

- The table below shows some of these properties.

<table>
<thead>
<tr>
<th>Some extensive properties</th>
<th>Some intensive properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Name</td>
<td>Symbol</td>
</tr>
</tbody>
</table>

### 1.18 The state of the system and the path of changing the state of the system

- **First: the state of the system:**
  - ✓ If we have a system and we know that it is not exposed to any internal changes or external interference that may change any of its properties, then we can confidently say that the system is in a state of equilibrium and all of its properties are fixed and can be known.
  - ✓ There are some properties of the system that play a key role more than other properties. We mean here that these properties are those that have control over the rest of the system properties in the sense that if any of these properties change, the rest of the properties follow it and also change. Let us, just for the sake of clarification, call these properties the "predominating properties".
  - ✓ If we are able to specify the "predominating properties", then we can be sure that we are able control the system.
  - ✓ Now, what are these "predominating properties"? Of course, the answer to this question differs from system to system, and from a situation of a system to another situation of the same system. However, we should not be pessimistic because scientific knowledge and experiences reveal that there are three properties that prove they are the best candidates for this task. These three properties are:
    1) The amount of the substance or its number of moles.
    2) The temperature.
    3) The pressure.
  - ✓ With much confidence we can say that if we achieved fixing those three properties for any system, we at the same time have fixed all other properties of the system.
  - ✓ We will see, and you might already have seen that the values of many properties such as densities, specific heats or enthalpies and many others are given at a specified temperature (usually 25 °C), specified pressure (usually 1 atm or 1 Par) and per a specified amount (usually one mole or one gram).
  - ✓ As a conclusion we say that the state of the system is its state a set of values of properties of the system that must be specified to reproduce the system and once a sufficient set of properties have been specified, values of all other properties of the system are uniquely determined. The number of values required to specify the state of the system depends on the system and is not
always known but the substance amount, temperature and pressure are the properties needed for *almost* all systems.

- **Second: the path of changing the state of the system**
  - When the system is in a certain state, say in an “*initial state*”, and then undergoes internal change or external interference, the system will be in a state that is different from the “*initial state*”. This new state is called the “*final state*”.
  - Changing the state of the system from an “*initial state*” to a “*final state*” must have occurred through a certain path.
  - The path taken to change the state of the system is the steps of the process that change the system from a state to another state.
  - Different persons can take different paths to transfer the system from the same initial state to the same final state. Changing the path has nothing to do with the state system.

1.19 The state functions and the path functions

- To understand the precise meaning of the state functions the path functions let us imagine the following case:
  - Both of you are standing beside each other at a certain point called “*the initial state*” at the bottom of a mountain. Both of you are at the same altitude.
  - Both of you want to reach a specified point called “*the final state*” at the top of the mountain. Both of you want to reach the same altitude.
  - You and your friend noticed that there are two paths:
    - Path X with a post says 1900 tasteful meters.
    - Path Y with a post says 1300 distasteful meters.
  - Again, imagine that you and your friend agreed that you are the one to take path X and he is the one to take path Y.
  - Without any stoppage, both of you started moving at the same time from the same initial state heading to the same final state but taking two different paths.
  - Your friend reached the final state after 35 minutes but you did not arrive except after 78 minutes.
  - Your speed was 24.36 meter/minute and his speed was 37.14 meter/minute.
  - Chatting with each other reveals that path X was tasteful because of its views was orchards and gardens and path X was distasteful because its views was wastes and rubbishes.
  - The conclusion that matter to us is that the initial state and altitude of both of you was the same and also the final state and altitude of both of you was the same. But the distances and the speeds of both of you are different.

- Although both of you have taken different paths with different distances and different speeds the final altitude of both of you were the same.
- We say that altitude of both of you does not depend on the path you chose because it’s a property of your initial and final state and has nothing to do with these two different paths or even any other path.
- However, the distance travelled. and the speed of you and of your friend are different. Therefore, we say that the distance and the speed do depend on the path and no one of them is a property of the initial or the final state of both of you.
- Finally, the altitude is a state function but the distance and the speed are path functions.
• Temperature, pressure or any other property of any system is a function of the state of the system.
• Heat absorbed or released by a system and work done by or on the system are examples of the path functions.

1.20 Processes and types of processes
• A process is the operation which change the state of a system. The change in the state of a system means that a certain process had been carried on it.
• When a process is carried out on a system, we should know how it was done.
• There are several four ways of carrying a process on a system:
  1) The isothermal process: The isothermal process is the process in which the final temperature of the system remains the same as its the initial temperatures. This typically occurs when a system is in contact with an outside thermal reservoir, and the change occurs slowly enough to allow the system to continually adjust to the temperature of the reservoir through heat exchange. In an isothermal process, the value of $\Delta T = 0$ but the value of $q \neq 0$.
  2) The adiabatic process: The adiabatic process is the process in which the initial and the final temperature of the system are different. This typically occurs when a system is closed or isolated to prevent any input or output of heat between the system and its surroundings. In an adiabatic process, the value of $\Delta T \neq 0$ but the value of $q = 0$.
  3) The isobaric process: The isobaric process is the process in which the final and the initial pressures of the system are the same. In an isobaric process, the value of $\Delta P = 0$.
  4) The isochoric process: The isochoric process is the process in which the final and initial volumes of the system are the same. In an isochoric process, the value of $\Delta V = 0$.

1.21 Cyclic processes
• First, carefully look and inspect the following graph which shows the relationship between the pressure and the volume of a fixed amount of a gas at constant temperature.

✓ At the beginning the gas was at state number 1. the gas pressure and volume were $P_A$ and $V_D$.
➢ Step A changes the gas from state number 1 to state number 2.

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At the state 2, the gas pressure remained $P_A$ but its volume changed to $V_B$.

- **Step B** changes the gas from state number 2 to state number 3.
  - At the state 3, the gas pressure changed to $P_C$ but its volume remained $V_B$.
- **Step C** changes the gas from state number 3 to state number 4.
  - At the state 4, the gas pressure remained $P_C$ but its volume changed to $V_D$.
- **Step D** changes the gas from state number 3 to state number 1.
  - At the state 1, the gas pressure changed to $P_A$ but its volume remained $V_D$.

✓ **At the end** the gas returned back to state number 1. the gas final pressure and final volume are the same as they were at the beginning.

- The cyclic process is a thermodynamic cycle which ends at where it started.
- In a thermodynamic cycle, the system returns to its original thermodynamic state.
- The cyclic process consists of consecutive steps of transferring heat and work into and out of the system by varying pressure, temperature, and other state variables of the system, and that eventually brings back the system to its initial state.
- At every point in the cycle, the system is in thermodynamic equilibrium, so the cycle process is reversible.
- At the end of the cyclic process all of the state functions of the system have the same values they had at the beginning of the cycle.

### 1.22 Irreversible and reversible processes

- **The irreversible process**: The irreversible process is the process that occurs in one fast and sudden step.
  ✓ In the irreversible process, any change in the state of a system and in all of its surroundings cannot be precisely restored to the initial state by infinitesimal changes in some property of the system without expenditure of energy.
  ✓ A system that undergoes an irreversible process may still be capable of returning to its initial state; however, the impossibility occurs in restoring the environment to its own initial conditions.
  ✓ An irreversible process increases the entropy\(^1\) of the universe: however, because entropy is a state function, the change in entropy of a system is the same whether the process is reversible or irreversible.
  ✓ All natural processes are irreversible.

✓ In the figure above, the state at top-left shows a gas in a perfectly insulated cylinder. The initial volume, pressure and temperature are $T_1$, $P_1$, and $V_1$. If the state changes to the top-right state where final volume, pressure and temperature become $T_2$, $P_2$, and $V_2$, the system cannot be restored to its initial

---

\(^1\) The concept of entropy will be discussed in chapter 4.
state. If we want to restore the initial pressure, the system will assume the bottom-left state instead, because energy is converted into heat.

- **The reversible process:** The reversible process is the process that occurs in many slow infinitesimal changes in some property of the system without entropy production or dissipation of energy.
  - Due to these infinitesimal changes, the system is in thermodynamic equilibrium throughout the entire process.
  - Since it would take an infinite amount of time for the reversible process to finish, perfectly reversible processes are impossible.
  - In a reversible cycle, the system and its surroundings will be exactly the same after each cycle.
  - An alternative definition of a reversible process is that it is the process that, after it has taken place, can be reversed without causing any change in either the system or its surroundings.

- In the figure above, the state at left state shows a gas in a perfectly insulated cylinder. The initial volume, pressure and temperature are $T_1$, $P_1$, and $V_1$. If the state changes to the state at right where final volume, pressure and temperature become $T_2$, $P_2$, and $V_2$, the system can be restored to its initial state.

### 1.23 Chemical thermodynamic equilibrium

**EQUILIBRIUM IS THE STATE OF BALANCE**

- Here, the words of this title imply very important indication. The title contains the word “chemical” and the word “thermodynamic”.
  - The word “chemical” means the matter composition of the system.
  - The word “thermodynamic” implies the action of heat and the action of mechanical forces.

- **The state of a chemical thermodynamic equilibrium:** The state of a thermodynamic equilibrium is the state of the system in which the system experiences no net flows of matter or of energy, no phase changes, and no unbalanced potentials (or driving forces) within the system and experiences no changes when it is isolated from its surroundings.

- **Types of equilibrium:**
  - **Chemical equilibrium**
    Chemical equilibrium is the state of the system in which the qualitative and quantitative chemical composition of the system remains the same without any change.
  - **Thermal equilibrium**
Thermal equilibrium is the state of the system in which the temperature of the system is the same everywhere and all over the system.

✓ **Mechanical equilibrium**
Mechanical equilibrium is the state of the system in which the forces acting upon any particle of the system is the same as the forces acting upon any other particle of the system.

✓ **Chemical thermodynamic equilibrium**
Chemical thermodynamic equilibrium is the state of the system in which the system is in chemical, thermal and mechanical equilibria.

### 1.24 The standard state, the standard temperature and pressure (STP), and the standard conditions

✓ **First:** The standard state: The standard state of a substance is a reference state of the substance used to calculate its properties under different conditions.

✓ The reference state of an element is its most stable form at a chosen standard-state pressure and for a given temperature. The table shows the reference states of some substances.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reference state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>grey arsenic</td>
</tr>
<tr>
<td>Bromine</td>
<td>liquid</td>
</tr>
<tr>
<td>Carbon</td>
<td>graphite</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>gas</td>
</tr>
<tr>
<td>Iodine</td>
<td>solid</td>
</tr>
<tr>
<td>Mercury</td>
<td>liquid</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>gas</td>
</tr>
<tr>
<td>Oxygen</td>
<td>gas</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>white phosphorus</td>
</tr>
<tr>
<td>Sulfur</td>
<td>rhombic sulfur</td>
</tr>
<tr>
<td>Tin</td>
<td>white tin, α-tin</td>
</tr>
</tbody>
</table>

✓ Selecting a state of a substance (pure substance, mixture or solution) to be the standard state of the substance means that it is selected to be its reference state that is used for calculating the properties of the substance at different conditions.

✓ The standard state of a substance is conventional and arbitrary.

✓ The IUPAC conventional standard states of a substance is its state at a pressure that is equal to 1 bar (100 kilopascals, 0.986 atmosphere).

✓ Temperature is not part of the definition of a standard state.

✓ Although temperature is not part of the definition of a standard state, most tables of thermodynamic quantities are compiled at specific temperatures, most commonly the room temperature (25 °C = 298.15 K).

✓ Many standard states are not real but hypothetical states, i.e., "non-physical states". Nevertheless, their thermodynamic properties are well-defined, usually by an extrapolation from some limiting condition, such as zero pressure or zero concentration, to a specified condition (usually unit concentration or pressure) using an ideal extrapolating function, such as ideal solution or ideal gas behavior, or by empirical measurements.

✓ Definition of the standard state for a substance depends on the its type:
If the substance is a gas its standard state is the hypothetical state it would have as a pure substance obeying the ideal gas equation at standard pressure. No real gas has perfectly ideal behavior, but this definition of the standard state of a gas allows corrections for non-ideality to be made consistently for all the different gases.

If the substance is a liquid or a solid its standard state is simply the state of the pure substance subjected to the standard pressure.

If the substance is a solute in a solution, the standard state is the hypothetical state it would have when the molality equals 1 mol kg\(^{-1}\) and, at the same time, it exhibits infinite-dilution behavior. The reason for this unusual definition is that the behavior of a solute at the limit of infinite dilution is described by equations which are very similar to the equations for ideal gases. Hence taking infinite-dilution behavior to be the standard state allows corrections for non-ideality to be made consistently for all the different solutes.

The standard state of a substance does not have to exist in nature: for example, it is possible to calculate values for steam at 25 °C and 1 bar, even though steam does not exist under these conditions. The advantage of this practice is that tables of thermodynamic properties prepared in this way are self-consistent.

- **Second: The standard temperature and pressure (STP):** The use of the term “Standard Temperature and Pressure”, which is abbreviated as STP, is restricted, only, on gases. When a gas is at STP, this means that its temperature is 0 °C (273.15 K) and its pressure is 1 atm (101325 Pa). Therefore, the standard state of a substance should not be confused with STP.

- **Third: The standard conditions:** The standard conditions are the conditions at which temperature is the room temperature (298 K), the prevailing pressure is the standard pressure (1 bar) and, in case of solutions, the concentration is 1 molal. The standard conditions are used for thermodynamics tables and problems.

### 1.25 The internal energy

- The internal energy is denoted "U" and is the total energy contained by a system. It excludes the energy to displace the system's surroundings, any energy associated with a move as a whole, or due to external force fields.
- The internal energy has two major components, the internal kinetic energy "U\(_{\text{kin}}\)" and the internal potential energy "U\(_{\text{pot}}\)"

\[
U = U_{\text{kin}} + U_{\text{pot}}
\]

- The internal kinetic energy "U\(_{\text{kin}}\)" is due to all kind of motions of the system's particles (translation, rotation, vibration). This kinetic energy portion "U\(_{\text{kin}}\)", as a part of the internal energy, is the energy behind the temperature of the system. This energy is often referred to as the thermal energy of a system, which makes it easy to relate this energy to the human experience and feelings of hotness and coldness.
- The internal potential energy "U\(_{\text{pot}}\)" is associated with the static constituents of matter, static electric energy of atoms within its particles and the static energy of chemical bonds.
- The internal energy excludes any potential energy a body may have because of its location in external gravitational or electrostatic field.
• The internal energy of a given system is the difference between its internal energy in a specified state and its internal energy at the absolute zero temperature.
• Since the absolute zero temperature is unattainable and cannot be reached, the total internal energy cannot be precisely measured or known. Only changes in the internal energy can be measured and known.
• Although it is impossible to calculate the total internal energy, it is not an obstacle in thermodynamics, because its chief concern is not the absolute values of the internal energy but the changes in its values.
• The internal energy of an isolated system is constant and cannot be changed.
• The internal energy is a state dependent and is a path independent, that is, it depends only on the condition of the system at the moment, and not on the path by which it arrived at that conditions.
• The internal energy is an extensive property, that is, its magnitude depends on the amount of the substance in a given state.
• The internal energy of a system can be changed by heating or cooling the system and/or by doing work on or by the system.

1.26 The enthalpy and the change in enthalpy
• Much of chemistry, and most of biology, takes place in vessels that are open to the atmosphere and subjected to constant pressure, not constrained to constant volume in a rigid, sealed container.
• In general, when a change takes place in a system open to the atmosphere, the volume of the system changes. For example, the thermal decomposition of 1.0 mol CaCO$_3$(s) at 1 bar and 800 °C results in an increase in volume of nearly 90 dm$^3$ on account of the carbon dioxide gas produced

$$\text{CaCO}_3\text{(s)} \overset{800 \degree \text{C}}{\longrightarrow} \text{CaO(s) + CO}_2\text{(g)}$$

• To create this large volume for the carbon dioxide to occupy, the surrounding atmosphere must be pushed back.

That is, the system must perform expansion work. The above figure shows that although a certain quantity of heat may be supplied to bring about the endothermic decomposition, the increase in internal energy of the system is not equal to the energy supplied as heat because some energy has been used to do work of expansion.
In other words, because the volume has increased, some of the heat supplied to the system has leaked back into the surroundings as work.

Another example is the oxidation of a fat, such as tristearin, to carbon dioxide in the body. The overall reaction is

$$2C_{57}H_{110}O_6(s) + 163O_2(s) \rightarrow 114CO_2(g) + 110H_2O(L)$$

In this exothermic reaction there is a net decrease in volume equivalent to the elimination of 49 mol (163 mol – 114 mol = 49 mol) of gas molecules for every 2 mol of tristearin molecules that react. The decrease in volume at 25 °C is about 600 cm$^3$ for the consumption of 1 g of fat. Because the volume of the system decreases, the atmosphere does work on the system as the reaction proceeds. That is, energy is transferred to the system as it contracts.

In effect, a weight has been lowered in the surroundings, so the surroundings can do less work after the reaction has occurred.

Some of surroundings’ energy has been transferred into the system. For this reaction, the decrease in the internal energy of the system is less than the energy released as heat because some energy has been restored by doing work.

We can avoid the complication of having to take into account the work of expansion by introducing a new property that will be at the center of our attention.

This property is the enthalpy, $H$, of a system.

The enthalpy, $H$, of a system is defined as

$$H = U + PV$$

Enthalpy of a system comprises the internal energy of the system plus the amount of work required to allow the system to occupy a space by displacing its surroundings and acquiring its own volume and pressure.

Enthalpy is a state function that depends only on the prevailing equilibrium state identified by the system’s internal energy, pressure, and volume.

The enthalpy differs from the internal energy by the addition of the product of the pressure, $P$, and the volume, $V$, of the system.

This expression ($H = U + PV$) applies to any system or individual substance: we should not be misled by the ‘PV’ term into thinking that equation ($H = U + PV$) applies only to a perfect gas.

Enthalpy is an extensive property, but the molar enthalpy, $H_m = \frac{H}{n}$, of a substance is an intensive property. The molar enthalpy differs from the molar internal energy by an amount proportional to the molar volume, $V_m$, of the substance:

$$H_m = U_m + PV_m$$

This relation is valid for all substances.

For a one mole of a perfect gas, where “PV = RT” we can write:

$$H_m = U_m + RT$$

At 25°C (298.15 K), $R \times T = 2.5 \frac{kJ}{mol}$, so the molar enthalpy of a perfect gas is greater than its molar internal energy by 2.5 $\frac{kJ}{mol}$. 

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Because the molar volume of a solid or liquid is typically about 1000 times less than that of a gas, we can also conclude that the molar enthalpy of a solid or liquid is only about 2.5 \( \frac{1}{\text{mol}} \) more than its molar internal energy, so the numerical difference is negligible.

A change in enthalpy (the only quantity we can measure in practice) arises from a change in the internal energy and a change in the product of \( P \times V \):

\[
\Delta H = \Delta U + \Delta(PV)
\]

Where \( \Delta(PV) = P_f V_f - P_i V_i \).

If the change takes place at constant pressure \( P \), the second term on the right simplifies to:

\[
\Delta(PV) = PV_f - PV_i = P(V_f - V_i) = P \Delta V
\]

and we can write:

At constant pressure: \( \Delta H = \Delta U + P\Delta V \)

We shall often make use of this important relation for processes occurring at constant pressure, such as chemical reactions taking place in containers open to the atmosphere.

Although the enthalpy and internal energy of a sample may have similar numerical values, the introduction of the enthalpy has very important consequences in thermodynamics:

- First, notice that because \( H \) is defined in terms of state functions (\( U \), \( P \), and \( V \)), therefore the enthalpy is a state function. The implication is that the change in enthalpy, \( \Delta H \), when a system changes from one state to another is independent of the path between the two states.

- Secondly, the change in enthalpy of a system can be identified with the heat transferred to it at constant pressure:

At constant pressure, no nonexpansion work: \( \Delta H = q_p \)

The equation “\( \Delta H = q_p \)” is enormously powerful because it expresses that at constant pressure, with no nonexpansion work, we can identify the energy transferred by heating with a change in enthalpy of the system.

The equation “\( \Delta H = q_p \)” relates a quantity we can measure (the energy transferred as heat at constant pressure) to the change in a state function (the enthalpy).

Dealing with state functions greatly extends the power of thermodynamic arguments, because we don’t have to worry about how we get from one state to another: all that matters are the initial and final states.

The equation “\( \Delta H = q_p \)” implies that if 10 kJ of energy is supplied as heat to the system that is free to change its volume at constant pressure, then the enthalpy of the system increases by 10 kJ, regardless of how much energy enters or leaves by doing work, and we write \( \Delta H = +10 \) kJ.

On the other hand, if the reaction is exothermic and releases 10 kJ of energy as heat when it occurs, then \( \Delta H = -10 \) kJ regardless of how much work is done.
• For the particular case of the combustion of tristearin mentioned earlier:

\[ 2\text{C}_{57}\text{H}_{110}\text{O}_6(\text{s}) + 163\text{O}_2(\text{s}) \rightarrow 114\text{CO}_2(\text{g}) + 110\text{H}_2\text{O(}\text{L}\text{)} \]

90 kJ of energy is released as heat, we would write \( \Delta H = -90 \text{ kJ} \).

• An endothermic reaction (\( q > 0 \)) taking place at constant pressure results in an increase in enthalpy (\( \Delta H > 0 \)) because energy enters the system as heat.

• On the other hand, an exothermic process (\( q < 0 \)) taking place at constant pressure corresponds to a decrease in enthalpy (\( \Delta H < 0 \)) because energy leaves the system as heat.

• All combustion reactions, including the controlled combustions that contribute to respiration, are exothermic and are accompanied by a decrease in enthalpy. These relations are consistent with the name “enthalpy”, which is derived from the Greek origins. “\( \text{en-} \)” means “within” and “thalpein” means “to heat”. Therefore, enthalpy means “heat content” meaning “heat inside”; the “heat inside” the system is increased if the process is endothermic and absorbs energy as heat from the surroundings; it is decreased if the process is exothermic and releases energy as heat into the surroundings.

• However, never forget that heat does not actually “exist” inside: only energy exists in a system; heat is a mean of recovering that energy or increasing it.

• Enthalpy is a is an extensive property.

• The term enthalpy means the heat content of the system.

• The enthalpy, \( H \), of a system cannot be measured but the change in it can be.

• If the state of the system changes from an initial state with an enthalpy \( H_i \) to a final state with an enthalpy \( H_f \) then:

\[ \Delta H = H_f - H_i \]

• The amount of “\( H \)” cannot be determined, but \( \Delta H \) can be.

• If the change in the state of the system makes \( \Delta H \) positive the change is described as an endothermic change, endothermic process or endothermic reaction.

• If the change in the state of the system makes \( \Delta H \) negative the change is described as an exothermic change, exothermic process or exothermic reaction.

• Endothermic and exothermic chemical reactions or physical transitions are usually depicted in figures such as those below.

**Endothermic reactions**

Reactants have less potential energy than products. Energy must be absorbed in order to raise the particles up to the upper energy level.
**Exothermic reactions**

Reactants have more potential energy than the products. Energy must be released in order to lower the particles to the lower energy level.
• **For processes at constant pressure**, \( \Delta H \) is equal to the change in the internal energy of the system, plus the PV-work done on \((w > 0)\) or by the system \((w < 0)\).
• Changes in the enthalpies for chemical substances are measured at the standard pressure \((1 \text{ bar})\).

### 1.27 The four laws of thermodynamics

- Without going through the historical development of the science of thermodynamics, the final results of all of the scientific findings are arranged and well established in such a fruitful way as to ensure the logical and scientific arrangements and sequence of subjects that is well agreed upon as the best way for the best understanding and underlying learning and teaching of thermodynamics.
- The thermodynamics main and pronounced feature is its four laws. Namely,
  1. The zeroth law
  2. The first law
  3. The second law
  4. The third law
- The question of why these laws are numbered starting from “zero” to “three” not from “one” to “four”, is a logical question.
- The reason of this firming and established numbering is due simply to the "zeroth law" which is the last-born of the four.
- After the first, the second and the third laws have acquired their names, and after scientists, students and professionals got familiar with these names, the fourth brother law is born.
- It was too late for changing the numerical arrangement.
- Therefore, the last-born law is given its present name "THE ZEROTH LAW".
- The answer of the question: why this law is not named "THE FOURT LAW" is because it is much more basic law than any of its other three brothers and presenting it before them gives a much clearer picture and understanding of the science of thermodynamics.
QUESTIONS AND PROBLEMS

1. A piston has an external pressure of 8.00 atm. How much work has been done if the cylinder goes from a volume of 0.140 liters to 0.450 liters.

2. Used in welding metals, the reaction of acetylene with oxygen is:
   \[ \text{C}_2\text{H}_2(g) + 2.5\text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) + 2\text{CO}_2(g) \]
   \[ \Delta H = -1255.5 \text{ kJ} \]
   How much PV work is done, in kJ, if the reaction of 6.5 g of acetylene at one atmospheric pressure decreased the volume by 2.8 L?

3. If a tricycle is pushed 50 feet with a force of 5 N, how much work is done on the tricycle?

4. How far, in meters, would a box travel if pushed with 7 N of force and 15 Joules of work is done on the box?

5. How much work, in J, is done by a gas that expands from 2 liters to 5 liters against an external pressure of 750 mmHg?

6. How much work is done by 0.54 moles of a gas that has an initial volume of 8 liters and expands under the following conditions: 30°C and 1.3 atm?

7. How much work is done by a gas (p=1.7 atm, V=1.56 L) that expands against an external pressure of 1.8 atm?

8. The rms speed of an unknown gas at 98 °C was found to be equal to the rms speed of N₂ gas at 37 °C. What is the molar mass of the unknown gas?

9. Knowing that the molar heat capacity of a gas at constant volume is 12.471 J/K mol, how many kilojoules of heat is needed to raise the temperature of 0.35 mol of it at constant volume by 15 K?

10. Knowing that the molar heat capacity of a gas at constant volume is 12.471 J/K mol, how many kilojoules of heat is needed to raise the temperature of 0.35 mol of it at constant pressure by 15 K?

11. Calculate the specific heat capacity of copper given that 204.75 J of energy raises the temperature of 15g of it from 25⁰ to 60⁰. (Cₚ,Cu = 0.39 J g⁻¹ K⁻¹).

12. 216 J of energy is required to raise the temperature of aluminum from 15⁰ to 35°C. Calculate the mass of aluminum. (Cₚ,Al = 0.9 J g⁻¹ °C⁻¹).

13. A 1.0 kg sample of metal with a specific heat of 0.50 kJ/Kg °C is heated to 100.0°C and then placed in a 50.0 g sample of water at 20.0 °C. What is the final temperature of the metal and the water?

14. A 2.8 kg sample of a metal with a specific heat of 0.43kJ/Kg °C is heated to 100.0 °C then placed in a 50.0 g sample of water at 30.0 °C. What is the final temperature of the metal and the water?
2. THE ZEROTH LAW OF THERMODYNAMICS
2 THE ZEROTH LAW OF THERMODYNAMICS

2.1 Temperature

- Establishment of the laws of thermodynamics relied and depended on investigating and knowing properties of the system and changes in them. Among properties of the system, temperature is the central one.
- In 1670 and after 28 years of the death of Galileo, Boyle was the first to use the word "temperature" to indicate the sense of hotness and coldness. It was derived from the Latin word "Temperatura" which was used by Galileo (1564 – 1642) as a connotation to the sense of the degree of hotness.
- Although the term "temperature" is in use since the seventeenth century, it is not until the twentieth century a law is established and formulated to state that "temperature" exists.
- Why did it become important to establish and formulate a law that recognizes the existence of temperature? The answer to this question lies on the fact that heat flow is associated with temperature gradients, and to understand firmly heat flow a natural law must lies behind this phenomenon and we should know it and bring it ahead of our eyes.
- Scientist felt that the framework of thermodynamics is not perfect. A law is missing to make the features of thermodynamics much clearer and in their best sequence.
- Also, the presence of a concrete and well-formulated statement of a law concerning this aspect is necessary to conceive how temperature measurements are made.
- This law waited for a long time before it was finally enunciated in 1939.
- This formulation of the law came so many years after the first, the second and the third laws of thermodynamics. Note that the enunciation of the first law was in 1850, the second law was in 1857, and third law was in 1912.
- Because this fourth law is more basic and fundamental than any of his other three brother-laws, it should be presented first. Could it be called "the fourth law" and at the same time present it before the first, the second and the third laws? This does not look wise or logical. Therefore, this choice is eliminated.
- The other available choice is to rename the three older laws in order to give chance for this newly born law to carry the name of the first law? This choice was also eliminated because the names of the three laws are firm and well established in books, literatures and among scientists, professionals, student and even publics.
- In 1931, the British physicist and astronomer Ralph Howard Fowler was the first to formulate the law in its present formulation. But it is not until 1939 when he named the law as "THE ZEROTH LAW."
- The zeroth law is the law which simply asserts that "regardless of how much energy two systems have, if we need to know the direction of heat flow between them, the temperature of the systems is the only thing we need to know." The zeroth law is the law which informs us in which direction heat will flow.

2.2 The statement of the zeroth law

If the system A and system B are in a thermal equilibrium with the system C, then the system A is in thermal equilibrium with the system B.
In thermodynamics literature, this statement of the zeroth law is usually accompanied with a figure that is drawn in so many fashions such as these below.

2.3 Thermometers

- Old fashioned thermometers
  - The knowing of the degree of hotness of objects and systems such as our bodies, drinks, foods, atmospheres…etc. Therefore, we need a tool that fulfill our needs as accurate as possible.
  - The old fashion ways such as “extremely hot, very hot, hot, fairly hot, fairly cold, cold, very cold, extremely cold etc.” are not satisfying the degree of human development.

- Galileo thermoscope and Galileo thermometer
  - In the last few centuries of the human development accumulated enormous piles of knowledge about the nature of matter and various properties. This paved the road to so many achievements. Thermometers is just one or tiny one of those achievements.
  - Historically, the idea of inventing a thermometer is widely attributed to Galilei Galileo because he discovered the principle that the density of a liquid changes in proportion to its degree of hotness
  - The name of the first thermometer was “thermoscope”. Thermoscope was invented by Galileo in 1593. The figure below shows one of these thermoscopes.
Thermoscope is sometimes called Galileo’s thermometer. However, because it is not calibrated and therefore measures only the difference in the degree of hotness, calling it a thermometer is inaccurate.

Decades after the invention of thermoscope, a thermometer was invented and called the “Galileo thermometer”. This so-called “Galileo thermometer” was not invented by Galileo but by a group of academics and technicians known as the among them Galileo’s pupil Torricelli.

The figure below shows the Galileo thermometer:

Fahrenheit and Celsius scales for thermometer

In 1724, the Dutch-German-Polish physicist Daniel Fahrenheit invented his thermometer that is based on the proposition that the human body temperature is 100 °F and accordingly the freezing and the boiling temperatures of water are 32 °F and 212 °F respectively. This scale is now obsoleted except in a few countries such as the USA and the UK.

In 1742, the Swedish astronomer Andres Celsius invented his famous thermometer. It is based on the proposition that the freezing and the boiling temperatures of water are 0 °C and 100 °C respectively. The Celsius scale is the scale being used all over the globe except a few countries.

The following figure shows a comparison between the Fahrenheit and the Celsius scales:
• The absolute temperature and the Kelvin scale for thermometer
  ✓ The absolute temperature is the temperature at which the fundamental particles of any matter has minimal vibrational motion.
  ✓ In 1848 Kelvin found that this absolute temperature is \(-273.15 \, ^\circ C\). The idea of this scale was given before Kelvin was born. Almost 150 years before Kevin was born Boyle was one of the scientists who discussed the possibility of a very low temperature “an absolute minimal temperature” and no way for any matter to have a temperature below it.
  ✓ Divisions of the Kelvin scale for temperatures is the same as those of the Celsius scale. However, the 0 point on the Kelvin scale equal to \(-273.15 \, ^\circ C\) and therefore the freezing and the boiling points of water in the Kelvin scale are 273.15 K and 373.15 K respectively.

2.4 Thermometers and the zeroth law
• To design a thermometer, we must choose a certain system that has a certain property that changes linearly as the temperature of the system changes.
• Although very few, systems which satisfies this strict condition are available. The most common are:
  1) The perfect (the ideal) gas with its volume.
  2) The mercury element with its volume.
  3) The platinum element with its electric resistance.
• The mercury thermometers are the most common.
  ✓ It consists of reservoir that is filled with mercury and a capillary tube that is evacuated of air and immersed upside down in the mercury.
  ✓ The reservoir of this system is put in contact with water that is a state of freezing. This state is the state of a dynamic equilibrium between the liquid and the solid states of water and their temperature is the freezing and, at the same time, the melting temperature of water.
  ✓ The mercury will assume a certain height in the capillary tube. This point is marked as 32 in the Fahrenheit scale and as 0 in the Celsius scale.
  ✓ Again, the reservoir of this system is put in contact with water that is a state of boiling. This state is the state of a dynamic equilibrium between the liquid and the gaseous states of water and their temperature is the boiling and, at the same time, the condensation temperature of water.
  ✓ The mercury will assume a certain height in the capillary tube. This point is marked as 212 in the Fahrenheit scale and as 100 in the Celsius scale.
  ✓ Finally, the distance between the two marks of the freezing and the boiling temperature are divided into equal parts (180 parts in the case of the Fahrenheit scaling and 100 parts in the case of the Celsius scaling).
  ✓ By accomplishing the last step, we get, in our hands, a thermometer that we can use to measure the temperature of any other object or system.
• This achievement would have not been achieved unless it is fact that: “when two systems (A and B) have the same temperature of a third system (C) then those two systems (A and B) must have been in thermal equilibrium with each other. This fact is by itself the Zeroth Law of Thermodynamics.
• The Zeroth Law is the scientific fundamental base of thermometers.
• The mathematical expression of the zeroth law is given by the following straight-line equation:

\[ t = a + b \times y \]
where “t” is the value of the temperature in any scale, “y” is the value of the property of the system which changes linearly with t, and of course “a” and “b” are constants where “a” represent the intercept and “b” represent the slope.

Example 2.1
A Pt thermometer resistance changes linearly with temperature according to the following equation:

\[
\text{Temperature in Kelvin scale} = a + b \times \text{resistance in ohm}
\]

If \(a = -1303.6 \degree C\) and \(b = 70.43 \Omega^{-1} \degree C\), calculate the temperature at which its resistance equals 33.1 Ω.

**Solution**

\[
\text{Temperature in Kelvin scale} = a + b \times \text{resistance in ohm}
\]

\[
t = -1303.6 \degree C + 70.43 \Omega^{-1} \degree C \times 33.1 \Omega
\]

\[
t = 1027.6 \degree C
\]

**Practice exercise**

The resistance of an element changes linearly with temperature as follows:

\[
\text{Temperature in Kelvin scale} = a + b \times \text{resistance in ohm}
\]

If the element resistance is 24.82 Ω at 444.6 °C and 33.6 Ω at 1063.0 °C, calculate the temperature at which its resistance equals 28.6 Ω.

Example 2.2

A property of a certain system is selected to measure temperatures of any other system. Why is this property and not any other is used?

**Solution**

Because this property meets the condition which says that it must change linearly with temperature.

**Practice exercise**

Give two examples of systems that are used thermometer.

Example 2.3

Define the boiling point.

**Solution**

The boiling point is the temperature at which a substance exists in its liquid and gaseous states in thermodynamic equilibrium at a specified vapor pressure.

**Practice exercise**

Give two examples of systems that are used thermometer.

### 2.5 The thermodynamic temperature

- Thermodynamic temperature is the absolute measure of temperature.
- Again, the graph below shows Charles law which illustrate the relation between the volume of a certain amount of a gas and its temperature at constant pressure.
- The figure shows that the volume of the gas decreases as its temperature decreases. It also shows that if we continue in decreasing temperature, we will reach a temperature at which the volume vanishes and become zero. The temperature at this point in the Celsius scale is –273.15 °C and in the Kelvin scale is 0 K.
• One Kelvin is defined as \( \frac{1}{273.16} \) of the temperature of the triple point of water, making absolute zero equals to \(-273.15^\circ C\) since the triple point of water is at 0.01°C (= 273.16 K) and 4.5881 torr (= 0.006037 atm = 0.6117 kPa).
• The thermodynamic temperature is the temperature measured according to the absolute, or Kelvin, scale.
• The zero temperature in this absolute scale (0 K) is the concern of the third law.
• The 0 K is the minimum temperature a system can reach. At this temperature:
  ✓ Particles of the system have the minimal possible motion,
  ✓ Particles of the system are at their lowest energy
  ✓ Particles of the system cannot be colder.
QUESTIONS AND PROBLEMS

1. A Pt thermometer resistance changes linearly with temperature. Its resistance is 24.82 Ω at 444.6 °C and 33.6 Ω at 1063.0 °C. Calculate its resistance at 800°C.

2. What form of the system energy is associated with its temperature?

3. Draw the graphical relation between the temperature and the volume of a certain quantity of an ideal gas if its pressure is kept constant. Show the minimum temperature that can be reached.

4. Carry on the following conversions:
   • –65.5 °C to K
   • 65.5 K to °C

5. Explain the bases of the Celsius scale of temperature.
3. THE FIRST LAW OF THERMODYNAMICS
3 THE FIRST LAW OF THERMODYNAMICS

3.1 The law of conservation of energy and the first law of thermodynamics

- Almost every argument and explanation in chemistry boils down to a consideration of some aspect of a single property: the energy.
- Energy determines what molecules may form, what reactions may occur, how fast they may occur, and in which direction a reaction has a tendency to occur.
- Energy is the capacity to do work which is done to achieve motion against an opposing force.
- These definitions imply that a raised weight of a given mass has more energy than one of the same mass resting on the ground because the former has a greater capacity to do work: it can do work as it falls to the level of the lower weight.
- The definition also implies that a gas at high temperature has more energy than the same gas at a low temperature: the hot gas has a higher pressure and can do more work in driving out a piston.
- People struggled for centuries to create energy from nothing, for they believed that if they could create energy, then they could produce work (and wealth) endlessly.
- However, without exception, despite strenuous efforts, many of which degenerated into deceit, they failed.
- As a result of their failed efforts, we have come to recognize that energy can be neither created nor destroyed but merely converted from one form into another or moved from place to place.
- This “law of the conservation of energy” is of great importance in chemistry.
- Most chemical reactions release energy or absorb it as they occur; so according to the law of the conservation of energy, we can be confident that all such changes must result only in the conversion of energy from one form into another or its transfer from place to place, not its creation or annihilation.
- The detailed study of that conversion and transfer is the domain of thermodynamics.

**The law of conservation of energy** is a natural law which states that the total energy of any isolated system is constant, this means that it is conserved over time and can neither be created nor destroyed but it can be transformed from one form of to another.

- Taking into consideration that the universe we live in is by itself an isolated system means that the total energy of the universe is constant from the beginning of its existence and forever as long as it is isolated.

**The first law of thermodynamics** is a manifestation of the principle of conservation of energy.

- The Mathematical Expression of the first law states that the change in the internal energy (\(\Delta U\)) of a system is equal to the heat (\(q\)) absorbed or released by the system plus the work done on or by the system. The mathematical equation of the first law is:

\[
\Delta U = q + w
\]
• Regarding heat (q), the convention states that if the system absorbs heat from its surroundings, its internal energy increases and the amount of heat is given a positive sign (q is positive) but if the system releases heat to its surroundings, its internal energy decreases and the amount of heat is given a negative sign (q is negative).

• Regarding work (w), the convention states that if the surroundings do work on the system, then the system internal energy increases and the amount of work is given a positive sign (w is positive) but if the system do work on its surroundings, then the system internal energy decreases and the amount of work is given a negative sign (w is negative).

• According to this convention the change in the internal energy of a system (ΔU) depends on the sign and the value of the heat (q) and the work (w).

• The positive sign reflects an increase in the energy of the system and vice versa.

• The following table summarizes this thermodynamics’ convention.

<table>
<thead>
<tr>
<th>SIGN OF q</th>
<th>SIGN OF w</th>
<th>SIGN OF ΔU</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>+</td>
<td>–</td>
<td>either + or –</td>
</tr>
<tr>
<td>–</td>
<td>+</td>
<td>either + or –</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

• We discussed in section 1.17 (page 21) that if the absorption (or release) of heat occurs at constant volume no PV-work is done and w = 0 but if it occurs at constant pressure a PV-work is done and w ≠ 0.

• As an example of the different ways of transferring energy, consider a chemical reaction that produces gases, such as the reaction of an acid with zinc:

\[
\text{Zn(s) + 2HCl(aq) } \rightarrow \text{ZnCl}_2(\text{aq}) + \text{H}_2(\text{g})
\]

✓ The following figure shows on the left a piece of Zn on the bottom of the cylinder and a flask containing a solution of HCl and shows on the right the flask inverted and the reaction between Zn and HCl has produced H2 which pushed the piston upward razing a weight in the surroundings.
In this case, energy has migrated to the surroundings as a result of the system doing work because a weight has been raised in the surroundings: that weight can now do more work, so it possesses more energy.

Some energy also migrates into the surroundings as heat. This can be detected by immersing the reaction vessel in an ice bath and noting that ice melts. We also can evaluate the quantity of melted ice.

Alternatively, we could let the same reaction take place in a vessel with a piston locked in position. No work will be done, because no weight is raised. However, because it will be found that more ice melts than in the first experiment, this means that more energy has migrated to the surroundings as heat.

- Because many chemical reactions produce gas, one very important type of work in chemistry is **expansion work**, the work done when a system expands against an opposing pressure.

- The action of acid on zinc mentioned previously is an example of a reaction in which expansion work is done in the process of making room for the gaseous product, hydrogen in this case.

- When a system expands through a volume ΔV against a constant external pressure $P_{ex}$ the work done is given by the following equation:

$$w = - P_{ex} \Delta V$$

- According to $w = - P_{ex} \Delta V$, the **external** pressure determines how much work a system does when it expands through a given volume:
  - the greater the external pressure, the greater the opposing force and the greater the work that a system does.
  - When the external pressure is zero, $w = 0$.

  - Expansion against zero external pressure is called **free expansion**.

**Example 3.1**

Calculate the work done by a system in which a reaction results in the formation of 1.0 mol CO$_2$(g) at 25°C and 100 kPa. *Hint.* The increase in volume will be 25 dm$^3$ under these conditions if the gas is treated as perfect.

**Solution**

$$w = - P_{ex} \Delta V$$

We need to know the change in volume ($\Delta V$).

The volume is increased by the value of CO$_2$(g) produced ($V_{CO_2}$).

$$\Delta V = V_{CO_2} = \frac{n \times R \times T}{P} = \frac{1 \text{ mol} \times 8.314 \text{ J/K mol} \times 288 \text{ K}}{100 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}}} = 0.0248 \frac{\text{J}}{\text{Pa}}$$

$$\Delta V = 0.0248 \frac{\text{J}}{\text{Pa}} \times \frac{1 \text{ Pa} \times \text{m}^3}{1 \text{ J}} = 0.0248 \text{ m}^3$$

$$w = - 100 \text{ kPa} \times \frac{1000 \text{ Pa}}{1 \text{ kPa}} \times 0.0248 \text{ m}^3 = 2480 \text{ Pa m}^3 = 2480 \text{ J}$$

$$w = - 2480 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -2.48 \text{ kJ}$$

- The equation “$w = - P_{ex} \Delta V$” shows us how to get the least expansion work from a system by reducing the external pressure to zero.
• But how can we achieve the greatest work for a given change in volume? According to equation \( w = -P_{ex} \Delta V \), the system does maximum work when the external pressure has its maximum value.
• The force opposing the expansion is then the greatest and the system must exert most effort to push the piston out. However, that external pressure cannot be greater than the pressure, \( P \), of the gas inside the system, for otherwise the external pressure would compress the gas instead of allowing it to expand.
• Therefore, maximum work is obtained when the external pressure is only infinitesimally less than the pressure of the gas in the system.
• In effect, the two pressures must be adjusted to be the same at all stages of the expansion.
• We call this balance of pressures a state of mechanical equilibrium. Therefore, we can conclude that a system that remains in mechanical equilibrium with its surroundings at all stages of the expansion does maximum expansion work.
• There is another way of expressing this condition: Because the external pressure is infinitesimally less than the pressure of the gas at some stage of the expansion, the piston moves out.
• However, suppose we increase the external pressure so that it became infinitesimally greater than the pressure of the gas; now the piston moves in. That is, when a system is in a state of mechanical equilibrium, an infinitesimal change in the pressure results in opposite directions of motion.
• A process that can be reversed by an infinitesimal change in a variable, in this case, the pressure, is said to be reversible.
• In everyday life “reversible” means a process that can be reversed; but in thermodynamics it has a stronger meaning, it means that a process can be reversed by an infinitesimal modification in some variable (such as the pressure). We can summarize this discussion by the following remarks:
  ✓ A system does maximum expansion work when the external pressure is equal to that of the system at every stage of the expansion (\( P_{ex} = P \)).
  ✓ A system does maximum expansion work when it is in mechanical equilibrium with its surroundings at every stage of the expansion.
  ✓ Maximum expansion work is achieved in a reversible change.
All three statements are equivalent, but they reflect different degrees of sophistication in the way the point is expressed.
• We cannot write down the expression for maximum expansion work simply by replacing \( P_{ex} \) in the equation \( w = -P_{ex} \Delta V \) by \( P \) (the pressure of the gas in the cylinder) because, as the piston moves out, the pressure inside the system falls.
• To make sure the entire process occurs reversibly, we have to adjust the external pressure to match the changing internal pressure.
• Suppose that we conduct the expansion isothermally (that is, at constant temperature) by immersing the system in a water bath held at a specified temperature.
• As we show in the equation \( w = -P_{ex} \Delta V \), the work of isothermal, reversible expansion of a perfect gas from an initial volume \( V_1 \) to a final volume \( V_2 \) at a constant temperature \( T \) is:

\[
w = -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2}
\]

\( n \) is the amount (number of moles) of gas molecules in the system.
• The equation “\(w = nRT \ln \frac{V_1}{V_2}\)” appears in thermodynamics in various uses that will be disclosed later on.

• The figure below shows that \(W\) of reversible isothermal expansion of a gas equals the area beneath the corresponding isotherm of \(P = \frac{nRT}{V}\) between the limits \(V_i\) and \(V_f\).

![Diagram](image-url)

• It is important to be able to interpret this equation rather than just remember it:
  1. In an expansion: \(V_2 > V_1\), \(\frac{V_2}{V_1} > 1\) and \(\ln \frac{V_2}{V_1} > 1\).

     Therefore, in an expansion, \(w\) is negative. That is what we should expect: energy *leaves* the system as the system does expansion work.

  2. For a given change in volume, we get more work the higher the temperature of the confined gas. That is also what we should expect: at high temperatures, the pressure of the gas is high, so we have to use a high external pressure, and therefore a stronger opposing force, to match the internal pressure at each stage.

• The following figure shows the work of reversible, isothermal expansion of a perfect gas.

• It appears from the figure that for a given change of volume and fixed amount of gas, the work is greater the higher the temperature.
Example 3.2
Calculate the work done when 1.0 mol Ar(g) confined in a cylinder of volume 1.0 dm³ at 25°C expands isothermally and reversibly to 2.0 dm³.

Solution

\[
\begin{align*}
    w &= -nRT \ln \frac{V_2}{V_1} \\
    &= -1 \text{ mol } \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \ln \frac{2 \text{ dm}^3}{1 \text{ dm}^3} \\
    &= 1717 \text{ J} = 1.72 \text{ kJ}
\end{align*}
\]

- The nature and the name of the heat absorbed or released at constant volume and at constant pressure are different.

3.2 Change in internal energy at constant volume and at constant pressure

- An important characteristic of the internal energy is that it is a state function. This simply means that it is a physical property that depends only on the present state of the system and is independent of the path by which that state was reached.
- If we were to change the temperature of the system, then change the pressure, then adjust the temperature and pressure back to their original values, the internal energy would return to its original value too.
- The fact that \( U \) is a state function implies that a change, \( \Delta U \), in the internal energy between two states of a system is independent of the path between them.
- If we climb a mountain between two fixed points, we make the same change in altitude regardless of the path we take between the two points. Likewise, if we compress a sample of gas until it reaches a certain pressure and then cool it to a certain temperature, the change in internal energy has a particular value.
- If, on the other hand, we change the temperature and then the pressure, but ensure that the two final values are the same as in the first experiment, then the overall change in internal energy is exactly the same as before.
- This path independence of the value of \( \Delta U \) is of the greatest importance in chemistry, as we shall soon see.
- Consider now an isolated system.
  ✓ No work can be done on or by an isolated system nor any kind of energy can be exchanged between it and its outsides. Therefore, the internal energy of an isolated system cannot change. That is,

  \[ \text{The internal energy of an isolated system is constant.} \]
  
  ✓ This statement is the First Law of thermodynamics. It is closely related to the law of conservation of energy but allows for transfers of energy as heat as well as by doing work.
  ✓ The definition of \( \Delta U \) in terms of \( w \) and \( q \) points to a very simple method for measuring the change in internal energy of a system when a reaction takes place.
  ✓ The work done by a system when it pushes against a fixed external pressure is proportional to the change in volume.
  ✓ If we carry out a reaction in a container of constant volume, the system can do no expansion work and provided it can do no other kind of work (such as electrical work), \( w = 0 \) and \( \Delta U = q \).
\[ \Delta U = q_v \]

The subscript “\(v\)” signifies that the volume of the system is constant.

- An example of a chemical system that can be approximated as a constant-volume container is an individual biological cell.
- To measure a change in internal energy, we should use a calorimeter that has a fixed volume and monitor the energy released as heat \((q < 0)\) or supplied \((q > 0)\).
- The figure below is an illustration of a **bomb calorimeter** which is an example of a constant-volume calorimeter: it consists of a sturdy, sealed, constant-volume vessel in which the reaction takes place, and a surrounding water bath.

![Bomb Calorimeter Diagram](image)

- To ensure that no heat escapes unnoticed from the calorimeter, it is immersed in a water bath with a temperature adjusted to match the rising temperature of the calorimeter.
- The fact that the temperature of the bath is the same as that of the calorimeter ensures that no heat flows from one to the other. That is, the arrangement is adiabatic.
- We can use equation “\(\Delta U = q_v\)” to obtain more insight into the heat capacity of a substance. The definition of heat capacity is given as \(C = \frac{q}{\Delta T}\).
- At constant volume, \(q\) may be replaced by the change in internal energy of the substance, so at constant volume:

\[ C_v = \frac{\Delta U}{\Delta T} \]

- In chapter 1, we defined that the change in enthalpy is the heat exchanged at constant temperature and pressure \((q_p)\). therefore,

\[ C_p = \frac{\Delta H}{\Delta T} \]
• The type of system we will discuss now is the simplest system which is “the perfect (ideal) gas”, and the type of work we will discuss is only the work of compression and expansion of an ideal gas (PV-work).

• The ideal gas is given by the following well-known equation:

\[ P \times V = n \times R \times T \]

• The equation of the PV-work is:

\[ w = -P \times \Delta V \]

We know for the equation “\( P \times V = n \times R \times T \)” that \( R \) is constant, therefore the value of \( P \times V \) remains constant unless the value of \( n, T \) or both is changed.

✓ If the change is in the value of \( n \), then:

\[
\begin{align*}
  w &= -P \times (V_2 - V_1) \\
  w &= - (P \times V_2) - (P \times V_1) \\
  w &= - (n_2 \times R \times T) - (n_1 \times R \times T) \\
  w &= -R \times T \times (n_2 - n_1) \\
  w &= -R \times T \times \Delta n_g
\end{align*}
\]

\[ w = -P \times \Delta V = -R \times T \times \Delta n_g \]

(Important note: the subscript \( g \) in \( \Delta n_g \) is to assert that the change is only in the number of moles gases)

✓ If the change is in the value of \( T \), then:

\[
\begin{align*}
  w &= - (P \times V_2) - (P \times V_1) \\
  w &= - (n \times R \times T_2) - (n \times R \times T_1) \\
  w &= -n \times R \times (T_2 - T_1) \\
  w &= -P \times \Delta V = -R \times T \times \Delta n_g = -n \times R \times \Delta T
\end{align*}
\]

• We already have discussed in section 1.17 (page 21) that if the absorption (or the release) of heat occurs at constant volume, no PV-work is done and \( w = 0 \) but if it occurs at constant pressure a PV-work is done and \( w \neq 0 \).

✓ \( \Delta U \) at constant volume

\[
\begin{align*}
  \Delta U &= q + w \\
  \Delta U &= q_v + 0 \\
  \Delta U &= q_v
\end{align*}
\]

This means that the heat transferred at constant temperature and volume (\( q_v \)) equals the change in internal energy of the gas.

✓ \( \Delta U \) at constant pressure

\[
\begin{align*}
  \Delta U &= q + w \\
  \Delta U &= q_p + w \\
  \Delta U &= q_p - P \times \Delta V = q_p - R \times T \times \Delta n_g = q_p - n \times R \times \Delta T
\end{align*}
\]

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This means that the heat transferred at constant temperature and pressure is $q_p$

✓ It is mentioned in chapter 1 (page 32) the heat absorbed or released by the system at constant temperature and pressure ($q_p$) equals the change in the enthalpy of the system ($\Delta H$). therefore,

$$\Delta U = \Delta H - P \times \Delta V = \Delta H - R \times T \times \Delta n_g = \Delta H - n \times R \times \Delta T$$

**Example 3.3**

Calculate $\Delta E$ for the following reaction at 1 atm and 25°C:

$$2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g) \quad \Delta U = -563.5\text{kJ}$$

**Solution**

$$\Delta H = \Delta U + R \times T \times \Delta n_g$$

$$\Delta n_g = (2 \text{ mol}) - (3 \text{ mol}) = -1 \text{ mol}$$

$$\Delta H = (-563.5 \text{ kJ}) + (8.314 \times 10^{-3} \text{ kJ/mol K} \times 298 \text{ K} \times -1 \text{ mol}) = -566.0 \text{ kJ}$$

**Practice Exercise**

What is $\Delta U$ for the formation of 1 mole of CO at 1 atm and 25°C?

$$\text{C(graphite)} + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}(g) \quad \Delta H = -110.5 \text{ kJ}$$

### 3.3 Applications of the first law

**RECOGNIZE THE SYMBOLS BELOW**

- Number of moles = $n$
- External pressure = $P_{ext}$
- Initial pressure = $P_1$
- Final pressure = $P_2$
- Initial volume = $V_1$
- Final volume = $V_2$
- Initial molarity = $M_1$
- Final molarity = $M_2$
- Initial temperature = $T_1$
- Final temperature = $T_2$
- Work done = $w$
- Heat capacity = $C$
- Heat capacity at constant volume = $C_v$
- Heat capacity at constant pressure = $C_p$
- Molar heat capacity = $C_m$
- Molar heat capacity at constant volume = $C_{m,v}$
- Molar heat capacity at constant pressure = $C_{m,p}$
- Heat transferred = $q$
- Heat transferred at constant volume = $q_v$
- Heat transferred at constant pressure = $q_p$
- Change in internal energy = $\Delta U$
- Change in enthalpy = $\Delta H$

#### 3.3.1 The isothermal processes if the system is a perfect (ideal) gas

$$\Delta T = T_2 - T_1 = 0$$

The values of $\Delta U$, $\Delta H$, $w$, and $q$, are as follows:
1) $\Delta U$

The internal energy of the perfect gas solely and exclusively depends on its kinetic energy, and we know that if the temperature of the gas is constant its kinetic energy is constant and consequently its internal energy is constant. Therefore,

$$\Delta U = 0$$

2) $\Delta H$

We already knew from chapter 1 that:

$$q_p = C_p \times (T_2 - T_1)$$

Therefore, at constant temperature:

$$\Delta H = 0$$

3) $q$ and $w$

From the first law $\Delta U = q + w$ and because $\Delta U = 0$ at constant temperature We deduce that at constant temperature:

$$q = -w$$

A) The value of “w” if the isothermal processes is reversible:

If, in addition to $T$, the gas amount is constant Boyle’s law “$P_1 V_1 = P_2 V_2$” applies and work can be calculated using the following equation:

$$w = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$$

B) The value of “w” if the isothermal processes is irreversible:

$$w = -P_{ext} (V_2 - V_1)$$

$$w = P_{ext} (V_1 - V_2) = P_{ext} \left( \frac{nRT}{P_1} - \frac{nRT}{P_2} \right)$$

$$w = nRT \left( \frac{P_{ext}}{P_1} - \frac{P_{ext}}{P_2} \right)$$

But if:

$$P_{ext} = P_2$$

$$w = nRT \left( \frac{P_2}{P_1} - 1 \right)$$

C) The difference between reversible and irreversible isothermal works:

$$w_{rev} - w_{irrev} = -\frac{nRT}{P_1P_2} (P_1 - P_2)^2$$

✓ $(P_1 - P_2)^2$ is always positive regardless which is higher P2 or P1.

✓ "$\frac{nRT}{P_1P_2} (P_1 - P_2)^2$" is always positive.
✓ This means that "\( w_{\text{rev}} - w_{\text{irrev}} \)" is always negative.

➢ **In expansion,**

\( w_{\text{rev}} - w_{\text{irrev}} \) is a negative sign
Both \( w_{\text{rev}} \) and \( w_{\text{irrev}} \) are negative
This means that the expansion work is higher when it is reversible

➢ **In compression,**

\( w_{\text{rev}} - w_{\text{irrev}} \) is a negative sign
Both \( w_{\text{rev}} \) and \( w_{\text{irrev}} \) are positive
This means that the compression work is higher when it is irreversible

---

**Example 3.4**

Calculate \( w, q, \Delta U \) and \( \Delta H \) as a result of the reversible expansion of 1 mol of an ideal gas at 27 °C from 2.28 m\(^3\) to 4.56 m\(^3\).

**Solution**

\[
\Delta U = \Delta H = 0
\]

\[
w = -q = nRT \ln \frac{V_1}{V_2}
\]

\[
w = 1 \text{ mol} \times 8.314 \times \frac{J}{\text{mol K}} \times 300 \text{ K} \times \ln \frac{2.28 \text{ m}^3}{4.56 \text{ m}^3} = -1729 \text{ J}
\]

\[
q = -w = +1729 \text{ J}
\]

**Practice exercise**

Calculate \( w, q, \Delta U \) and \( \Delta H \) as a result of the reversible compression of 40 g of O\(_2\)(g) at 21 °C from 0.5 atm to 3.5 atm.

---

**Example 3.5**

Calculate \( w, q, \Delta U \) and \( \Delta H \) as a result of the isothermal sudden expansion of 2 moles of an ideal gas from 10 atm and 0 °C to a pressure equals the external pressure which is 0.4 atm.

**Solution**

\[
\Delta U = \Delta H = 0
\]

\[
w = nRT \left( \frac{P_2}{P_1} - 1 \right)
\]

\[
w = 2 \text{ mol} \times 8.314 \times \frac{J}{\text{mol K}} \times 273 \text{ K} \times \left( \frac{0.4 \text{ atm}}{10 \text{ atm}} - 1 \right) = -4357.9 \text{ J}
\]

\[
q = -w = +4357.9 \text{ J}
\]

**Practice exercise**

Calculate \( w, q, \Delta U \) and \( \Delta H \) as a result of the isothermal sudden expansion of 2 moles of an ideal gas from 10 atm and 0 °C to 4 atm at against an external pressure of 1 atm.

---

### 3.3.2 The adiabatic processes if the system is a perfect (ideal) gas

- In the adiabatic processes no release or absorbance of heat:

\[
q = 0
\]

\[
T_1 \neq T_2
\]

\[
P_1 V_1^{\gamma} = P_2 V_2^{\gamma}
\]

\[
\frac{c_{\text{m,p}}}{c_{\text{m,v}}} P_1 V_1^{\gamma} = \frac{c_{\text{m,p}}}{c_{\text{m,v}}} P_2 V_2^{\gamma}
\]

\[
P_1 V_1^{2.5R} = P_2 V_2^{2.5R}
\]

\[
P_1 V_1^{2.5R} = P_2 V_2^{2.5R}
\]

\[
P_1 V_1^{1.67} = P_2 V_2^{1.67}
\]
Example 3.6
Calculate the final pressure as a result of the adiabatic reversible compression of a fixed quantity of an ideal gas initially at 9.5 atm 4.5 dm$^3$ if its final a volume became 3.5 dm$^3$.
Solution
\[ P_1 V_1^{1.67} = P_2 V_2^{1.67} \]
\[ 9.5 \text{ atm} \times 4.5^{1.67} \text{ dm}^3 = P_2 \times 3.5^{1.67} \text{ dm}^3 \]
\[ P_2 = 14.45 \text{ atm} \]

Practice exercise
Calculate the final pressure as a result of the adiabatic reversible expansion of a fixed quantity of an ideal gas initially at 9.5 atm 3.5 dm$^3$ if its final volume became 4.5 dm$^3$.

A) The value of “w” if the adiabatic processes is reversible:
The values of $\Delta U$, $\Delta H$, and $w$, are as follows:
1) $\Delta U$ and $w$
Because $\Delta U = q + w$, and $q = 0$ the values of $\Delta U$ and $w$ are equal in the adiabatic process and can be calculated using the heat capacity at constant volume using the following equation:
\[ \Delta U = w = C_v \Delta T \]

2) $\Delta H$
Because $\Delta H$ equals the heat absorbed or released at constant pressure, it can be calculated using the equation mentioned in chapter 1:
\[ \Delta H = C_p \Delta T \]

- It is clear that the main task in adiabatic processes is knowing the temperature after the change ($T_2$) which depends on whether the adiabatic process is reversible or irreversible.

A) The value of $T_2$ in the adiabatic reversible processes

\[ T_1 V_1^{\frac{R}{C_m,v}} = T_2 V_2^{\frac{R}{C_m,v}} \]
\[ T_1 V_1^{1.67} = T_2 V_2^{1.67} \]
\[ T_1 V_1^{0.67} = T_2 V_2^{0.67} \]

********************

\[ \frac{T_1}{P_1^{\frac{R}{C_p}}} = \frac{T_2}{P_2^{\frac{R}{C_p}}} \]
\[ \frac{T_1}{P_1^{1.67}} = \frac{T_2}{P_2^{1.67}} \]
\[ \frac{T_1}{P_1^{0.4}} = \frac{T_2}{P_2^{0.4}} \]

********************

\[ T_2 = T_1 \times \left( \frac{V_1}{V_2} \right)^{0.67} = T_1 \times \left( \frac{P_2}{P_1} \right)^{0.4} \]
Example 3.7
Calculate the final temperature of 2.5 mole of an ideal gas after an adiabatic reversible compression from 4.5 dm$^3$ at 298 K to 3.5 dm$^3$. Calculate also q, $\Delta U$, w, and $\Delta H$.

($C_{m,v} = 12.471$ J/mol K)

Solution

\[ T_2 = T_1 \times \left( \frac{V_1}{V_2} \right)^{0.67} \]

\[ T_2 = 298 \text{ K} \times \left( \frac{4.5 \text{ dm}^3}{3.5 \text{ dm}^3} \right)^{0.67} \]

\[ T_2 = 352.65 \text{ K} \]

\[ q = 0 \]

\[ \Delta U = C_v \times \Delta T = C_{m,v} \times n \times \Delta T \]

\[ \Delta U = 12.471 \ \frac{\text{J}}{\text{mol K}} \times 2.5 \text{ mol} \times (352.65 - 298) \text{ K} \]

\[ \Delta U = 1703.85 \text{ J} \]

\[ w = \Delta U = 1703.85 \text{ J} \]

\[ \Delta H = C_p \times \Delta T = C_{m,p} \times n \times \Delta T = (C_{m,v} + R) \times n \times \Delta T \]

\[ \Delta H = (12.471 \ \frac{\text{J}}{\text{mol K}} + 8.314 \ \frac{\text{J}}{\text{mol K}}) \times 2.5 \text{ mol} \times (352.65 - 298) \text{ K} \]

\[ \Delta H = 2839.75 \text{ J} \]

Practice exercise
Calculate the final temperature of 2.5 mole of an ideal gas after an adiabatic reversible compression from 9.5 atm at 298 K to 14.45 atm.

B) The value of $T_2$ in the adiabatic irreversible processes:

\[ T_2 = T_1 \times \left( \frac{C_{m,v} + R \frac{p_{ext}}{p_1}}{C_{m,v} + R \frac{p_{ext}}{p_2}} \right) = T_1 \times \left( \frac{1.5R + R \frac{p_{ext}}{p_1}}{1.5R + R \frac{p_{ext}}{p_2}} \right) \]

\[ T_2 = T_1 \times \left( \frac{1.5 + \frac{p_{ext}}{p_1}}{1.5 + \frac{p_{ext}}{p_2}} \right) \]

But if $p_{ext} = p_2$:

\[ T_2 = T_1 \times \left( \frac{1.5 + \frac{p_2}{p_1}}{1.5 + 1} \right) \]

\[ T_2 = T_1 \times \left( \frac{1.5 + \frac{p_2}{p_1}}{2.5} \right) \]

\[ \frac{p_2}{p_1} = \left( \frac{V_1}{V_2} \right)^{1.67} \]

\[ T_2 = T_1 \times \left( \frac{1.5 + \left( \frac{V_1}{V_2} \right)^{1.67}}{2.5} \right) \]

Example 3.8
If the external pressure and final pressure of the gas are equal, calculate the final temperature of 2.5 mole of an ideal gas after an adiabatic irreversible compression from 4.5 dm$^3$ at 298 K to 3.5 dm$^3$. Calculate also q, $\Delta U$, w, and $\Delta H$.

($C_{m,v} = 12.471$ J/mol K)

Solution

\[ T_2 = T_1 \times \left( \frac{1.5 + \left( \frac{V_1}{V_2} \right)^{1.67}}{2.5} \right) \]
\[
T_2 = 298 \text{ K} \times \left(1.5 + \frac{4.5 \text{ dm}^3}{3.5 \text{ dm}^3} \right)^{1.67} \times \frac{2.5}{2.5}
\]

\[
T_2 = 404.52 \text{ K}
\]

\[
q = 0
\]

\[
\Delta U = C_v \times \Delta T = C_{m,v} \times n \times \Delta T
\]

\[
\Delta U = 12.471 \text{ J/mol K} \times 2.5 \text{ mol} \times (404.52 - 298) \text{ K}
\]

\[
\Delta U = 3321.03 \text{ J}
\]

\[
w = \Delta U = 3321.03 \text{ J}
\]

\[
\Delta H = C_p \times \Delta T = C_{m,p} \times n \times \Delta T = (C_{m,v} + R) \times n \times \Delta T
\]

\[
\Delta H = \left(12.471 \text{ J/mol K} + 8.314 \text{ J/mol K}\right) \times 2.5 \text{ mol} \times (404.52 - 298) \text{ K}
\]

\[
\Delta H = 5535.05 \text{ J}
\]

**Practice exercise**

If the external pressure is 1.2 atm, calculate the final temperature of 2.5 mole of an ideal gas after an adiabatic irreversible compression from 13.59 atm at 298 K to 23.72 atm. Calculate also \( q, \Delta U, w, \) and \( \Delta H \).

\((C_{m,v} = 12.471 \text{ J/mol K})\)
# Table of Summarization

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TABLE OF COMPARISON BETWEEN VARIABLES IN EXPANSION AND IN COMPRESSION

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<td>Work done is more when the process is isothermal regardless whether it is reversible or irreversible.</td>
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<tr>
<td>Final volume in an isothermal process is the same in reversible and irreversible processes, and this makes $\Delta U$ and $\Delta H$ the same too.</td>
<td>Final volume and temperature in an adiabatic process are not the same in reversible and irreversible processes, and this what makes $\Delta U$ and $\Delta H$ different.</td>
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<td>In an adiabatic, decrease in U, which equals the work done, decreases T in reversible process more than in irreversible process.</td>
<td>In an adiabatic, increase in U, which equals the work done, increases T in irreversible process more than in reversible process.</td>
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QUESTIONS AND PROBLEMS

1. Calculate w, q, ΔU and ΔH as a result of the reversible expansion of 1 mole of an ideal gas at 27 ºC from 2.28 m³ to 4.56 m³.

2. Calculate the minimum work needed to compress 16 g of O₂(g) from 1.01325 × 10⁵ Pa to 1.01325 × 10⁷ Pa at 300K. Calculate, also, q, ΔU and ΔH.

3. Calculate w, q, ΔU and ΔH as a result of vaporization of 1 mole of benzene at its normal boiling point (80.02 ºC) against a constant external pressure of 101325 Pa, knowing that the vaporization of 1 g of benzene at constant temperature and pressure requires 395 J.

4. Calculate w, q, ΔU and ΔH as a result of the isothermal sudden expansion of 2 moles of an ideal gas from 10 atm and 0 ºC to 0.4 atm.

5. Calculate q, w, P₂, ΔU and ΔH as a result of the isothermal quick expansion of 5 moles of an ideal gas from 10 atm to 4 atm against an external pressure of 1 atm.

6. Calculate q, w, P₂, ΔU and ΔH as a result of the adiabatic reversible expansion of a quantity of an ideal gas having an initial volume of 1.43 dm³ at 303975 Pa and 298 K, if its final volume becomes 2.86 dm³.

7. Calculate q, w, ΔU and ΔH as a result of the sudden expansion of 0.1 kg of N₂(g) to 1 × 10⁴ Pa without exchanging heat with surroundings, knowing that its initial temperature and pressure were 298 K and 3 × 10⁴ Pa, and Cᵥ,m = 12.471 J k⁻¹ mol⁻¹.

8. Calculate q, w, ΔU and ΔH as a result of expansion of 1 mole of an ideal gas at 300 K from 1 × 10⁶ Pa to 1 × 10⁵ Pa, knowing that Cᵥ,m = 12.471 J k⁻¹ mol⁻¹, if the expansion occurs in a process that is:
   A) isothermal and reversible.   B) isothermal and irreversible.
   C) adiabatic and reversible.   D) adiabatic and irreversible.
4. THERMOCHEMISTRY
4. THERMOCHEMISTRY

4.1 Introduction

- The heat absorbed or released, at constant temperature and constant volume or pressure as a result of any change is called "heat of change".
- The term "heat of change" is rarely used, instead, "heat of reaction" is the mostly used.
- The heat absorbed or released, at constant temperature and volume, equals the increase or decrease in the internal energy:

\[ q_v = \Delta U \]

- The heat absorbed or released, at constant temperature and pressure, equals the increase or decrease in the enthalpy:

\[ q_p = \Delta H \]

- Definition of the enthalpy was given in chapter 1 (page 32).
- Because most processes are carried out at constant temperature and pressure, rather than at constant temperature and volume, changes in enthalpy, \( \Delta H \), is more important to chemists than changes in internal energy, \( \Delta U \).
- The change in the enthalpy, \( \Delta H \), has several names: enthalpy of change, heat of change, enthalpy of reaction, heat of reaction. Among all these names, enthalpy of reaction is the term used commonly and is denoted \( \Delta H_{\text{rxn}} \).

4.2 Enthalpy of reaction (\( \Delta H_{\text{rxn}} \))

- Any system in a certain state has a certain amount of energy stored in it as kinetic energy and is called the heat content of the system or the enthalpy of the system and is denoted by \( H \).
- Let the system be (A).
- Changing this system from its initial state, \( A_1 \), to its final state, \( A_2 \), at constant temperature and pressure, will change its enthalpy from \( H_1 \) to \( H_2 \).
- This means that a change (an increase or a decrease) in enthalpy by \( \Delta H \) has occurred and:

\[ \Delta H = H_2 - H_1 \]

- If:

\[
\begin{align*}
\text{Temperature} &= 25 ^\circ \text{C} = 298 \text{ K} \\
\text{Pressure} &= \text{the standard pressure} = 1 \text{ atm} = 101325 \text{ Pa}
\end{align*}
\]

Then the initial enthalpy is the initial standard enthalpy (\( H_1^\circ \)), the final enthalpy is the final standard enthalpy (\( H_2^\circ \)) and the change in enthalpy is the change in the standard enthalpy (\( \Delta H_{\text{rxn}}^\circ \))

\[ \Delta H_{\text{rxn}}^\circ = H_2^\circ - H_1^\circ \]

- \( \Delta H_{\text{rxn}}^\circ \) is called the standard change in enthalpy of reaction.
• Depending on whether \( H_2 \) is more or less than \( H_1 \), \( \Delta H \) will have either a positive or a negative sign.
  ✓ If \( \Delta H \) is positive the change or the reaction is described as **endothermic**.
  ✓ If \( \Delta H \) is negative the change or the reaction is described as **exothermic**.

\[
\Delta H = + \text{ve (endothermic)} \\
\Delta H = - \text{ve (exothermic)}
\]

4.3 Thermochemical equation and the units of \( \Delta H \)

• **First: Thermochemical equation**
  ✓ Thermochemical equation is an equation which shows, in addition to what a regular balanced chemical equation shows, both the physical state of each substance written immediately after the substance between brackets \( (s), (L), (g), (aq); \) and the enthalpy of reaction, \( (\Delta H) \), shown immediately after the equation. The following is just an example:

\[
2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(L) \quad \Delta H = + 197 \text{ kJ}
\]

So, any thermochemical equation has the following **musts**:

a) It **must** be balanced.

b) State of each substance **must** be specified.

c) The enthalpy of reaction, \( (\Delta H) \), **must** be written.

✓ The unit of \( \Delta H \) is the unit of energy. It is usually \( \text{kJ} \).

✓ Thermochemical equation represents a reaction at a certain temperature and pressure. Temperature and pressure are usually 25 \(^\circ\)C and 1 atm. If the reaction is at these condition \( \Delta H_{\text{rxn}} \) is the symbol of its enthalpy and is called the standard enthalpy of the reaction.

✓ If the reaction is not at these condition, \( \Delta H_{\text{rxn}} \) is the symbol of its enthalpy and is called the enthalpy of the reaction and the conditions then are specified.

✓ Thermochemical equation can be reversed. This means that substances on the left become on the write, substances on the write become on the left, and the sign of \( \Delta H \) takes the opposite sign. For example, if:

\[
2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(L) \quad \Delta H = + 197 \text{ kJ}
\]

its correct reverse is:

\[
\text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(L) \rightarrow 2\text{NaHCO}_3(s) \quad \Delta H = - 197 \text{ kJ}
\]

**Example 4.1**

Knowing that:

\[
4\text{NO(g)} + 6\text{H}_2\text{O(L)} \rightarrow 4\text{NH}_3(g) + 5\text{O}_2(g) \quad \Delta H = + 1170 \text{ kJ}
\]

What is \( \Delta H \) of the following reaction:

\[
4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(L)} \quad \Delta H = ?
\]

**Solution**

Because the reaction in question is the opposite of the given reaction:

\[
4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(L)} \quad \Delta H = - 1170 \text{ kJ}
\]

**Practice exercise**

Knowing that:

\[
\text{N}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{NO}_2(L) \quad \Delta H = + 67.6 \text{ kJ}
\]

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What is $\Delta H$ of the following reaction:
$$2\text{NO}_2(\text{L}) \rightarrow \text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \quad \Delta H = ?$$

✓ Thermochemical equation can be multiplied by any value (0.5, 1.5, 2, etc.). This will change the coefficients of substances. Accordingly, the value of $\Delta H$ will change too. For example, if the following equation:
$$2\text{NaHCO}_3(\text{s}) \rightarrow \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{L}) \quad \Delta H = + 197 \text{ kJ}$$
is multiplying by 0.5, 1.5, or 2, the result will be the following thermochemical equations:
$$\text{NaHCO}_3(\text{s}) \rightarrow 0.5\text{Na}_2\text{CO}_3(\text{s}) + 0.5\text{CO}_2(\text{g}) + 0.5\text{H}_2\text{O}(\text{L}) \quad \Delta H = + 98.5 \text{ kJ}$$
$$3\text{NaHCO}_3(\text{s}) \rightarrow 1.5\text{Na}_2\text{CO}_3(\text{s}) + 1.5\text{CO}_2(\text{g}) + 1.5\text{H}_2\text{O}(\text{L}) \quad \Delta H = + 295.5 \text{ kJ}$$
$$4\text{NaHCO}_3(\text{s}) \rightarrow 2\text{Na}_2\text{CO}_3(\text{s}) + 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{L}) \quad \Delta H = + 394 \text{ kJ}$$

Note that the values of $\Delta H$ is also multiplied by the same number.

Example 4.2
Knowing that:
$$\text{N}_2(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{L}) \quad \Delta H = + 67.6 \text{ kJ}$$

What is $\Delta H$ of the following reaction:
$$4\text{NO}_2(\text{L}) \rightarrow 2\text{N}_2(\text{g}) + 4\text{O}_2(\text{g}) \quad \Delta H = ?$$

Solution
Because the reaction in question is half of the opposite of the given reaction, the value of its the $\Delta H$ is:
$$2\text{NH}_3(\text{g}) + 2.5\text{O}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + 3\text{H}_2\text{O}(\text{L}) \quad \Delta H = - 585 \text{ kJ}$$

Practice exercise
Knowing that:
$$\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g}) \quad \Delta H = -2035 \text{ kJ}$$
$$3\text{H}_2\text{O}(\text{g}) \rightarrow 3\text{H}_2\text{O}(\text{L}) \quad \Delta H = -132 \text{ kJ}$$
$$3\text{H}_2\text{O}(\text{L}) \rightarrow 3\text{H}_2(\text{g}) + 1.5\text{O}_2(\text{g}) \quad \Delta H = 858 \text{ kJ}$$
$$2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g}) \quad \Delta H = 36 \text{ kJ}$$

the result is following equation:
$$2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ}$$

✓ Thermochemical equations can be added together to produce a new thermochemical equation with a $\Delta H$ that is equal to the sum of all $\Delta H$ values of these equations. For example, if we sum the following equations:

$$\text{B}_2\text{H}_6(\text{g}) + 3\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g}) \quad \Delta H = -2035 \text{ kJ}$$
$$3\text{H}_2\text{O}(\text{g}) \rightarrow 3\text{H}_2\text{O}(\text{L}) \quad \Delta H = -132 \text{ kJ}$$
$$3\text{H}_2\text{O}(\text{L}) \rightarrow 3\text{H}_2(\text{g}) + 1.5\text{O}_2(\text{g}) \quad \Delta H = 858 \text{ kJ}$$
$$2\text{B}(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow \text{B}_2\text{H}_6(\text{g}) \quad \Delta H = 36 \text{ kJ}$$

the result is following equation:
$$2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ}$$

✓ This fact is known as "**Hess's Law**" or "**Hess's Law of Heat Summation**". This law is stated in many different ways such as:

➢ "**Enthalpy of a reaction is the same regardless of the way it is carried out.**"
"If a reaction takes place in several steps then its enthalpy is the sum of the enthalpies of these steps."

"The heat evolved or absorbed in a chemical process is the same whether the process takes place in one step or in several steps."

Example 4.3
Knowing that:
1) \(2\text{C(graph)} + 3\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH(L)}\) \(\Delta H = -277\text{ kJ}\)
2) \(\text{H}_2\text{O(L)} \rightarrow \text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g})\) \(\Delta H = + 285.8\text{ kJ}\)
3) \(\text{C(graph)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})\) \(\Delta H = -393.5\text{ kJ}\)

Calculate \(\Delta H\) of the following reaction:
4) \(\text{CH}_3\text{CH}_2\text{OH(L)} + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O(L)}\)

Solution
First reverse the first equation, reverse the second equation and multiply by 3 and finally multiply the third equation by 2, and finally add these equations together:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{OH(L)} & \rightarrow 2\text{C(graph)} + 3\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \quad \Delta H = +277\text{ kJ} \\
3\text{H}_2(\text{g}) + 1.5\text{O}_2(\text{g}) & \rightarrow 3\text{H}_2\text{O(L)} \quad \Delta H = -857.4\text{ kJ} \\
2\text{C(graph)} + 2\text{O}_2(\text{g}) & \rightarrow 2\text{CO}_2(\text{g}) \quad \Delta H = -787\text{ kJ}
\end{align*}
\]

\(\Delta H = -1367.4\text{ kJ}\)

Practice exercise
Knowing that:
\(\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O(L)}\) \(\Delta H = -890.34\text{ kJ}\)
\(\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O(L)}\) \(\Delta H = -285.84\text{ kJ}\)
\(\text{C(graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})\) \(\Delta H = -393.5\text{ kJ}\)

calculate \(\Delta H\) and \(\Delta U\) of the following reaction:
\(\text{C(graphite)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})\)

Second: The units of \(\Delta H\)
✓ Let us look to the following thermochemical equation:

\[
2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273\text{ kJ}
\]

What does \(-1273\text{ kJ}\) mean?
It means that in this reaction, 1273 kJ is released per 2 moles of \(\text{B}_2(\text{s})\).
It also means that in this reaction, 1273 kJ is released per 1.5 mole of \(\text{O}_2(\text{g})\).
It also means that in this reaction, 1273 kJ is released per 1 mole of \(\text{B}_2\text{O}_3(\text{s})\).
✓ In thermochemical equations the unit of \(\Delta H\) is \(\text{kJ}\) not \(\text{kJ/mol}\).
✓ Is the following thermochemical equation written accurately?

\[
2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273\text{ kJ/mol of B}_2\text{O}_3(\text{s})
\]

The answer is yes.
✓ Is the following thermochemical equation written accurately?

\[
2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273\text{ kJ}/1.5 \text{ mol of O}_2(\text{g})
\]

The answer is yes.
✓ Is the following thermochemical equation written accurately?

\[
2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273\text{ kJ}/2 \text{ mol of B}_2(\text{s})
\]
The answer is yes.
✓ Is the following thermochemical equation written accurately?

\[ 2\text{B}_2(\text{s}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{B}_2\text{O}_3(\text{s}) \quad \Delta H = -1273 \text{ kJ/mol} \]

The answer is a big NO. The reason is due to our knowledge that "mol" is the unit of the amount of the substance, and when we say "per mol" we must specify per mole of what substance.
✓ It is true that we see this inaccurate writing of thermochemical equations in textbooks, references and even research papers. However, this does mean that it is an accurate way of writing a thermochemical equation. It can be accurate in only one case where all coefficient in the equation are one.

4.4 Factors affecting the enthalpy of reaction

1) Chemical nature of substances
The heat content of a substance differs from that of any other substance. This makes the amount of heat absorbed (or released) different as result of changes occurring for different substances. For example, dissociation of one mole of water vapor to hydrogen gas and oxygen gas requires 285.83 kJ, while dissociation of the same amount of hydrogen sulfide gas at the same conditions to hydrogen gas and solid sulfur requires 20.36 kJ:

\[ \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = 241.82 \text{ kJ} \]
\[ \text{H}_2\text{S}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{8}\text{S}_8(\text{s}) \quad \Delta H = 26.36 \text{ kJ} \]

The reason behind this is that the enthalpy (heat content) of water vapor is different from that of hydrogen sulfide gas; and the enthalpy (heat content) of oxygen gas is different from that solid sulfur.

2) Physical nature of substances (solid, liquid, gas, and aqueous)
The heat content of a substance in its solid state is lower than in its liquid state and much lower than in its gaseous state. For example, dissociation of one mole of water requires 241.82 kJ, the same amount of liquid water at the same conditions requires 285.80 kJ dissociate:

\[ \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = 241.82 \text{ kJ} \]
\[ \text{H}_2\text{O}(\text{L}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = 285.80 \text{ kJ} \]

The reason behind this is that the enthalpy (heat content) of water vapor is higher than that of liquid water.

3) Amount of substance (number of moles of substance)
The enthalpy of reaction depends on the amount of the substance. The following equations shows that the dissociation of one mole of water vapor requires the absorption of 241.82 kJ of heat, while the dissociation of two moles of water vapor at the same conditions requires 483.64 kJ.

\[ \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \quad \Delta H = 241.82 \text{ kJ} \]
\[ 2\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \quad \Delta H = 483.64 \text{ kJ} \]
4) **Temperature**
The heat content of a substance at a certain temperature differs from that at any other temperature. Therefore, the enthalpy of a certain and specified reaction differs if it is done at different temperature. This effect of temperature will be discussed in more details later.

5) **Pressure**
The heat content of a substance at a certain pressure differs from that at any other pressure. Therefore, the enthalpy of a certain and specified reaction differs if it is done at different pressure. Also, this effect of pressure will be discussed in more details later.

**Example 4.5**
Knowing that:

\[ 2\text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(L) \quad \Delta H = + 197 \text{ kJ} \]

Calculate the

a) The quantity of heat absorbed, \( q \), as a result of dissociating 0.4 mol of \( \text{NaHCO}_3(g) \).

b) The quantity of heat produced, \( q \), as a result of producing 54 g of \( \text{H}_2\text{O}(g) \).

**Solution**

a) From the equation:

\[ 2 \text{ mol NaHCO}_3(s) \Rightarrow + 197 \text{ kJ} \]

\[ 0.4 \text{ mol NaHCO}_3(s) \Rightarrow q \]

\[ q = 0.4 \text{ mol} \times \frac{197 \text{ kJ}}{2 \text{ mol}} = 39.4 \text{ kJ} \]

b) From the equation:

\[ 1 \text{ mol H}_2\text{O}(s) \Rightarrow + 197 \text{ kJ} \]

\[ \frac{54 \text{ g}}{18 \text{ g mol}^{-1}} = 3 \text{ mol H}_2\text{O}(s) \Rightarrow q \]

\[ q = 3 \text{ mol} \times \frac{197 \text{ kJ}}{1 \text{ mol}} = 591 \text{ kJ} \]

**Practice exercise**
Knowing that:

\[ \text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g) \quad \Delta H = -2035 \text{ kJ} \]

Calculate the

a) The quantity of heat released, \( q \), as a result of oxidation of 0.4 mol of \( \text{B}_2\text{H}_6(g) \).

b) The quantity of heat produced, \( q \), as a result of producing 54 g of \( \text{H}_2\text{O}(g) \).

### 4.5 Enthalpies of physical changes and chemical changes

- Physical changes are called **transitions** while chemical changes are called **reactions**. However, both physical changes and chemical changes are often called "reactions".

- Enthalpies of physical transitions and chemical reactions carry the same names of the physical transitions and of the chemical reactions, and denoted "\( \Delta H_{\text{rxn}} \)". where, "\( \Delta H \)" is the enthalpy of change and the subscript "\( \text{rxn} \)" stands for the word "reaction"; and it changes depending on the type of change taking place, for example:
  - If the change is the vaporization of a liquid, its enthalpy is called enthalpy of vaporization and denoted "\( \Delta H_{\text{vap}} \)".
If the change is the sublimation of a solid, its enthalpy is called enthalpy of sublimation and denoted "\(\Delta H_{\text{subl}}\).

If the change is the chemical reaction called “combustion” its enthalpy is called enthalpy of combustion and denoted "\(\Delta H_{\text{comb}}\).

If the change is the chemical reaction of hydrogenation, its enthalpy is called enthalpy of hydrogenation and is denoted "\(\Delta H_{\text{hydrog}}\).

If the physical or the chemical change is at the standard conditions, i.e. at 1 atm, and at 298 K, its enthalpy is called "standard enthalpy of reaction" and denoted "\(\Delta H_{\text{rxn}}\)." Here we have the “dot” superscript "°" which means that the change is at standard conditions.

4.5.1 Enthalpies of physical changes

In any physical change no reactant disappears and no new product appears. i.e. no chemical changes occur. The substance before and after the physical change occur is the same substance but its physical form, state, appearance or existence changes.

The physical changes that will be discussed are:
1) Crystal transition which is changing the crystal structure of a solid to another crystal structure.
2) Fusion of a solids.
3) Vaporization of liquids.
4) Sublimation of a solids.
5) Breaking bonds between atoms of the same element. Here we confined breaking bonds to those between the atoms of the same element because breaking bond between atoms of in compounds is in fact a chemical change. However, when we come to talk about breaking bonds we will include these bonds in our discussion.
6) Atomization
7) Electron loss from elements (usually called ionization).
8) Electron gain by elements (usually called electron affinity).
9) Dissolving a solute in a solvent.

According to the previous point, in physical changes no new chemical bonds are formed and no new substances are formed.

A phase is a specific state of matter that is uniform throughout in composition and physical state.

The liquid and vapor states of water are two of its phases. The term “phase” is more specific than “state” because a substance may exist in more than one solid form, each one of which is a solid phase. Thus, when the element sulfur is in its solid phase it may be found as rhombic sulfur form or as monoclinic sulfur form; these two forms are in the solid phase but they differ in the manner in which the S₈ molecules stack together.

Many substances exist in a variety of solid phases:
- Carbon, for instance, exists as graphite, diamond, and a variety of forms based on fullerene structures.
- Calcium carbonate exists as calcite and aragonite.
- There are at least twelve forms of ice; the last was discovered in 2006.

No substance has more than one gaseous phase, so “gas phase” and “gaseous state” are effectively synonyms.

The only substance that exists in more than one liquid phase is helium.
The conversion of one phase of a substance to another phase is called a phase transition:
✓ Vaporization (liquid → gas) is a phase transition
✓ Transition between solid phases (rhombic sulfur → monoclinic sulfur) is a phase transition.

Of course, any physical change, at constant temperature and pressure, is accompanied by an absorbance or a release of a quantity of heat called “enthalpy of transition”. Although we know that any physical change is not a chemical reaction, its enthalpy is sometimes called enthalpy of reaction. Not all chemists are bound by the terms they know. Enthalpy of transition is denoted as $\Delta H_{\text{trans}}$.

If the physical change is at the standard pressure, it is called the standard enthalpy of transition, $\Delta H_{\text{trans}}^\circ$.

Types of physical transitions is limited and the following is a discussion of the enthalpies of the different physical changes.

**First: Enthalpies of phase transitions**

1) **Enthalpy of crystal transition, and standard enthalpy of crystal transition**
✓ Enthalpy of crystal transition is the quantity of heat absorbed or released, at constant temperature and pressure, as a result of changing the crystalline state of a solid from a crystalline form to another crystalline form.
✓ If the amount is one mole and the change is at the standard conditions it is called the standard enthalpy of crystal transition.
✓ Changing one mole of carbon from diamond to graphite at standard conditions, releases 1.87 kJ, and we say that this quantity of heat is the standard enthalpy of crystal transition of one mole of carbon from diamond to graphite, $\Delta H_{\text{diam→graph}}^\circ$:

$$C(\text{diam}) \rightarrow C(\text{graph}) \quad \Delta H_{\text{diam→graph}}^\circ = -1.87 \text{ kJ}$$

2) **Enthalpy of fusion, and standard enthalpy of fusion**
✓ Fusion, or melting is the transition of a substance from its solid phase to its liquid phase.
✓ Fusion requires absorption of a certain amount of heat called enthalpy of fusion. All enthalpies of fusion are positive.
✓ Enthalpy of fusion is the quantity of heat absorbed, at constant temperature and pressure, as a result of changing a substance from its solid state to its liquid state.
✓ If the amount is one mole and the change is at the standard conditions the it is called the standard enthalpy of fusion, $\Delta H_{\text{fus}}^\circ$.
✓ Changing one mole of water from its solid phase to its liquid phase at the standard conditions, requires 6.01 kJ, we say that this quantity of heat is the standard enthalpy of fusion of water, $\Delta H_{\text{fus,water}}^\circ$:

$$\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(L) \quad \Delta H_{\text{fus,water}}^\circ = + 6.01 \text{ kJ}$$

✓ The reverse process of fusion is called freezing, its enthalpy is negative and is called the enthalpy of freezing.

$$\text{H}_2\text{O}(L) \rightarrow \text{H}_2\text{O}(s) \quad \Delta H_{\text{freez,H}_2\text{O}}^\circ = -6.01 \text{ kJ}$$
3) **Enthalpy of vaporization, and standard enthalpy of vaporization**

- Vaporization is the transition of a substance from its liquid phase to its gaseous phase.
- Vaporization requires absorption of a certain amount of heat called enthalpy of vaporization. All enthalpies of vaporization are positive.
- Enthalpy of vaporization is the quantity of heat absorbed, at constant temperature and pressure, as a result of changing the state of a substance from its liquid state to its gaseous state.
- If the amount is one mole and the change is at the standard conditions the it is called the **standard enthalpy of vaporization, \( \Delta H^\circ_{\text{vap}} \)**.
- Changing one mole of water from liquid to vapor (gas) at the standard conditions, requires 40.70 kJ, we say that this quantity of heat is the standard enthalpy of vaporization of water, \( \Delta H^\circ_{\text{vap,H}_2\text{O}} \)

\[
\text{H}_2\text{O}(L) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{vap,H}_2\text{O}} = + 40.70 \text{ kJ}
\]

- The reverse process of vaporization is called condensation, its enthalpy is negative and is called the enthalpy of condensation.

\[
\text{H}_2\text{O}(L) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{cond,H}_2\text{O}} = - 40.70 \text{ kJ}
\]

4) **Enthalpy of sublimation, and standard enthalpy of sublimation**

- Sublimation is the transition of a substance from its solid phase to its gaseous phase.
- Sublimation requires absorption of a certain amount of heat called enthalpy of sublimation. All enthalpies of sublimation are positive.
- Enthalpy of sublimation is the quantity of heat absorbed, at constant temperature and pressure, as a result of changing the state of a substance from its solid state to its gaseous state.
- If the amount is one mole and the change is at the standard conditions the it is called the **standard enthalpy of sublimation, \( \Delta H^\circ_{\text{subl}} \)**.
- Changing one mole of water from liquid to vapor (gas) at the standard conditions, requires 46.71 kJ, we say that this quantity of heat is the standard enthalpy of vaporization of water, \( \Delta H^\circ_{\text{subl,H}_2\text{O}} \)

\[
\text{H}_2\text{O}(L) \rightarrow \text{H}_2\text{O}(g) \quad \Delta H^\circ_{\text{vap,H}_2\text{O}} = + 46.71 \text{ kJ}
\]

- Another example is solid carbon dioxide (the dry ice). When one mole of it is supplied with 26.3 kJ at standard conditions we say that this quantity of heat is the standard enthalpy of sublimation of carbon, \( \Delta H^\circ_{\text{subl,CO}_2} \)

\[
\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H^\circ_{\text{sublim,CO}_2} = + 25.2 \text{ kJ}
\]

- The opposite process of sublimation is called precipitation, its enthalpy is the enthalpy precipitation.
- Before we move to the fifth type of physical changes, let us look at the following figure which shows the difference in the degree of closeness
between molecules in the solid phase (a), the liquid phase (b) and the gaseous phase (c).

The figure reveals that particles of the substance is closely compact when it is in its solid state, loosely attracted to each other when it is in its liquid state and completely separated from each other when it is in its gaseous state.

Now, let us look at the following table below which gives the standard enthalpies of fusion and vaporization and sublimation of some substances.

<table>
<thead>
<tr>
<th>substance</th>
<th>$\Delta H_{\text{fus}}^{\circ}$/kJ mol$^{-1}$</th>
<th>$\Delta H_{\text{vap}}^{\circ}$/kJ mol$^{-1}$</th>
<th>$\Delta H_{\text{subl}}^{\circ}$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia, NH$_3$</td>
<td>5.65</td>
<td>23.4</td>
<td>29.05</td>
</tr>
<tr>
<td>Argon, NH$_3$</td>
<td>1.2</td>
<td>6.5</td>
<td>7.7</td>
</tr>
<tr>
<td>Benzene, C$_6$H$_6$</td>
<td>10.59</td>
<td>30.8</td>
<td>41.39</td>
</tr>
<tr>
<td>Ethanol, CH$_3$CH$_2$OH</td>
<td>4.6</td>
<td>43.5</td>
<td>48.1</td>
</tr>
<tr>
<td>Mercury, Hg</td>
<td>2.292</td>
<td>59.30</td>
<td>61.592</td>
</tr>
<tr>
<td>Methane, CH$_4$</td>
<td>0.94</td>
<td>8.2</td>
<td>9.14</td>
</tr>
<tr>
<td>Methanol, CH$_3$OH</td>
<td>3.16</td>
<td>35.3</td>
<td>38.46</td>
</tr>
<tr>
<td>Propanone, CH$_3$CO CH$_3$</td>
<td>5.72</td>
<td>29.1</td>
<td>34.82</td>
</tr>
<tr>
<td>Water, H$_2$O</td>
<td>6.01</td>
<td>40.7</td>
<td>46.71</td>
</tr>
</tbody>
</table>

- **First**, we notice that the enthalpy of fusion is much less than the enthalpy of vaporization. Of course, the reason is that the difference between the degree of closeness of particles in their solid and liquid states is much less than the difference between the degree of closeness of particles in their gaseous state and either the solid or the liquid state.

- **Second**, we notice that the enthalpy of sublimation equals the sum of the enthalpies of fusion and vaporization. Of course, the reason behind this is the fact that enthalpy of any substance is a function of its state. In other words, the difference between the enthalpy of the substance in its gaseous state and its enthalpy in its gaseous state is the same whether it changes from its solid state to its gaseous state directly or its first changes to its liquid state then changes to its gaseous state.

5) **The bond dissociation energy (bond energy)**

✓ When atoms (of the same element or of different elements) combine together, bonds are said to be formed between them. This is accompanied by releasing energy (the process is exothermic and $\Delta H$ is negative.)
When atoms (of the same element or of different elements) are separated from each other, bonds are said to be broken. This is accompanied by absorbing energy (the process is endothermic and $\Delta H$ is positive.)

Of course, having knowledge about bonds’ dissociation and the energy involved, at the same time, means that knowledge about bonds’ formation and the energy involved is also known. This is because formation of a bond is exactly the opposite of its dissociation.

The word "dissociation" is used when we talk about breaking bonds between atoms and about the energy involved. Hence the energy involved is called "bond energy" or "bond dissociation energy". They are given the symbol "B" or sometimes the symbol "BE".

Bond energy or bond dissociation energy is also called bond enthalpy $\Delta H_{\text{bond}}$.

Let’s take methane gas, CH$_4$(g):

\[
\begin{align*}
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Methane has four bonds between the carbon and the four hydrogen atoms. At first glance, we would expect that the amount of energy needed to break any one of them is the same as for any of the other three. Fortunately (or unfortunately), the case is not as we expect. The first bond needs 435 kJ mol$^{-1}$ to break:

\[
\text{CH}_3\text{H} \rightarrow \text{CH}_3 + \text{H} \quad \Delta H = 435 \text{ kJ mol}^{-1}
\]

But once is broken the bond strength between the carbon atom and the remaining three hydrogen atoms changes, so the energies required to break them becomes different:

\[
\begin{align*}
\text{CH}_2\text{H} & \rightarrow \text{CH}_2 + \text{H} \quad \Delta H = 444 \text{ kJ mol}^{-1} \\
\text{CH}\text{H} & \rightarrow \text{CH} + \text{H} \quad \Delta H = 444 \text{ kJ mol}^{-1} \\
\text{C}\text{H} & \rightarrow \text{C} + \text{H} \quad \Delta H = 339 \text{ kJ mol}^{-1}
\end{align*}
\]

Let’s take water, H$_2$O (L) as another example:

\[
\begin{align*}
\text{H} & \quad \text{O} \\
\text{H} & \quad \text{H}
\end{align*}
\]

Breaking the first bond needs 493.4 kJ mol$^{-1}$:

\[
\text{HO}\text{H} \rightarrow \text{HO} + \text{H} \quad \Delta H = 493.4 \text{ kJ mol}^{-1}
\]
But once this bond is broken the energy required to break the second bond becomes less:

\[ \text{H–O} \rightarrow \text{O + H} \quad \Delta H = 424.4 \text{ kJ mol}^{-1} \]

✓ Furthermore, the dissociation-bond energy differs for the same bond in different compounds. For example, dissociation-bond energy of the C–H bond in CH₄ differs from that in CH₂CH₃ and from that of CH₂CH₂ or CHCH

✓ Sum up the above; it appears that it is much more useful to talk about an "AVERAGE BOND ENERGY, D₀". The average energy for C–H bond in CH₄ is 414 kJ mol⁻¹, for O–H in H₂O is 458.9 kJ mol⁻¹.

✓ The "AVERAGE BOND ENERGY" is also called "BOND ENERGY".

✓ If the amount of bonds broken is one mole (6.022 × 10²³ bonds), and the conditions are the standard conditions, it is called standard bond energy, B°, standard bond enthalpy, ∆H° bond or average standard bond-dissociation energy, D₀).

✓ The table below shows, according to a reference, the average dissociation energy of some of the bonds.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H – H</td>
<td>436</td>
<td>N – N</td>
<td>160</td>
</tr>
<tr>
<td>C – H</td>
<td>413</td>
<td>N = O</td>
<td>631</td>
</tr>
<tr>
<td>N – H</td>
<td>393</td>
<td>N triple N</td>
<td>941</td>
</tr>
<tr>
<td>P – H</td>
<td>297</td>
<td>N – O</td>
<td>201</td>
</tr>
<tr>
<td>C – C</td>
<td>347</td>
<td>N – H</td>
<td>388</td>
</tr>
<tr>
<td>C – O</td>
<td>358</td>
<td>O – H</td>
<td>464</td>
</tr>
<tr>
<td>C – N</td>
<td>305</td>
<td>O – S</td>
<td>265</td>
</tr>
<tr>
<td>C – Cl</td>
<td>397</td>
<td>O – Cl</td>
<td>269</td>
</tr>
<tr>
<td>C = C</td>
<td>607</td>
<td>O – O</td>
<td>204</td>
</tr>
<tr>
<td>C = O</td>
<td>805</td>
<td>C – F</td>
<td>552</td>
</tr>
<tr>
<td>O = O</td>
<td>498</td>
<td>C – S</td>
<td>259</td>
</tr>
</tbody>
</table>

✓ While the other table below shows them, in kJ/mol, according to another reference. It appears how values are not the same.

<table>
<thead>
<tr>
<th>Diatomic molecules</th>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–H</td>
<td>O=O</td>
<td>497</td>
<td>F–F</td>
<td>155</td>
</tr>
<tr>
<td>N=N</td>
<td>O=O</td>
<td>428</td>
<td>H–F</td>
<td>565</td>
</tr>
<tr>
<td>O=H</td>
<td>C=O</td>
<td>1074</td>
<td>Cl–Cl</td>
<td>242</td>
</tr>
<tr>
<td>H–Cl</td>
<td>H–I</td>
<td>299</td>
<td>O–H</td>
<td>204</td>
</tr>
<tr>
<td>H–CN</td>
<td>F–F</td>
<td>155</td>
<td>O–Cl</td>
<td>269</td>
</tr>
<tr>
<td>H–C≡C</td>
<td>I–I</td>
<td>151</td>
<td>C≡C</td>
<td>552</td>
</tr>
<tr>
<td>H–C≡N</td>
<td>Cl–Cl</td>
<td>242</td>
<td>C≡C</td>
<td>299</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polyatomic molecules</th>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
<th>Bond</th>
<th>Energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H–CH₃</td>
<td>H–NH₂</td>
<td>460</td>
<td>H–OH</td>
<td>492</td>
</tr>
<tr>
<td>H–CH₂</td>
<td>O₂N–NO₂</td>
<td>54</td>
<td>HO–OH</td>
<td>213</td>
</tr>
<tr>
<td>H₂C=CH₃</td>
<td>O=CO</td>
<td>531</td>
<td>HO–CH₃</td>
<td>377</td>
</tr>
<tr>
<td>H₃C=CH₂</td>
<td>Cl–CH₃</td>
<td>352</td>
<td>Cl–Cl</td>
<td>242</td>
</tr>
<tr>
<td>H₂O=CH</td>
<td>Br–CH₃</td>
<td>295</td>
<td>Br–Br</td>
<td>366</td>
</tr>
<tr>
<td>H₃C=CH</td>
<td>I–I</td>
<td>237</td>
<td>I–I</td>
<td>299</td>
</tr>
</tbody>
</table>

✓ There are known reasons behind the variation of these values between references. These reasons are out of our scope and will not be discussed. However, it is always advisable to deal with values of the same reference
and avoid taking values from a reference once and from a different reference once again.

✓ Bond energy is very useful due to its use in calculating the enthalpy of any reaction using the following equation is the equation used to do these calculations:

\[ \Delta H_{\text{rxn}}^\circ = \sum B^\circ(r) - \sum B^\circ(p) \]

**Example 4.5**

Calculate \( \Delta H_{\text{rxn}}^\circ \) of the following reaction:

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

Use data given in the previous table.

**Solution**

\[ \Delta H_{\text{rxn}}^\circ = \sum B^\circ(r) - \sum B^\circ(p) \]

\[ \Delta H_{\text{rxn}}^\circ = \{(941 \text{ kJ}) + (3 \times 436 \text{ kJ})\} - \{(2 \times 3 \times 388 \text{ kJ})\} \]

\[ \Delta H_{\text{rxn}}^\circ = \{(941 \text{ kJ}) + (1308 \text{ kJ})\} - \{(2328 \text{ kJ})\} \]

\[ \Delta H_{\text{rxn}}^\circ = 2249 \text{ kJ} - 2328 \text{ kJ} \]

\[ \Delta H_{\text{rxn}}^\circ = -97 \text{ kJ} \]

**Practice exercise**

Knowing that:

<table>
<thead>
<tr>
<th>Bond</th>
<th>H─H</th>
<th>C─H</th>
<th>C─C</th>
<th>C≡C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol(^{-1})</td>
<td>436</td>
<td>413</td>
<td>347</td>
<td>607</td>
</tr>
</tbody>
</table>

Calculate, in kJ mol\(^{-1}\), \( \Delta H_{\text{hydrogenation, ethene gas}}^\circ \).

<table>
<thead>
<tr>
<th>Bond</th>
<th>H─H</th>
<th>O=O</th>
<th>O─H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol(^{-1})</td>
<td>436</td>
<td>498</td>
<td>464</td>
</tr>
</tbody>
</table>

**Example 4.6**

Knowing that:

<table>
<thead>
<tr>
<th>Bond</th>
<th>H─H</th>
<th>O=O</th>
<th>O─H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol(^{-1})</td>
<td>436</td>
<td>498</td>
<td>464</td>
</tr>
</tbody>
</table>

Calculate \( \Delta H_{\text{rxn}}^\circ \) for the thermal decomposition of 2 moles of liquid water:

**Solution**

\[ 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \]

\[ \Delta H_{\text{rxn}}^\circ = \sum B^\circ(r) - \sum B^\circ(p) \]

\[ \Delta H_{\text{rxn}}^\circ = \{(4 \times 464 \text{ kJ})\} - \{(2 \times 436 \text{ kJ} + (498 \text{ kJ})\} \]

\[ \Delta H_{\text{rxn}}^\circ = \{(1856 \text{ kJ})\} - \{(872 \text{ kJ})\} + \{(498 \text{ kJ})\} \]

\[ \Delta H_{\text{rxn}}^\circ = 1856 \text{ kJ} - 1370 \text{ kJ} \]

\[ \Delta H_{\text{rxn}}^\circ = +484 \text{ kJ} \]

**Practice exercise**

Knowing that:

<table>
<thead>
<tr>
<th>Bond</th>
<th>H─H</th>
<th>C─H</th>
<th>C─C</th>
<th>C≡C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol(^{-1})</td>
<td>?</td>
<td>413</td>
<td>347</td>
<td>607</td>
</tr>
</tbody>
</table>

\( \Delta H_{\text{hydrogenation,1-propane gas}}^\circ = -130 \text{ kJ/mol of propane} \)

Calculate, in kJ mol\(^{-1}\), the bond energy of H\(_2\).

✓ The types and strengths of the bonds that the elements can make to other elements are additional factors.

✓ A complication when dealing with bond enthalpies is that their values depend on the molecule in which the two linked atoms occur.
For instance, the total standard enthalpy changes for the atomization (the complete dissociation into atoms) of water

\[
\text{H}_2\text{O}(g) \rightarrow 2\text{H}(g) + \text{O}(g) \quad \Delta H = +927 \text{ kJ}
\]

is not twice the O—H bond enthalpy in H\(_2\)O even though two O—H bonds are dissociated. There are in fact two different dissociation steps:

- In the first step, an O—H bond is broken in an H\(_2\)O molecule:
  
  \[
  \text{H}_2\text{O}(g) \rightarrow \text{HO}(g) + \text{H}(g) \quad \Delta H = +499 \text{ kJ}
  \]

- In the second step, the O—H bond is broken in an OH radical:
  
  \[
  \text{HO}(g) \rightarrow \text{H}(g) + \text{O}(g) \quad \Delta H = +428 \text{ kJ}
  \]

The sum of the two steps is the atomization of the molecule. 

*Atomization will be discussed in more details once we finish our discussion on bond dissociation energy.*

As can be seen from this example, the O—H bonds in H\(_2\)O and HO have similar but not identical bond enthalpies.

Although accurate calculations must use bond enthalpies for the molecule in question and its successive fragments, when such data are not available there is no choice but to make estimates by using **mean or averaged bond enthalpies**, \(\Delta H_B\), which are the averages of bond enthalpies over a related series of compounds which some are given in the following table.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Cl</th>
<th>Br</th>
<th>I</th>
<th>S</th>
<th>P</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>436</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>412</td>
<td>348(1)</td>
<td>612(2)</td>
<td>838(3)</td>
<td>518 (a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>388</td>
<td>305 (1)</td>
<td>163 (1)</td>
<td>613 (2)</td>
<td>400 (2)</td>
<td>890 (3)</td>
<td>945 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>463</td>
<td>360 (1)</td>
<td>157</td>
<td>146 (1)</td>
<td>743 (2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>565</td>
<td>494</td>
<td>270</td>
<td>185</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>431</td>
<td>338</td>
<td>200</td>
<td>203</td>
<td>254</td>
<td>242</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>366</td>
<td>276</td>
<td></td>
<td>219</td>
<td>193</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>299</td>
<td>238</td>
<td></td>
<td>210</td>
<td>178</td>
<td>151</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>338</td>
<td>259</td>
<td></td>
<td>496</td>
<td>250</td>
<td>212</td>
<td>264</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>322</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>318</td>
<td>374</td>
<td>466</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>226</td>
</tr>
</tbody>
</table>

For example, the mean HO bond enthalpy, \(\Delta H_{B,H-O} = 463 \text{ kJ mol}^{-1}\), is the mean of the O—H bond enthalpies in H\(_2\)O and several other similar compounds, including methanol, CH\(_3\)OH.

**Example 4.7**

Estimate the enthalpy change for the combustion of liquid ethanol to carbon dioxide and liquid water under standard conditions by using the bond enthalpies, mean bond
enthalpies, and the appropriate standard enthalpies of vaporization. Use the following information.

<table>
<thead>
<tr>
<th>Bond</th>
<th>H—H</th>
<th>O=O</th>
<th>C—H</th>
<th>C—O</th>
<th>O—H</th>
<th>C=O</th>
<th>C—C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean bond enthalpy (kJ/mol)</td>
<td>436</td>
<td>497</td>
<td>412</td>
<td>360</td>
<td>463</td>
<td>743</td>
<td>348</td>
</tr>
</tbody>
</table>

**Solution**

The thermochemical equation of combustion of 1 mol of liquid methanol is:

$$C_2H_5OH(L) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(L)$$

**First:** Bond in the reactants are five C—H bonds, one C—C bond, one C—O bond, one O—H bond and two O=O bonds. The total enthalpy of bonding for all these bonds is calculated as follows:

$$\Delta H_{B,\text{reacta.}} = (5 \text{ mol} \times 412 \text{ kJ}) + (1 \text{ mol} \times 348 \text{ kJ}) + (1 \text{ mol} \times 360 \text{ kJ}) + (1 \text{ mol} \times 463 \text{ kJ}) + (2 \text{ mol} \times 497 \text{ kJ})$$

$$\Delta H_{B,\text{reacta.}} = + 4255 \text{ kJ}$$

**Second:** Bond in the products are four C=O bonds and six O—H bonds. The total enthalpy of bonding for all these bonds is calculated as follows:

$$\Delta H_{B,\text{prod.}} = (4 \text{ mol} \times 743 \text{ kJ}) + (6 \text{ mol} \times 463 \text{ kJ})$$

$$\Delta H_{B,\text{prod.}} = + 5750 \text{ kJ}$$

$$\Delta H_{\text{reaction}} = \Delta H_{B,\text{reacta.}} - \Delta H_{B,\text{prod.}}$$

$$\Delta H_{\text{reaction}} = (+4255 \text{ kJ}) - (+5750 \text{ kJ}) = -1495 \text{ kJ}$$

6) **The atomization energy**

✓ Atomization is the breaking of all bonds in the substance (element or compound) to get its atoms in individual gaseous atoms. The following are examples of atomization:

$$Na_2CO_3(s) \rightarrow 2Na(g) + C(g) + 3O(g)$$
$$H_2O(L) \rightarrow 2H(g) + O(g)$$
$$H_2O(s) \rightarrow 2H(g) + O(g)$$
$$Fe(s) \rightarrow Fe(g)$$
$$H_2(g) \rightarrow 2H(g)$$

✓ Energy or enthalpy of atomization is the quantity of heat that is absorbed at constant temperature and pressure to break all bonds in the substance to get its atoms in individual gaseous atoms.

✓ In atomization, all bonds in the substance are broken and none are formed. Therefore, enthalpies of atomization are always positive.

✓ If the atomization is for an element and the quantity of the produced gaseous atoms is one mole, or if the atomization is for one mole of a compound, and the conditions are the standard conditions, it is called **standard enthalpy of atomization, \(\Delta H^\circ_{\text{atom}}\)** of the element or the compound.

✓ If the atomized substance is a compound, the sum of its bond dissociation energies is its enthalpy of atomization. The following is an example:

$$C_6H_6 \ (L) \rightarrow 6C(g) + 6H(g) \quad \Delta H^\circ_{\text{atom}} = + 5559.9 \text{ kJ mol}^{-1}$$

✓ If the atomized substance is an element in its solid state, its enthalpy of atomization is its enthalpy of sublimation. The following is an example:
Fe(s) → Fe(g) \[ \Delta H_{\text{atom}}^\circ = +415 \, \text{kJ mol}^{-1} \]

✓ If the atomized substance is an element in its liquid state, its enthalpy of atomization is its enthalpy of vaporization. The following is an example:

Br(L) → Br(g) \[ \Delta H_{\text{atom}}^\circ = +112 \, \text{kJ mol}^{-1} \]

✓ If the atomized substance is a poly-atomic element like N\(_2\) or O\(_3\), its standard enthalpy of atomization is the energy required to break bonds to get one mole of gaseous atoms. The following is equation:

\[ \frac{1}{2}\text{Cl}_2(g) \rightarrow \text{Cl}(g) \quad \Delta H_{\text{atom}}^\circ = +121.29 \, \text{kJ mol}^{-1} \]

✓ The following is an example of how bond energies and atomization energies are useful tools to determine the enthalpies of reactions.

<table>
<thead>
<tr>
<th>Example 4.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knowing that:</td>
</tr>
</tbody>
</table>
| \begin{tabular}{|c|c|c|c|}
| Substance & C(g) & H\(_2\)(g) & O\(_2\)(g) \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| \Delta H_{\text{atom}}^\circ / \text{kJ mol}^{-1} \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 716.68 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 217.97 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 249.2 \end{tabular} \\
| \end{tabular} |
| and: |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| Bond energy / \text{kJ mol}^{-1} \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 413 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 348 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 351 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 463 \end{tabular} \\
| \end{tabular} |
| Calculate \( \Delta H_{\text{rxn}}^\circ \) for the following reaction: |
| \( 2\text{C(graphite)} + 3\text{H}_2(g) + 0.5\text{O}_2(g) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(L) \) \quad \Delta H_{\text{rxn}}^\circ = ? |
| Solution |
| \[ \Delta H_{\text{rxn}}^\circ = \sum \Delta B^\circ (r) - \sum \Delta B^\circ (p) \]
| \[ \sum \Delta B^\circ (r) = [2 \times \Delta H_{\text{atom},\text{C(graphite)}}^\circ + 6 \times \Delta H_{\text{atom},\text{H(g)}}^\circ + \Delta H_{\text{atom},\text{O(g)}}^\circ] \]
| \[ \sum \Delta B^\circ (p) = [5 \times \Delta H_{\text{bonding},(C=\text{H})}^\circ + \Delta H_{\text{bonding},(C=\text{C})}^\circ + \Delta H_{\text{bonding},(C=\text{O})}^\circ + \Delta H_{\text{bonding},(O=\text{H})}^\circ] \]
| \[ \Delta H_{\text{rxn}}^\circ = (2990.38) - (3227) = -236.62 \, \text{kJ} \]
| Practice exercise |
| Knowing that: |
| \begin{tabular}{|c|c|c|}
| Substance & C(g) & O(g) \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| \Delta H_{\text{atom}}^\circ / \text{kJ mol}^{-1} \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 716.68 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 217.97 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 249.2 \end{tabular} \\
| \end{tabular} |
| and: |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| Bond energy / \text{kJ mol}^{-1} \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 413 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 351 \end{tabular} \\
| \end{tabular} |
| \begin{tabular}{|c|}
| \hline
| \begin{tabular}{|c|}
| \hline
| 464 \end{tabular} \\
| \end{tabular} |
| Calculate \( \Delta H_{\text{rxn}}^\circ \) for the following esterification of methanoic acid: |
| \( \text{HCOOCH}_3(L) \rightarrow 2\text{C(graphite)} + 2\text{H}_2(g) + \text{O}_2(g) \) \quad \Delta H_{\text{rxn}}^\circ = ? |

Example 4.8

Estimate the standard enthalpy change for the reaction:

\( \text{C(s, graphite)} + 2\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(L) \)

Use the following information:

\[ \begin{array}{|c|c|c|c|c|c|c|}
| H—H | O=O | C—H | C—O | O=H | C(s,\text{graph.}) | \text{CH}_3\text{OH(g)} |
\end{array} \]
<table>
<thead>
<tr>
<th>Mean bond enthalpy (kJ/mol)</th>
<th>463</th>
<th>497</th>
<th>412</th>
<th>360</th>
<th>463</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enthalpy of atomization (kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>716.68</td>
</tr>
<tr>
<td>Enthalpy of condensation (kJ/mol)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>– 38</td>
</tr>
</tbody>
</table>

**Solution**

The thermochemical equation for this process is the sum of the three following equations:

First: \[2\text{H}_2(g) + \text{C(s,graph)} + \frac{1}{2}\text{O}_2(g) \rightarrow 4\text{H}(g) + \text{C}(g) + \text{O}(g)\]

Second: \[\text{C}(g) + 4\text{H}(g) + \text{O}(g) \rightarrow \text{CH}_3\text{OH}(g)\]

Third: \[\text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{OH}(L)\]

If we manage to calculate \(\Delta H\) for the three equations the \(\Delta H\) of the equation in question can be obtained.

**First equation:**

\(\Delta H\) of dissociating 2 mol \(\text{H}_2(g)\) = 2 mol \(\times 463\) kJ/mol = 926 kJ

Dissociation of 2 mol \(\text{H}_2(g)\): \[2\text{H}_2(g) \rightarrow 4\text{H}(g)\] \(\Delta H = + 926\) kJ

Atomization of 1 mol \(\text{C(s,graph)}\): \[\text{C(s,graph)} \rightarrow \text{C}(g)\] \(\Delta H = + 716.68\) kJ

Dissociation of 1/2 mol \(\text{O}_2(g)\): \[\frac{1}{2}\text{O}_2(g) \rightarrow \text{O}(g)\] \(\Delta H = + 249.17\) kJ

Overall, so far:

\[2\text{H}_2(g) + \text{C(s,graph)} + \frac{1}{2}\text{O}_2(g) \rightarrow 4\text{H}(g) + \text{C}(g) + \text{O}(g)\] \(\Delta H = + 1891.85\) kJ

**Second equation:**

Second equation is the reverse of the following equation, which is the equation of atomization of \(\text{CH}_3\text{OH}(g)\):

\[\text{CH}_3\text{OH}(g) \rightarrow \text{C}(g) + 4\text{H}(g) + \text{O}(g)\]

\(\text{CH}_3\text{OH}\) has three \(\text{C}—\text{H}\) bonds, one \(\text{C}—\text{O}\) bond and one \(\text{O}—\text{H}\) bond. Therefore, the atomization energy of \(\text{CH}_3\text{OH}(g)\), \(\text{AE}_{\text{methanol}}\), is:

\[\text{AE}_{\text{methanol}} = (3\ \text{mol} \times 412\ \text{kJ}) + (1\ \text{mol} \times 360\ \text{kJ}) + (1\ \text{mol} \times 463\ \text{kJ}) = + 2059\ \text{kJ}\]

\[\text{C}(g) + 4\text{H}(g) + \text{O}(g) \rightarrow \text{CH}_3\text{OH}(g)\] \(\Delta H = – 2059\) kJ

**Third equation:**

Third equation is the condensation of gaseous methanol:

\[\text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{OH}(L)\] \(\Delta H = – 38\) kJ

\[\text{C(s)} + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{C}(g) + 4\text{H}(g) + \text{O}(g)\] \(\Delta H = + 1891.85\) kJ

\[\text{C}(g) + 4\text{H}(g) + \text{O}(g) \rightarrow \text{CH}_3\text{OH}(g)\] \(\Delta H = – 2059\) kJ

\[\text{CH}_3\text{OH}(g) \rightarrow \text{CH}_3\text{OH}(L)\] \(\Delta H = – 38\) kJ

\[\text{C(s)} + 2\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CH}_3\text{OH}(L)\] \(\Delta H = – 205.15\) kJ

The experimental value is – 239.00 kJ

7) **Enthalpy of electron loss (ionization)**

✓ Ionization is the physical process by which electrons are removed from atoms.
✓ Ionization requires energy absorption and therefore is an endothermic process.
✓ Enthalpy of Ionization is the quantity of heat absorbed, at constant temperature and pressure, as a result of removal of electrons from gaseous atoms.
✓ If the number of atoms is Avogadro’s number (one mole) and the removal of electrons is at the standard conditions it is called the standard enthalpy of ionization, $\Delta H_{\text{ion}}$. It is also called the ionization energy.
✓ Ionization of hydrogen atoms is an example:

$$H(g) \rightarrow H^+(g) + e^-(g) \quad \Delta H = + 1312 \text{ kJ}$$

The equations states that the standard enthalpy of ionization of hydrogen atoms is 1312 kJ mol$^{-1}$. This means that 1312 kJ of energy must be supplied as heat to ionize 1 mol H(g) at standard conditions.

✓ The table below gives the values of the ionization enthalpies for a number of elements; note that all enthalpies of ionization are positive.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>He</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>902</td>
<td>1760</td>
<td>799</td>
<td>1090</td>
<td>2350</td>
<td>2860</td>
<td>3390</td>
<td>3370</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>519</td>
<td>1451</td>
<td>7740</td>
<td>11 690</td>
<td>577</td>
<td>1820</td>
<td>2740</td>
<td>11 690</td>
</tr>
<tr>
<td>3</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
<td>Ar</td>
<td>Ca</td>
<td>Ga</td>
</tr>
<tr>
<td>4</td>
<td>494</td>
<td>538</td>
<td>1451</td>
<td>7740</td>
<td>11 690</td>
<td>577</td>
<td>1820</td>
<td>2740</td>
<td>11 690</td>
<td>590</td>
</tr>
<tr>
<td>5</td>
<td>K</td>
<td>Ca</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
<td>Kr</td>
<td>Rb</td>
<td>Sr</td>
</tr>
<tr>
<td>6</td>
<td>418</td>
<td>548</td>
<td>656</td>
<td>707</td>
<td>833</td>
<td>679</td>
<td>1010</td>
<td>1770</td>
<td>2650</td>
<td>1060</td>
</tr>
<tr>
<td>7</td>
<td>Cs</td>
<td>Ba</td>
<td>TI</td>
<td>Pb</td>
<td>Bi</td>
<td>Po</td>
<td>At</td>
<td>Rn</td>
<td>Cs</td>
<td>502</td>
</tr>
</tbody>
</table>

✓ We often need to consider a succession of ionizations, such as the conversion of magnesium atoms to Mg$^+$ ions, the ionization of these Mg$^+$ ions to Mg$^{2+}$ ions, and so on.
✓ The successive molar enthalpy changes are called, respectively, the first ionization enthalpy, the second ionization enthalpy, and so on.
✓ For magnesium, these enthalpies refer to the processes

$$\text{Mg}(g) \rightarrow \text{Mg}^+(g) + e^-(g) \quad \Delta H = + 738 \text{ kJ}$$
$$\text{Mg}^+(g) \rightarrow \text{Mg}^{2+}(g) + e^-(g) \quad \Delta H = + 1451 \text{ kJ}$$

✓ Note that the second ionization enthalpy is larger than the first because more energy is needed to separate an electron from a positively charged ion than from the neutral atom.
✓ Note also that enthalpies of ionization refer to the ionization of the gas phase atom or ion, not to the ionization of an atom or ion in a solid.

90
### Example 4.9
The standard enthalpy of sublimation of magnesium (molar mass = 24.31 g/mol) at 25 °C is 148 kJ mol\(^{-1}\) and its first and second ionization enthalpies are 148 kJ/mol and 738 kJ/mol respectively. How much energy as heat (at constant temperature and pressure) must be supplied to 1.00 g of solid magnesium metal to produce a gas composed of Mg\(^{2+}\) ions and electrons?

**Solution**
The enthalpy change for the overall process is a sum of the steps, sublimation followed by the two stages of ionization, into which it can be divided. Then, the heat required for the specified process is the product of the overall molar enthalpy change and the number of atoms; the latter is calculated from the given mass and the molar mass of the substance.

The overall process is:

\[
\text{Mg(s)} \rightarrow \text{Mg}^{2+}(g) + 2\text{e}^-(g)
\]

The thermochemical equation for this process is the sum of the following thermochemical equations:

<table>
<thead>
<tr>
<th>Step</th>
<th>Equation</th>
<th>(\Delta H) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublimation</td>
<td>(\text{Mg(s)} \rightarrow \text{Mg(g)})</td>
<td>+148</td>
</tr>
<tr>
<td>First ionization</td>
<td>(\text{Mg(g)} \rightarrow \text{Mg}^+(g) + \text{e}^-(g))</td>
<td>+738</td>
</tr>
<tr>
<td>Second ionization</td>
<td>(\text{Mg}^+(g) \rightarrow \text{Mg}^{2+}(g) + \text{e}^-(g))</td>
<td>+1451</td>
</tr>
<tr>
<td>Overall (sum)</td>
<td>(\text{Mg(s)} \rightarrow \text{Mg}^{2+}(g) + 2\text{e}^-(g))</td>
<td>+2337</td>
</tr>
</tbody>
</table>

\[
n_{\text{Mg}} = \frac{m_{\text{Mg}}}{M_{\text{Mg}}} = \frac{1 \text{ g}}{24.31 \text{ g/mol}} = 0.0411 \text{ mol}
\]

\[
q_p = \frac{2337 \text{ kJ/mol}}{0.0411 \text{ mol}} = 96.05 \text{ kJ}
\]

### Example 4.10
The enthalpy of sublimation of aluminum (molar mass = 26.98 g/mol) is 326 kJ mol\(^{-1}\). Use this information and the ionization enthalpies in table provided above to calculate the energy that must be supplied as heat (at constant pressure) to convert 1.00 g of solid aluminum metal to a gas of Al\(^{3+}\) ions and electrons at 25°C.

**Solution**
The enthalpy change for the overall process is a sum of the steps, sublimation followed by the three stages of ionization, into which it can be divided. Then, the heat required for the specified process is the product of the overall molar enthalpy change and the number of atoms; the latter is calculated from the given mass and the molar mass of the substance.

The overall process is:

\[
\text{Al(s)} \rightarrow \text{Al}^{3+}(g) + 3\text{e}^-(g)
\]

The thermochemical equation for this process is the sum of the following thermochemical equations:

<table>
<thead>
<tr>
<th>Step</th>
<th>Equation</th>
<th>(\Delta H) (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublimation</td>
<td>(\text{Al(s)} \rightarrow \text{Al(g)})</td>
<td>+326</td>
</tr>
<tr>
<td>First ionization</td>
<td>(\text{Al(g)} \rightarrow \text{Al}^+(g) + \text{e}^-(g))</td>
<td>+577</td>
</tr>
</tbody>
</table>
Second ionization: $$\text{Al}^+(\text{g}) \rightarrow \text{Al}^{2+}(\text{g}) + e^- (\text{g}) \quad \Delta H = +1820 \text{ kJ}$$
Second ionization: $$\text{Al}^{2+}(\text{g}) \rightarrow \text{Al}^{3+}(\text{g}) + e^- (\text{g}) \quad \Delta H = +2740 \text{ kJ}$$
Overall (sum): $$\text{Al}(\text{s}) \rightarrow \text{Al}^{3+}(\text{g}) + 3e^- (\text{g}) \quad \Delta H = +5463 \text{ kJ}$$

\[
n_{\text{Al}} = \frac{m_{\text{Al}}}{M_{\text{Al}}} = \frac{1 \text{ g}}{26.98 \text{ g/mol}} = 0.0371 \text{ mol}
\]

\[
q_p = +5463 \frac{\text{kJ}}{\text{mol}} \cdot 0.0371 \text{ mol} = 202.48 \text{ kJ}
\]

8) **Enthalpies of electron gain**

✓ While ionization is the loss of electrons from atoms, electron gain is the gain of electrons by atoms.

✓ Yes, the meaning of the word gain is the opposite of the meaning of the word loss, but in chemistry “electron loss” and “electron gain” are terms with specified conventional meanings.

✓ Unfortunately, many chemists and even some respectful chemistry book authors overlook the conventional meanings of terms and replace it with merely its linguistical meaning. Therefore, many chemists say and write: “electron gain is the reverse of ionization”, but in reality, the reverse of ionization is not the electron gain:

➢ By definition, the ionization of hydrogen is written as:

$$\text{H}(\text{g}) \rightarrow \text{H}^+(\text{g}) + \text{electron}$$

➢ The reverse of the ionization of hydrogen must be:

$$\text{H}^+(\text{g}) + \text{electron} \rightarrow \text{H}(\text{g})$$

➢ By definition, the electron gain of hydrogen is written as:

$$\text{H}(\text{g}) + \text{electron} \rightarrow \text{H}^-(\text{g})$$

From these equations, it is so obvious that electron loss is not the reverse of the ionization.

✓ Enthalpy of electron gain is the quantity of heat release, at constant temperature and pressure, as a result of gaining electrons by gaseous atoms.

✓ If the number of atoms is Avogadro’s number (one mole) and the gain of electrons is at the standard conditions it is called the **standard enthalpy of electron gain**, $$\Delta H_{\text{eg}}^\circ$$ It is also called the electron affinity.

$$\text{Cl}(\text{g}) + e^- (\text{g}) \rightarrow \text{Cl}^-(\text{g}) \quad \Delta H = -349 \text{ kJ}$$

it follows that the electron gain enthalpy of Cl atoms is $$-349 \text{ kJ mol}^{-1}$$. Notice that electron gain by Cl is an exothermic process, so heat is released when a Cl atom captures an electron and forms an ion.

✓ It can be seen from the table below, which lists a number of electron gain enthalpies, that some electron gains are exothermic and others are endothermic, so we need to include their sign.
For example, electron gain by an \( \text{O}^- \) ion is strongly endothermic because it takes energy to push an electron on to an already negatively charged species:

\[
\text{O}^- (g) + e^- (g) \rightarrow \text{O}^{2-} (g) \quad \Delta H = +844 \text{ kJ}
\]

9) **Enthalpies of solution (dissolutions)**

- Let us look at the following figure:

- The figure shows that dissolving a solid in solute, comprises three actions:
  1) *The breaking of attractions within solute particles.* Here \( \Delta H_1 \) is positive.
  2) *The breaking of attractions within solvent particles.* Here \( \Delta H_2 \) is also positive.
  3) *The emergence of attractions between solute and solvent particles which is called “solvation”.* Here \( \Delta H_3 \) is negative.

(Note: If the solvent is water, solvation is given the special term “hydration”).
✓ Enthalpy of solution equals the sum of the enthalpies of the three actions or steps.

\[ \Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3 \]

✓ In most cases, \( \Delta H_3 \), which is negative, does not compensate for \( \Delta H_1 \) and \( \Delta H_2 \), which both are positive:

\[ \Delta H_1 + \Delta H_2 \neq \Delta H_3 \]

\[ \Delta H_{\text{solution}} > 0 \text{ or } \Delta H_{\text{solution}} < 0 \]

This makes the enthalpy of solution either positive (\( \Delta H_{\text{soln}} > 0 \)) as in the case of dissolving potassium chloride in water (\( \Delta H_{\text{soln,KCl}} = 17.2 \text{ kJ/mol} \)), or negative (\( \Delta H_{\text{solution}} < 0 \)) as in the case of dissolving potassium hydroxide in water (\( \Delta H_{\text{soln,KOH}} = -57.6 \text{ kJ/mol} \)).

✓ Solutions with negative values of enthalpy of solution form stronger bonds and have lower vapor pressure.

✓ If the attractive and repulsive properties of solvent and solute are equal the solution is called **ideal solution**. The enthalpy of solution of an ideal solution is zero:

\[ \Delta H_1 + \Delta H_2 = \Delta H_3 \]

\[ \Delta H_{\text{solution}} = 0 \]

✓ From this above discussion, enthalpy of solution is the quantity of heat absorbed or released, at constant temperature and pressure, as a result of the dissolving a solute in a solvent. If the amount of solute is one mole, the mass of solvent is 1 kg and the process is at standard conditions it is called the **standard enthalpy of solution**, \( \Delta H_{\text{soln}}^0 \).

✓ Enthalpy of solution of a certain quantity of a solute, at certain temperature and pressure, is not constant but differs as the amount of solute differs. However, it becomes constant if the solution is at infinite dilution. It is then called **standard enthalpy of solution at infinite dilution**, \( \Delta H_{\text{infin.dilution}}^0 \).

✓ Solution at infinite dilution can be understood by the following illustration:

<table>
<thead>
<tr>
<th>1 mol of HCl(g) is dissolved in</th>
<th>5</th>
<th>25</th>
<th>Large</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number moles of H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δ( H_{\text{solution}} )(kJ)</td>
<td>–63.995</td>
<td>–72.177</td>
<td>–75.076</td>
</tr>
</tbody>
</table>

- It is clear that when HCl(g) is dissolved in H₂O(L) heat is released.
- It is clear that more heat is released as solution becomes more diluted.
- It is clear that there is a certain degree of dilution beyond which no more heat can be released.

The degree of dilution beyond which no more heat can be released, is called **INFINITE DILUTION**.
4.5.2 Enthalpies of chemical changes

- In contrast to physical transitions, chemical reactions lead to the disappearance of substances (reactants) and the appearance of new substances (products).
- In chemical reactions, chemical bonds of reactants are broken and those of products are formed.
- Of course, any chemical reaction, at constant temperature and pressure, is accompanied by an absorbance or a release of a quantity of heat called the enthalpy of the reaction. It is denoted as $\Delta H_{\text{rxn}}$.
- If the reaction is at the standard conditions, it is called standard enthalpy of reaction, $\Delta H_{\text{rxn}}^\circ$.
- Because number of chemical reactions is tremendous, chemical reactions and their enthalpies are classified to many different types.
- The enthalpy changes accompanying chemical reactions carry the name of the chemical reaction. For example, if the reaction is hydrogenation such as the hydrogenation of ethene the enthalpy change is called “the enthalpy of hydrogenation”:

$$\text{CH}_2=\text{CH}_2(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_3(g) \quad \Delta H = -137 \text{ kJ}$$

The value of $\Delta H$ given here signifies that the enthalpy of the system decreases by 137 kJ (and, if the reaction takes place at constant pressure, that 137 kJ of energy is released by heating the surroundings) when, at standard conditions, 1 mol CH$_2$=CH$_2$(g) combines with 1 mol H$_2$(g) to give 1 mol CH$_3$CH$_3$(g).
- Because reactions are defined as breaking of existing bonds and forming of new emerging bonds, it will be necessary, before we discuss the enthalpies of some chemical reactions, our discussion we previously have done regarding the "bond energy or the bond enthalpy” and on the “atomization energy or atomization enthalpy” is very useful and helpful in understanding the enthalpies of different chemical reactions.
- The following is a discussion of only the chemical reactions that are mostly useful in our daily life and in studying the subject of thermochemistry.

1) Enthalpy of combustion and standard enthalpy of combustion

- **Combustion** or burning is a chemical reaction between a fuel and an oxidant accompanied by the production of heat and conversion of chemical species. The release of heat can result in the production of light in the form of either glowing or a flame:
  - Fuels are organic compounds (especially hydrocarbons) in the gas, liquid or solid phase.
  - In a complete combustion reaction, a compound reacts with an oxidizing element, such as oxygen or fluorine, and the products are compounds of each element in the fuel with the oxidizing element.
  - The oxidizing agent used in almost all combustion reactions is oxygen.
  - The amount of heat released, at constant temperature and pressure, as a result of combusting a substance is called enthalpy of combustion.

- If the amount combusted is one mole, and the conditions are the standard conditions, it is called standard enthalpy of combustion, $\Delta H_{\text{comb}}^\circ$. Below are some examples:

$$\text{H}_2(g) + 0.5\text{O}_2(g) \rightarrow \text{H}_2\text{O}(L) \quad \Delta H_{\text{comb}}^\circ = -285.83 \text{ kJ}$$
\[
\begin{align*}
H_2(g) + 0.5O_2(g) & \rightarrow H_2O(g) \quad \Delta H_{\text{comb}}^\circ = -241.82 \text{ kJ} \\
C(\text{graph}) + O_2(g) & \rightarrow CO_2(g) \quad \Delta H_{\text{comb}}^\circ = -393.51 \text{ kJ} \\
CH_4(g) + 2O_2(g) & \rightarrow CO_2(g) + 2H_2O(L) \quad \Delta H_{\text{comb}}^\circ = -890 \text{ kJ}
\end{align*}
\]

✓ The following table shows the enthalpies ofcombusting only one gram ofsome fuels:

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Enthalpies (kJ/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>– 141.9</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>– 54.0</td>
</tr>
<tr>
<td>Propane</td>
<td>– 49.9</td>
</tr>
<tr>
<td>Butane</td>
<td>– 49.2</td>
</tr>
<tr>
<td>Gasoline</td>
<td>– 47.0</td>
</tr>
<tr>
<td>Diesel</td>
<td>– 45.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>– 29.7</td>
</tr>
<tr>
<td>Coal (Anthracite)</td>
<td>– 27.0</td>
</tr>
<tr>
<td>Coal (Lignite)</td>
<td>– 15.0</td>
</tr>
<tr>
<td>Wood</td>
<td>– 15.0</td>
</tr>
</tbody>
</table>

✓ The following table shows the standard enthalpy ofcombustion ofsome substances:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Combustion reaction</th>
<th>(\Delta H_{\text{comb}}^\circ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methane</td>
<td>CH(_4)(g) + 2O(_2)(g) \rightarrow CO(_2)(g) + 2H(_2)O(L)</td>
<td>– 890</td>
</tr>
<tr>
<td>ethane</td>
<td>C(_2)H(_6)(g) + 3.5O(_2)(g) \rightarrow 2CO(_2)(g) + 3H(_2)O(L)</td>
<td>– 1560</td>
</tr>
<tr>
<td>propane</td>
<td>C(_3)H(_4)(g) + 5O(_2)(g) \rightarrow 3CO(_2)(g) + 4H(_2)O(L)</td>
<td>– 2200</td>
</tr>
<tr>
<td>butane</td>
<td>C(_4)H(_10)(g) + 7.5O(_2)(g) \rightarrow 4CO(_2)(g) + 5H(_2)O(L)</td>
<td>– 2874</td>
</tr>
<tr>
<td>octane</td>
<td>C(_8)H(_18)(g) + 12.5O(_2)(g) \rightarrow 8CO(_2)(g) + 9H(_2)O(L)</td>
<td>– 5460</td>
</tr>
<tr>
<td>methanol</td>
<td>(\text{CH}_3\text{OH}(L) + 1.5O_2(g) \rightarrow CO_2(g) + 2H_2O(L))</td>
<td>– 726</td>
</tr>
<tr>
<td>ethanol</td>
<td>(\text{C}_2\text{H}_5\text{OH}(L) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(L))</td>
<td>– 1368</td>
</tr>
<tr>
<td>propan-1-ol</td>
<td>(\text{C}_3\text{H}_7\text{OH}(L) + 4.5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(L))</td>
<td>– 2021</td>
</tr>
<tr>
<td>butan-1-ol</td>
<td>(\text{C}_4\text{H}_9\text{OH}(L) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(L))</td>
<td>– 2671</td>
</tr>
</tbody>
</table>

✓ Enthalpies of combustion are commonly measured by using a bomb calorimeter, a device in which energy is transferred as heat at constant volume. Therefore, it measures \(q_v\). We know that \(q_v = \Delta U\), consequently the bomb calorimeter actually measures the change in internal energy, \(\Delta U\), not the change in enthalpy, \(\Delta H\). But the equation “\(\Delta H = \Delta U + RT\Delta n_g\)” enables us to calculate \(\Delta H\). For example, the energy released as heat when glycine is burned in a bomb calorimeter is 969.6 kJ mol\(^{-1}\) at 298.15 K:

\[
\text{NH}_2\text{CH}_2\text{COOH}(s) + \frac{9}{4}O_2(g) \rightarrow 2\text{CO}_2(g) + \frac{5}{2}\text{H}_2\text{O}(L) + \frac{1}{2}\text{N}_2(g) \\
\Delta U_{\text{comb}} = -969.6 \text{ kJ mol}^{-1}
\]

The chemical equation shows that: \(\Delta n_g = (2 + \frac{1}{2}) + (\frac{9}{4}) = 0.25\) mol. Therefore:

\[
\Delta H = \Delta U + RT\Delta n_g
\]
\[ \Delta H = (-969.6 \text{ kJ}) + (8.314 \frac{J}{\text{mol K}} \times 1\text{kJ} \times 1000J \times 298.15 \text{ K} \times 0.25 \text{ mol}) \]
\[ \Delta H = -969.0 \text{ kJ} \]

2) **Enthalpy of neutralization and standard enthalpy of neutralization**

✓ **Neutralization** is the reaction between an acid and a base.

✓ **Neutralization** is the reaction between H\(^+\)(aq) and OH\(^-\)(aq), to produce liquid water H\(_2\)O(L):

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(L) \]

The heat released, at constant temperature and pressure, as a result of reaction between H\(_3\)O\(^+\)(aq), and OH\(^-\)(aq) to produce liquid water H\(_2\)O(L) is called the enthalpy of neutralization \(\Delta H_{\text{neut}}\). If the amount of water produced is one mole, and the conditions are the standard conditions, it is called **standard enthalpy of neutralization**, \(\Delta H_{\text{neut}}^o\) and it equals \(-57 \text{ kJ}\):

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(L) \quad \Delta H_{\text{neut}}^o = -57 \text{ kJ} \]

✓ This means that when 1 mole of an aqueous H\(^+\) is neutralized with 1 mole of an aqueous OH\(^-\) at the standard conditions, 57 kJ of heat is released.

✓ The question is: "How can we get an aqueous H\(^+\) and an aqueous OH\(^-\)?"

✓ We can get H\(^+\)(aq) from an acid and OH\(^-\)(aq) from a base.

✓ Therefore, no wonder that the common definition of the neutralization reaction is that it is the reaction between an acid and a base.

✓ **Strong acids and bases**

Strong acids and bases are solutions of ionic compounds that dissociate in water and provide their aqueous H\(^+\) and OH\(^-\) ions. Therefore, one mole of a strong acid like HCl gives one mole of H\(^+\)(aq), and one mole of a strong base like NaOH gives one mole of OH\(^-\):

\[ \text{HCl}(g) + \text{H}_2\text{O}(L) \rightarrow \text{Cl}^-(aq) + \text{H}_3\text{O}^+(aq) \]
\[ \text{NaOH}(s) + \text{H}_2\text{O}(L) \rightarrow \text{OH}^-(aq) + \text{Na}^+(aq) \]

Consequently, the reaction between one mole of each will produce one mole of liquid H\(_2\)O and 57 kJ of heat:

\[ \text{H}^+(aq) + \text{Cl}^-(aq) + \text{Na}^+(aq) + \text{OH}^-(aq) \rightarrow \text{Na}^+(aq) + \text{Cl}^-(aq) + \text{H}_2\text{O}(L) \]

This reaction is usually written in a simplified equation as follows:

\[ \text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(L) \quad \Delta H_{\text{neut}}^o = -57 \text{ kJ} \]

This simplified equation justifies defining neutralization reaction as the reaction between H\(^+\)(aq) and OH\(^-\)(aq).

✓ **Weak acids and bases**

Weak acids and bases are partially ionized. Therefore, one mole of a weak acid like CH\(_3\)COOH gives less than one mole of H\(^+\). Also, one mole of a weak base like NH\(_3\) gives less than one mole of OH\(^-\):
CH$_3$COOH(L) + H$_2$O(L) $\rightleftharpoons$ CH$_3$COO$^-$ (aq) + H$_3$O$^+$ (aq)

NH$_3$(g) + H$_2$O(L) $\rightleftharpoons$ OH$^-$ (aq) + NH$_4^+$ (aq)

Because these reactions are reversible they do not proceed to completion. Consequently, if the neutralization reaction involves weak acids or bases, water produced is less than if none of them is involved. However, when the weak acid and the weak base is involved their available H$_3$O$^+$ and OH$^-$ (aq) combines to produce H$_2$O and energy. This consumption of ions must be compensated for by using the energy released to ionize the unionized molecules of the acid and the base. Eventually, all the reactants are consumed but some of the 57 kJ was used for the ionization, which means that we end up with less than 57 kJ. Although one mole of H$_2$O is produced as a result of the reaction between weak acids and bases and 57 kJ must have been released, the net amount of energy released is less than 57 kJ by the amount consumed to complete ionization.

This is the reason why, at standard conditions, neutralization involving strong acids and bases releases 57 kJ while it releases less than 57 kJ when it involves weak acids and bases.

3) **Enthalpy of formation and standard enthalpy of formation**

- Any substance can be prepared in labs and manufactured in industrial plants by so many different ways, any of which can be called a formation reaction of the substance.
- If we chose CO$_2$(g) as an example, we see that it can be formed in hundreds or more ways. The following are just a few of them:
  
  CO(g) + 0.5O$_2$(g) $\rightarrow$ CO$_2$(g)  
  CaCO$_3$(s) $\rightarrow$ CO$_2$(g) + CaO(s)  
  C(graph) + O$_2$(g) $\rightarrow$ CO$_2$(g)  
  CH$_4$(g) + 2O$_2$(g) $\rightarrow$ CO$_2$(g) + 2H$_2$O(L)  
  CH$_4$(g) + 2O$_2$(g) $\rightarrow$ CO$_2$(g) + 2H$_2$O(L)

- Any other substance we chose is the same. It can be formed by so many different ways.
- In chemical thermodynamics, not any reaction that produces a certain substance is named its **formation reaction**.
- In chemical thermodynamics convention, the formation reaction of a substance is only the reaction which forms only one mole of the substance from the reaction which happens between the elements of the substance while they are in their standard states.
- The **reference state** of an element is its most stable form under the prevailing conditions. We need to be cautious not to confuse “reference state” with “standard state”: the reference state of carbon at 25°C is graphite; the standard state of carbon is any specified phase of the element at standard pressure. For example, the standard enthalpy of formation of H$_2$O(L) at 25°C is obtained from the following thermochemical equation and is:

  H$_2$(g) + O$_2$(g) $\rightarrow$ H$_2$O(L)  \hspace{1cm} \Delta H_f^{\circ}$,H$_2$O(L) = −286 kJ

- The table below shows the reference state of some elements.
It is clear that this definition of the formation reaction has three **musts**:
1) The amount of the substance formed **must** be one mole.
2) The reactants **must** be elements.
3) The reacting elements **must** be in their standard states.

Regarding the previous equations concerning CO₂(g) only one of them satisfies these three **musts**, and therefore is named the formation reaction of CO₂(g), it is this reaction below:

\[
\text{C(graph)} + \text{O}_2(g) \rightarrow \text{CO}_2(g)
\]

Even though all of the other reactions produce CO₂(g), no one of them is considered, in chemical thermodynamics, the formation reaction of CO₂(g).

The formation reaction of H₂O(L) is no reaction except:

\[
\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(L)
\]

Why do we call the previous reaction "the formation reaction of H₂O(L)?"
The answer is: Because it is the reaction that produces only one mole of H₂O(L) from its elements while they are in their standard states. Any other way to produce H₂O(L) such as the following is not its formation reaction:

\[
\begin{align*}
\text{H}_2(g) + \text{O}(g) &\rightarrow \text{H}_2\text{O}(L) \\
\text{H}_2\text{O}(s) &\rightarrow \text{H}_2\text{O}(L) \\
\text{CH}_4(g) + 2\text{O}_2(g) &\rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(L)
\end{align*}
\]

The heat absorbed or released, at constant temperature and pressure, as a result of the formation of a substance is its **enthalpy of formation**, ∆\(\text{H}_f\). If the amount formed, is one mole, and the pressure is the standard pressure, it is called the **standard enthalpy of formation**, ∆\(\text{H}_f^\circ\).

Below are some thermochemical equation representing the formation reaction of some substances:

\[
\begin{align*}
\text{H}_2(g) + 0.5\text{O}_2(g) &\rightarrow \text{H}_2\text{O}(L) \quad \Delta\text{H}_f^\circ = -285.83 \text{ kJ} \\
\text{C(graph)} + 1.5\text{O}_2(g) &\rightarrow \text{CO}_2(g) \quad \Delta\text{H}_f^\circ = -393.51 \text{ kJ}
\end{align*}
\]
0.5H₂(g) + C(graph) + 0.5N₂(g) → HCN(L) \[ \Delta H_f^o = + 108.78 \text{ kJ} \]
Cd(s) + C(graph) + 1.5O₂(g) → CdCO₃(s) \[ \Delta H_f^o = -750.6 \text{ kJ} \]
0.5H₂(g) → H*(g) \[ \Delta H_f^o = + 218 \text{ kJ} \]
0.5H₂(g) → H(g) \[ \Delta H_f^o = + 436 \text{ kJ} \]

✓ According to this specified definition, if our substance, by itself, is an element in its standard state, it has no formation reaction. Therefore, the standard enthalpy of formation of any element in its standard state is **zero**. This is simply because their formation is the null reaction:

Element in its standard state → Element in its standard state

✓ Note, however, that the standard enthalpy of formation of an element in a state other than its reference state is not zero. The following is an example:

C(s, graphite) → C(s, diamond) \[ \Delta H_f^o = + 1.895 \text{ kJ} \]

Therefore, although \( \Delta H_{f,C,\text{graphite}}^o = 0 \), \( \Delta H_{f,C,\text{diamond}}^o = + 1.895 \text{ kJ mol}^{-1} \).

✓ The reference states of the elements define a thermochemical “sea level”, and enthalpies of formation can be regarded as thermochemical “altitudes” above or below sea level.

✓ The figure below shows that the “sea level” is the elements in its reference state from which a compound is made and the enthalpy of formation acts as a kind of thermochemical “altitude” of the compound with respect to the “sea level”. Endothermic formation reactions of a substance have positive enthalpies of formation; exothermic formation reactions of a substance have negative energies of formation.

✓ Substances that have negative standard enthalpies of formation (such as water) are classified as **exothermic substances**, because they lie at a lower enthalpy than their component elements (they lie below thermochemical sea level). Opposite to the are classified as **endothermic substances**.

✓ Some reactions can have more than one name. For example, formation reaction of CO₂(g) is, at the same time, its combustion reaction.

✓ In major chemistry books, the enthalpies of formation of substances are always tabulated. An example of such tables is presented here.
<table>
<thead>
<tr>
<th>compound</th>
<th>ΔH_f° (kJ/mol)</th>
<th>compound</th>
<th>ΔH_f° (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr(s)</td>
<td>−99.5</td>
<td>C_2H_2(g)</td>
<td>+226.7</td>
</tr>
<tr>
<td>AgCl(s)</td>
<td>−127.0</td>
<td>C_2H_4(g)</td>
<td>+52.3</td>
</tr>
<tr>
<td>AgI(s)</td>
<td>−62.4</td>
<td>C_2H_6(g)</td>
<td>−84.7</td>
</tr>
<tr>
<td>Ag_2O(s)</td>
<td>−30.6</td>
<td>C_3H_4(g)</td>
<td>−103.8</td>
</tr>
<tr>
<td>Ag_2S(s)</td>
<td>−31.8</td>
<td>n-C_4H_{10}(g)</td>
<td>−124.7</td>
</tr>
<tr>
<td>Al_2O_3(s)</td>
<td>−1669.8</td>
<td>n-C_5H_{12}(l)</td>
<td>−173.1</td>
</tr>
<tr>
<td>BaCl_2(s)</td>
<td>−860.1</td>
<td>C_2H_5OH(l)</td>
<td>−277.6</td>
</tr>
<tr>
<td>BaCO_3(s)</td>
<td>−1218.8</td>
<td>CoO(s)</td>
<td>−239.3</td>
</tr>
<tr>
<td>BaO(s)</td>
<td>−558.1</td>
<td>Cr_2O_3(s)</td>
<td>−1128.4</td>
</tr>
<tr>
<td>BaSO_4(s)</td>
<td>−1465.2</td>
<td>CuO(s)</td>
<td>−155.2</td>
</tr>
<tr>
<td>CaCl_2(s)</td>
<td>−795.0</td>
<td>Cu_2O(s)</td>
<td>−166.7</td>
</tr>
<tr>
<td>CaCO_3</td>
<td>−1207.0</td>
<td>CuS(s)</td>
<td>−48.5</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>−635.5</td>
<td>CuSO_4(s)</td>
<td>−769.9</td>
</tr>
<tr>
<td>Ca(OH)_2(s)</td>
<td>−986.6</td>
<td>Fe_2O_3(s)</td>
<td>−822.2</td>
</tr>
<tr>
<td>CaSO_4(s)</td>
<td>−1432.7</td>
<td>Fe_3O_4(s)</td>
<td>−1120.9</td>
</tr>
<tr>
<td>CCl_4(l)</td>
<td>−139.5</td>
<td>HBr(g)</td>
<td>−36.2</td>
</tr>
<tr>
<td>CH_4(g)</td>
<td>−74.8</td>
<td>HCl(g)</td>
<td>−92.3</td>
</tr>
<tr>
<td>CH_3OH(l)</td>
<td>−238.6</td>
<td>HI(g)</td>
<td>+25.9</td>
</tr>
<tr>
<td>CO(g)</td>
<td>−110.5</td>
<td>HNO_3(l)</td>
<td>−173.2</td>
</tr>
<tr>
<td>CO_2(g)</td>
<td>−393.5</td>
<td>H_2O(g)</td>
<td>−241.8</td>
</tr>
<tr>
<td>H_2O(l)</td>
<td>−285.8</td>
<td>NH_3Cl(s)</td>
<td>−315.4</td>
</tr>
<tr>
<td>H_2O_2(l)</td>
<td>−187.6</td>
<td>NH_4NO_3(s)</td>
<td>−365.1</td>
</tr>
<tr>
<td>H_2S(g)</td>
<td>−20.1</td>
<td>NO(g)</td>
<td>+90.4</td>
</tr>
<tr>
<td>H_2SO_4(l)</td>
<td>−811.3</td>
<td>NO_2(g)</td>
<td>+33.9</td>
</tr>
<tr>
<td>HgO(s)</td>
<td>−90.7</td>
<td>NiO(s)</td>
<td>−244.3</td>
</tr>
<tr>
<td>HgS(s)</td>
<td>−58.2</td>
<td>PbBr_2(s)</td>
<td>−277.0</td>
</tr>
<tr>
<td>KBr(s)</td>
<td>−392.2</td>
<td>PbCl_2(s)</td>
<td>−359.2</td>
</tr>
<tr>
<td>KCl(s)</td>
<td>−435.9</td>
<td>PbO(s)</td>
<td>−217.9</td>
</tr>
<tr>
<td>KClO_3(s)</td>
<td>−391.4</td>
<td>PbO_2(s)</td>
<td>−276.6</td>
</tr>
<tr>
<td>KF(s)</td>
<td>−562.6</td>
<td>Pb_3O_4(s)</td>
<td>−734.7</td>
</tr>
<tr>
<td>MgCl_2(s)</td>
<td>−641.8</td>
<td>PCl_3(g)</td>
<td>−306.4</td>
</tr>
<tr>
<td>MgCO_3(s)</td>
<td>−1113</td>
<td>PCl_5(g)</td>
<td>−398.9</td>
</tr>
<tr>
<td>MgO(s)</td>
<td>−601.8</td>
<td>SiO_2(s)</td>
<td>−859.4</td>
</tr>
<tr>
<td>Mg(OH)_2(s)</td>
<td>−924.7</td>
<td>SnCl_2(s)</td>
<td>−349.8</td>
</tr>
<tr>
<td>MgSO_4(s)</td>
<td>−1278.2</td>
<td>SnCl_4(l)</td>
<td>−545.2</td>
</tr>
<tr>
<td>MnO(s)</td>
<td>−384.9</td>
<td>SnO(s)</td>
<td>−286.2</td>
</tr>
<tr>
<td>MnO_2(s)</td>
<td>−519.7</td>
<td>SnO_2(s)</td>
<td>−580.7</td>
</tr>
<tr>
<td>NaCl(s)</td>
<td>−411.0</td>
<td>SO_2(g)</td>
<td>−296.1</td>
</tr>
<tr>
<td>NaF(s)</td>
<td>−569.0</td>
<td>SO_3(g)</td>
<td>−395.2</td>
</tr>
<tr>
<td>NaOH(s)</td>
<td>−426.7</td>
<td>ZnO(s)</td>
<td>−348.0</td>
</tr>
<tr>
<td>NH_3(g)</td>
<td>−46.2</td>
<td>ZnS(s)</td>
<td>−202.9</td>
</tr>
</tbody>
</table>

✓ With the introduction of the standard enthalpies of formation, the enthalpy of any reaction can be determined using the following equation:

\[ \Delta H_{rxn}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants}) \]
The right side of the equation consists of two terms. The first term is the sum of the standard enthalpies of formation of all the products; the second is the sum of the standard enthalpies of formation of all the reactants.

**Example 4.11**
From the table below,

<table>
<thead>
<tr>
<th></th>
<th>LiOH(s)</th>
<th>CO₂(g)</th>
<th>Li₂CO₃(s)</th>
<th>H₂O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°f / kJ mol⁻¹</td>
<td>−484.9</td>
<td>−393.5</td>
<td>−1216.0</td>
<td>−241.8</td>
</tr>
</tbody>
</table>

Calculate the standard enthalpy change of the following reaction:

\[ 2\text{LiOH(s)} + \text{CO}_2(g) \rightarrow \text{Li}_2\text{CO}_3(s) + \text{H}_2\text{O}(g) \quad \Delta H°_{\text{rxn}} = ? \]

**Solution**

\[ \Delta H°_{\text{rxn}} = \sum \Delta H°_f(\text{products}) - \sum \Delta H°_f(\text{reactants}) \]

\[ \Delta H°_{\text{rxn}} = \sum \{(−1216.0) + (−241.8)\} - \sum \{2 \times (−484.9) + (−393.5)\} \]

\[ \Delta H°_{\text{rxn}} = −94.5 \text{ kJ} \]

**Practice exercise**
From the table below,

<table>
<thead>
<tr>
<th></th>
<th>PbO(s)</th>
<th>CO(g)</th>
<th>CO₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH°f / kJ mol⁻¹</td>
<td>−219</td>
<td>−111</td>
<td>−394</td>
</tr>
</tbody>
</table>

Calculate the standard enthalpy change of the following reaction:

\[ \text{PbO(s)} + \text{CO}(g) \rightarrow \text{Pb}(s) + \text{CO}_2(g) \quad \Delta H°_{\text{rxn}} = ? \]

---

4) **Lattice Energy** (E_L) and Born-Haber Cycle

- Ionic compounds are formed from the strong electrostatic attractions between cations and anions known as ionic bonds.
- The strength of an ionic bond is the energy released as a result of forming an ionic compound, such as sodium chloride (NaCl) from the reaction between its gaseous ions; or by the energy absorbed as a result of dissociating ionic compound to its gaseous ions:

\[ \text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s) \]

or

\[ \text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \]

Of course, the values of ΔH are the same but their signs are not.

- The **lattice energy** which is also called the **enthalpy of lattice** is defined as the amount of heat released, at constant temperature and pressure, as a result of forming an ionic substance from its gaseous ions; or the amount of heat absorbed, at constant temperature and pressure, as a result of dissociating an ionic substance to its gaseous ions.

- If the amount formed or dissociated, is one mole, and the pressure is the standard pressure, it is called the **standard enthalpy of lattice**, ΔH°_lattice; or **standard lattice energy**, E_L.

- It appears that its sign can be either negative or positive depending on wither the ionic substance is formed or dissociated.

- We will stick to the following definition for Standard Lattice Energy:

\[ \text{Standard Lattice Energy is the energy absorbed to produce gaseous ions from 1 mole of the crystalline ionic solid at the standard conditions.} \]
• The precise value of the lattice energy may not be determined experimentally, because of the impossibility of preparing an adequate number of gaseous cations and anions and measuring the energy released during their attractions to form the solid.

• In 1916 and to calculate the lattice energies, the German scientists Born and Haber devised a thermochemical cycle, known as Born-Haber cycle.

• NaCl is the most common ionic compound usually used as an example to illustrate the Born-Haber cycle.

• It’s found that at standard conditions, producing Na$^+(g)$ and Cl$^-(g)$ from one mole of NaCl(s) requires the absorption of 787.25 kJ.

• The thermochemical equation representing the lattice energy of NaCl(s) is:

\[ \text{NaCl(s)} \rightarrow \text{Na}^+(g) + \text{Cl}^-(g) \quad \Delta H_{\text{lattice}} = + 787.25 \text{ kJ} \]

• Taking NaCl as an example, below is one way of presenting how the Born-Haber cycle is used to obtain the values of its lattice energy:

  NaCl(s) → Na$^+(g)$ + Cl$^-(g)$ \hspace{1cm} \Delta H_{\text{lattice}} = + 787.25 \text{ kJ}

  - The born-Haber consists of the following five steps:
    Step 1: absorption of 411 kJ to decompose 1 mole of NaCl(s) to 1 mole of Na(s) and 0.5 mole of Cl$_2$(g).
      \[ \text{NaCl(s)} \rightarrow \text{Na(s)} + 0.5\text{Cl}_2(g) \quad \Delta H_1 = + 411.15 \text{ kJ} \]
      This is the opposite of the formation of NaCl(s):
      \[ \text{NaCl(s)} \rightarrow \text{Na}(s) + 0.5\text{Cl}_2(g) \quad \Delta H_1 = + 411.15 \text{ kJ} \]
Step 2: absorption of 107.32 kJ to atomize one mole of Na(s) to one mole of Na(g):

\[ \text{Na}(s) \rightarrow \text{Na}(g) \quad \Delta H_2 = +107.32 \text{ kJ} \]

Step 3: absorption of 121 kJ to atomize 0.5 mole of \( \text{Cl}_2(g) \):

\[ 0.5\text{Cl}_2(g) \rightarrow \text{Cl}(g) \quad \Delta H_3 = +121.68 \text{ kJ} \]

Step 4: absorption of 498.3 kJ to ionize one mole of Na(g):

\[ \text{Na}(g) \rightarrow \text{Na}^+ (g) + e^- \quad \Delta H_4 = +498.3 \text{ kJ} \]

Step 5: release of 351.2 kJ to ionize one mole of Cl(g):

\[ \text{Cl}(g) + e^- \rightarrow \text{Cl}^- (g) \quad \Delta H_5 = -351.2 \text{ kJ} \]

- Our aim is to calculate the value of \( \Delta H \) of the following equation:

\[ \text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^- (g) \quad \Delta H_6 = \Delta H_{\text{lattice}}^\circ = ? \]

- By applying Hess’s law of heat summation on the five steps of born-Haber cycle we achieve our aim.

\[ \begin{align*}
\text{NaCl}(s) & \rightarrow \text{Na}(s) + 0.5\text{Cl}_2(g) \\
\text{Na}(s) & \rightarrow \text{Na}(g) \\
0.5\text{Cl}_2(g) & \rightarrow \text{Cl}(g) \\
\text{Na}(g) & \rightarrow \text{Na}^+(g) + e^- \\
\text{Cl}(g) + e^- & \rightarrow \text{Cl}^- (g)
\end{align*} \]

\[ \Delta H_1 = +411.15 \text{ kJ} \]

\[ \Delta H_2 = +107.32 \text{ kJ} \]

\[ \Delta H_3 = +121.68 \text{ kJ} \]

\[ \Delta H_4 = +498.3 \text{ kJ} \]

\[ \Delta H_5 = -351.2 \text{ kJ} \]

\[ \Delta H_{\text{lattice}, \text{NaCl}} = +787.25 \text{ kJ} \]

This is the standard lattice energy of NaCl(s) obtained by the Born-Haber cycle.

- The value of \( \Delta H_{\text{lattice}}^\circ \) for any ionic compound can easily be determined using this cycle.

**Example 4.12**

Use the information below and Born-Haber method to calculate \( \Delta H_{\text{lattice}, \text{NaCl}}^\circ \).

<table>
<thead>
<tr>
<th>( \Delta H_{\text{f,NaF}}^\circ )</th>
<th>( \Delta H_{\text{atom,Na}}^\circ )</th>
<th>( \Delta H_{\text{atom,Cl}}^\circ )</th>
<th>( \Delta H_{\text{ioniz,Na}}^\circ )</th>
<th>( \Delta H_{\text{elec,aff,F}}^\circ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>kJ mol(^{-1})</td>
<td>-569.00</td>
<td>107.32</td>
<td>155.00</td>
<td>498.3</td>
</tr>
</tbody>
</table>

Draw the relevant diagram.

**Solution**

The born-Haber consists of the following five steps:

**Step 1**: absorption of 569.00 kJ to decompose 1 mole of NaF(s) to 1 mole of Na(s) and 0.5 mole of F\(_2\)(g).

This is the opposite of the formation of NaF(s):

\[ \text{NaF}(s) \rightarrow \text{Na}(s) + 0.5\text{F}_2(g) \quad \Delta H_1 = +569.00 \text{ kJ} \]

**Step 2**: absorption of 107.32 kJ to atomize one mole of Na(s) to one mole of Na(g):

\[ \text{Na}(s) \rightarrow \text{Na}(g) \quad \Delta H_2 = +107.32 \text{ kJ} \]

**Step 3**: absorption of 155.00 kJ to atomize 0.5 mole of F\(_2\)(g):

\[ 0.5\text{F}_2(g) \rightarrow 2\text{F}(g) \quad \Delta H_3 = +155.00 \text{ kJ} \]

\[ \text{Na}(g) \rightarrow \text{Na}^+(g) + e^- \quad \Delta H_4 = +498.3 \text{ kJ} \]

\[ \text{Cl}(g) + e^- \rightarrow \text{Cl}^- (g) \quad \Delta H_5 = -351.2 \text{ kJ} \]

\[ \Delta H_{\text{lattice}, \text{NaCl}} = +787.25 \text{ kJ} \]
Our aim is to calculate the value of $\Delta H$ of the following equation:

By applying Hess's law of heat summation on the five steps of Born-Haber cycle we achieve our aim.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>$\Delta H$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>$0.5F_2(g) \rightarrow F(g)$</td>
<td>$\Delta H_3 = +155.00$</td>
</tr>
<tr>
<td>5</td>
<td>absorption of 500 kJ to ionize one mole of Na(g):</td>
<td>$\Delta H_4 = +498.3$</td>
</tr>
<tr>
<td></td>
<td>$Na(g) \rightarrow Na^+(g) + e^-$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>release of 364 kJ to ionize one mole of F(g):</td>
<td>$\Delta H_5 = -328.00$</td>
</tr>
<tr>
<td></td>
<td>$F(g) + e^- \rightarrow F^-(g)$</td>
<td></td>
</tr>
</tbody>
</table>

This is the standard lattice energy of NaF(s) obtained by the Born-Haber cycle. 

The relevant diagram for NaF is similar to that discussed above for NaCl except that we should replace Cl by F.

**Practice exercise**

Choose an ionic compound. Obtain from literature the necessary data needed to find its lattice energy. Apply Born-Haber cycle and draw the relevant diagram.

### 4.6 Effect of pressure and temperature on the enthalpies of reactions

- The factors affecting the enthalpies of reaction were mentioned on page 70. It was mentioned that the effect of pressure and temperature will be discussed later.
- Here we will not discuss the effect of changing pressure because whatever changes we do in pressure stays within the limits that do not effectively make noticeable changes in the enthalpies of reactions. Therefore, our discussion is limited to the effect of changing temperature at which reactions are carried out in their enthalpies.
- $\Delta H$ of a specified reaction is constant as long as the reaction occurs at the same temperature and pressure. Changing the reaction temperature and/or pressure changes the value of its $\Delta H$.
- It often happens that we have data at one temperature but need it at another temperature. For example, we might want to know the enthalpy of a particular reaction at body temperature, 37°C, but may have data available for 25°C.
- Another type of question might be whether the oxidation of glucose is more exothermic when it takes place inside an Arctic fish that inhabits water at 0°C than when it takes place at mammalian body temperatures.
- Similarly, we may need to predict whether the synthesis of ammonia is more exothermic at a typical industrial temperature of 450°C than at 25°C.
- The enthalpy of a substance increases with temperature. Therefore, if the total enthalpy of the reactants increases by a different amount from that of the products, the reaction enthalpy will change with temperature.
- The change in enthalpy is given as:

$$\Delta H = C_p \Delta T$$
In 1858, the German physicist Gustav Robert Kirchhoff had studied the effect of temperature on enthalpies of reactions, and gave the law known as **Kirchhoff law** which is derived as follows:

\[
\int_{T_1}^{T_2} d\Delta H^{\circ}_{\text{rxn}} = \int_{T_1}^{T_2} dC_p \, dT
\]

\[
\Delta H^{\circ}_{\text{rxn},T_2} - \Delta H^{\circ}_{\text{rxn},T_1} = \Delta C_p \, (T_2 - T_1)
\]

\[
\Delta H^{\circ}_{\text{rxn},T_2} = \Delta H^{\circ}_{\text{rxn},T_1} + \Delta C_p \, (T_2 - T_1)
\]

Of course, this is true only if \(C_p\) does not change as temperature changes, or if its change is negligible. This law makes it easy to calculate \(\Delta H\) of any reaction at any temperature provided that we know its \(\Delta H\) at a certain temperature.

The value of \(\Delta C_p\) is given as:

\[
\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})
\]

We can therefore expect the dependence of the reaction enthalpy on temperature is related to the difference in heat capacities of the products and the reactants.

As a simple example, consider the following reaction:

\[
2H_2(g) + O_2(g) \rightarrow 2H_2O(L)
\]

\[
\Delta C_p = \{2 \times C_{p,m,H_2O(L)}\} - \{2 \times C_{p,m,H_2(g)} + C_{p,m,O_2(g)}\}
\]

**Kirchhoff’s law** states that the standard reaction enthalpy at one temperature can be calculated from the standard reaction enthalpy at another temperature provided we know the standard molar constant-pressure heat capacities of all the substances.

**Kirchhoff’s law** supposes that the heat capacities are constant over the range of temperature of interest, so the law is best restricted to small temperature differences (of no more than 100 K or so).

### Example
The standard enthalpy of formation of gaseous water at 25°C is \(-241.82\) kJ mol\(^{-1}\). Estimate its value at 100°C.

**Use the following information.**

<table>
<thead>
<tr>
<th>(C_{p,m}/\text{J K}^{-1}\text{ mol}^{-1})</th>
<th>H(_2)O(g)</th>
<th>H(_2) (g)</th>
<th>O(_2) (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>33.58</td>
<td>28.48</td>
<td>29.37</td>
</tr>
</tbody>
</table>

**Solution**

The chemical equation is:

\[
\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})
\]

The law to be used is the Kirchhoff’s law:

\[
\Delta H^{\circ}_{\text{rxn},T_2} = \Delta H^{\circ}_{\text{rxn},T_1} + \Delta C_p \, (T_2 - T_1)
\]

\[
\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})
\]

\[
\Delta C_p = C_{p}(\text{H}_2\text{O,L}) - \{C_{p,H_2(g)} + C_{p,O_2(g)}\}
\]

\[
\Delta C_p = 1 \text{ mol} \times 33.5 \frac{\text{J}}{\text{K mol}} - \{1 \text{ mol} \times 28.48 \frac{\text{J}}{\text{K mol}} + 0.5 \text{ mol} \times 29.37 \frac{\text{J}}{\text{K mol}}\}
\]

\[
\Delta C_p = -9.95 \frac{\text{J}}{\text{K mol}}
\]

\[
(T_2 - T_1) = 373 \text{ K} - 298 \text{ K} = 75 \text{ K}
\]
\[ \Delta H_{\text{rxn}, T_2} = \Delta H_{\text{rxn}, T_1} + \Delta C_p (T_2 - T_1) \]
\[ \Delta H_{\text{rxn}, T_2} = (1 \text{ mol} \times -241.82 \text{ kJ mol}^{-1}) + (-9.95 \frac{1}{R} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 75 \text{ K}) \]
\[ \Delta H_{\text{rxn}, T_2} = -242.57 \text{ kJ} \]

**Practice exercise**

The standard enthalpy of formation of gaseous ammonia at 298 K is −46.11 kJ mol⁻¹. Estimate its value at 400 K.

Use the following information.

<table>
<thead>
<tr>
<th></th>
<th>NH₃(g)</th>
<th>N₂(g)</th>
<th>H₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{p,m} )/J K⁻¹ mol⁻¹</td>
<td>35.06</td>
<td>29.125</td>
<td>28.824</td>
</tr>
</tbody>
</table>

- The calculations in the previous two examples show that the standard reaction enthalpy at the higher temperatures is only slightly different from those at 25°C.
- The reason is that the change in reaction enthalpy is proportional to the difference between the molar heat capacities of the products and the reactants, which is usually not very large.
- It is generally the case that, provided the temperature range is not too wide, enthalpies of reactions vary only slightly with temperature.
- A reasonable first approximation is that standard reaction enthalpies are independent of temperature especially when the temperature difference is within 100 K.

**Example**

Formaldehyde can be prepared from ethanol as follows. From the data given below at 298 K, calculate \( \Delta H_{\text{rxn}} \) of the following reaction at 398 K. Assume that heat capacities are the same at both temperatures.

\[ \text{H}_3\text{O}(\text{L}) \rightarrow \text{CH}_2\text{O}(\text{g}) + \text{H}_2(\text{g}) \]

<table>
<thead>
<tr>
<th></th>
<th>CH₃OH</th>
<th>CH₂O</th>
<th>H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta H_f )/kJ mol⁻¹</td>
<td>-234.7</td>
<td>-115.90</td>
<td></td>
</tr>
<tr>
<td>( C_{m,p} )/J mol⁻¹ K⁻¹</td>
<td>81.11</td>
<td>35.4</td>
<td>28.836</td>
</tr>
</tbody>
</table>

**Solution**

\[ \Delta H_{\text{rxn}} = \sum \Delta H_f^o(\text{products}) - \sum \Delta H_f^o(\text{reactants}) \]
\[ \Delta H_{\text{rxn}} = \sum \{(-115.90) + (0)\} \text{ kJ} - \sum (-234.7) \text{ kJ} \Delta H_{\text{rxn}} = +118.8 \text{ kJ} \]
\[ \Delta C_p = \sum C_p(\text{reactants}) - \sum C_p(\text{reactants}) \]
\[ \Delta C_p = (1 \text{ mol} \times 35.4 \text{ J mol}^{-1} \text{ K}^{-1} + 1 \text{ mol} \times 28.836 \text{ J mol}^{-1} \text{ K}^{-1}) - \\
(1 \text{ mol} \times 81.11 \text{ J mol}^{-1} \text{ K}^{-1}) \]
\[ \Delta H_{398} = \left[ (118.8 \text{ kJ}) + \left( -16.874 \text{ J K}^{-1} \right) \times (398 - 298) \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \right] \]
\[ \Delta H_{398} = 117.11 \text{ kJ} \]

**Practice exercise**

Knowing that \( \Delta H_{\text{diss}, H_2O(g)} = 241.75 \text{ kJ mol}^{-1} \) at 18 °C and 1 atm, use the information below to calculate \( \Delta H_{\text{diss}, H_2O(g)} \) at 68 °C and 1 atm.

<table>
<thead>
<tr>
<th></th>
<th>H₂O(g)</th>
<th>H₂(g)</th>
<th>O₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_p )/J K⁻¹ mol⁻¹</td>
<td>33.56</td>
<td>28.83</td>
<td>29.12</td>
</tr>
</tbody>
</table>
4.7 Hess's law of heat summation
- Hess is the famous Swiss-Russian chemist who, in 1840 and before the first law of thermodynamic was formulated as it appears now, introduced his law of heat summation. Therefore, Hess is considered a father of thermodynamics and the father of thermochemistry.
- His law was introduced on page 68 during our discussion of the thermochemical equation.

4.8 The different ways of finding values of enthalpies of reactions
The following is a summary of the methods used to find the value of enthalpies of any reaction. All these methods have already been discussed previously.

1. Use of the values of (∆U)
   While ∆H is the heat of reaction at constant temperature and pressure, ∆U is the heat of reaction at constant temperature and volume. If ∆U of any change is known is ∆H can be calculated from the following equation:

   $$\Delta H_{\text{rxn}}^{\circ} = \Delta U_{\text{rxn}}^{\circ} + PV = \Delta U_{\text{rxn}}^{\circ} + RT\Delta n_g$$

   This was illustrated section 3.2, chapter 3 page 53.

2. Use of Hess's Law
   Hess’s law shows that the value of ∆H of a reaction can be calculated from knowing the values of ∆H of some other reactions. This was illustrated on pages 68 and 69 when we talked about properties of thermochemical equations under the section titled “thermochemical equation and the units of ∆H”.

3. Use of the bond dissociation and the atomization energies
   Any reaction is simply the breaking of the old bonds between atoms of the reactants, and the formation of the new bonds between atoms of the products. The value of energy (heat) released from the formation of a bond is the negative value of the energy (heat) absorbed to break it. But the tabulated values of bond dissociation energies are all positive because they are the values to break bonds. It is possible to calculate:
   - The energy absorbed to break all reactants bonds ∑B(r), i.e. sum of the bond energies of all broken bonds in reactants.
   - The amount of energy absorbed to break all products bonds ∑B(p), i.e. the negative of the sum of the energy released as a result of forming all products bonds.

   These two values can be used to calculate the ∆H_{\text{rxn}}^{\circ} as follows:

   $$\Delta H_{\text{rxn}}^{\circ} = \sum B'(r) - \sum B'(p)$$

   This was explained and illustrated in solved examples when we talked about the bond dissociation energy (bond energy) on page 75; and the atomization energy on page 81.

4. Use of the values of enthalpies of formations
   The enthalpies of formation are the most useful and simplest tool used to calculate enthalpies of reactions. ∆H_{\text{rxn}}^{\circ} equals the sum of the standard enthalpies of formation of its reactants subtracted from the sum of enthalpies of formation of its products:
\[ \Delta H_{\text{rxn}}^\circ = \sum \Delta H_i^\circ (\text{products}) - \sum \Delta H_i^\circ (\text{reactants}) \]

This was illustrated on the example page 95 “enthalpy of formation and standard enthalpy of formation” on page 91.

5. **Use of the value of \( \Delta H \) at a certain temperature**

On page 66 we Kirchhoff’s Law was discussed on page 66:

\[ \Delta H_{\text{rxn}T_2}^\circ = \Delta H_{\text{rxn}T_1}^\circ + \Delta C_p (T_2 - T_1) \]

It makes it easy to us to calculate \( \Delta H_{\text{rxn}}^\circ \) of any reaction at any temperature provided that we know its value at a certain temperature.

This was discussed and illustrated in a solved example when we discussed “the effect of pressure and temperature on the enthalpies of reactions” on pages 97 and 99.
Questions and problems

1. Knowing that the formation of 1 mol of SO$_3$(g), in a bomb calorimeter, from the reaction between SO$_2$(g) and O$_2$(g) produces 97030 J of heat at 298 K, calculate $\Delta H$.

2. Evaluate $\Delta n_e$ in the following reactions:
   A) C(graphite) + O$_2$(g) $\rightarrow$ CO$_2$(g)
   B) C(graphite) + 0.5O$_2$(g) $\rightarrow$ CO(g)
   C) CH$_4$(g) + 2O$_2$(g) $\rightarrow$ CO$_2$(g) + 2H$_2$O(L)
   D) AgNO$_3$(s) + HCl(g) $\rightarrow$ AgCl(s) + HNO$_3$(L)

3. Calculate $\Delta U$ of the following reactions at 25 ºC:
   A) C(graphite) + O$_2$(g) $\rightarrow$ CO$_2$(g) $\Delta H = -393.5$ kJ
   B) C(graphite) + 0.5O$_2$(g) $\rightarrow$ CO(g) $\Delta H = -110.5$ kJ
   C) CH$_4$(g) + 2O$_2$(g) $\rightarrow$ CO$_2$(g) + 2H$_2$O(L) $\Delta H = -89.35$ kJ
   D) AgNO$_3$(s) + HCl(g) $\rightarrow$ AgCl(s) + HNO$_3$(L) $\Delta H = -85.30$ kJ

4. Knowing that at 25 ºC:
   COCl$_2$(g) + H$_2$S(g) $\rightarrow$ 2HCl(g) + COS(g) $\Delta H = -78.705$ kJ
   H$_2$O(L) + CS$_2$(s) $\rightarrow$ H$_2$S(g) + COS(g) $\Delta H = -3.420$ kJ
   calculate $\Delta H$ of the following reaction:
   COCl$_2$(g) + 2H$_2$S(g) $\rightarrow$ 2HCl(g) + H$_2$O(L) + CS$_2$(g)

5. Knowing that:
   CH$_4$(g) + 2O$_2$(g) $\rightarrow$ 2CO$_2$(g) + 2H$_2$O(L) $\Delta H = -890.34$ kJ
   H$_2$(g) + 0.5O$_2$(g) $\rightarrow$ H$_2$O(L) $\Delta H = -285.84$ kJ
   C(graphite) + O$_2$(g) $\rightarrow$ CO$_2$(g) $\Delta H = -393.5$ kJ
   calculate $\Delta U$ of the following reaction:
   C(graphite) + 2H$_2$(g) $\rightarrow$ CH$_4$(g) $\Delta H =$ ?

6. Knowing that $\Delta H_f^\circ$, in kJ mol$^{-1}$, of CO$_2$(g) = −393.5, and H$_2$O(L) = −285.8; and:
   C$_4$H$_{10}$(g) + 6.5O$_2$(g) $\rightarrow$ 4CO$_2$(g) + 5H$_2$O(L) $\Delta H_{\text{comb}}^\circ = -2878.5$ kJ
   Calculate $\Delta H_f^\circ$, C$_4$H$_{10}$(g)$^\circ$.

7. Knowing that:
<table>
<thead>
<tr>
<th>Substance</th>
<th>C$<em>4$H$</em>{10}$(g)</th>
<th>CO$_2$(g)</th>
<th>H$_2$O(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f^\circ / \text{kJ mol}^{-1}$</td>
<td>124.5</td>
<td>-393.5</td>
<td>-285.8</td>
</tr>
</tbody>
</table>
   Calculate, in kJ mol$^{-1}$, $\Delta H_{\text{comb}, \text{C}_4\text{H}_{10}(g)}^\circ$.

8. Knowing that:
<table>
<thead>
<tr>
<th>Substance</th>
<th>C(g)</th>
<th>H(g)</th>
<th>O(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{atom}}^\circ / \text{kJ mol}^{-1}$</td>
<td>716.68</td>
<td>217.97</td>
<td>249.2</td>
</tr>
</tbody>
</table>
   and:
<table>
<thead>
<tr>
<th>Bond</th>
<th>C$\cdots$H</th>
<th>C$\cdots$C</th>
<th>C$\cdots$O</th>
<th>O$\cdots$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol$^{-1}$</td>
<td>413</td>
<td>348</td>
<td>351</td>
<td>463</td>
</tr>
</tbody>
</table>
   Calculate, in kJ mol$^{-1}$, $\Delta H_f^\circ$, CH$_3$CH$_2$OH(L)$^\circ$.

9. Knowing that:
<table>
<thead>
<tr>
<th>Bond</th>
<th>H$\cdots$H</th>
<th>C$\cdots$H</th>
<th>C$\cdots$C</th>
<th>C$\equiv$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy / kJ mol$^{-1}$</td>
<td>426</td>
<td>413</td>
<td>348</td>
<td>610</td>
</tr>
</tbody>
</table>
   Calculate, in kJ mol$^{-1}$, $\Delta H_f^\circ$, hydrogenation, ethylene gas$^\circ$.

10. Knowing that:
    | Substance       | H$_2$O(g) | H$_2$S(g) | O$_2$(g) |
    |-----------------|-----------|-----------|----------|
    | $C_p,m / \text{J K}^{-1} \text{mol}^{-1}$ | 33.56     | 28.83     | 29.12    |
    and $\Delta H_{\text{dissociation}, \text{H}_2\text{O(g)}}^\circ$ at 101325 Pa and 18 ºC, is 241.75 kJ mol$^{-1}$, calculate $\Delta H_{\text{dissociation}, \text{H}_2\text{O(g)}}^\circ$ at 101325 Pa and 68 ºC.
5. THE SECOND LAW
5. THE SECOND LAW

5.1 Carnot cycle
- Carnot cycle is an example of a reversible cycle. It was named after the French engineer Nicolas Sadi Carnot (1769-1832).
- It is the manifestation of a heat engine.
- In this cycle an ideal gas undergoes:
  ✓ Two reversible expansions, one is isothermal and the other is adiabatic.
  ✓ Two reversible compressions, one is isothermal and the other is adiabatic.

5.1.1 The four processes of Carnot’s cycle
1) First process (from state 1 to state 2):
  ✓ This is a reversible isothermal expansion from volume “V₁” to volume “V₂”.
  ✓ Heat is absorbed by the gas at constant high temperature “T_H” and an expansion work is done by the gas:

\[
Q_1 = nR T_H \ln \frac{V_2}{V_1} \\
w_1 = nRT_H \ln \frac{V_1}{V_2}
\]

2) Second process (from state 2 to state 3):
  ✓ This is a reversible adiabatic expansion from volume “V₂” to volume “V₃”.
  ✓ No heat is absorbed or released by the gas but an expansion work is done by the gas. This means that temperature will decrease from the high temperature “T_H” to a lower temperature “T_L”:

\[
Q_2 = 0 \\
w_2 = C_v (T_L - T_H)
\]

3) Third process (from state 3 to state 4):
  ✓ This is a reversible isothermal compression from volume “V₃” to volume “V₄”.
✓ Heat is released by the gas at the low temperature \((T_L)\) and a compression work is done on the gas:

\[
Q_L = nRT_L \ln \frac{V_4}{V_3}
\]

\[
w_{3,4} = nRT_L \ln \frac{V_3}{V_4}
\]

4) **Fourth and final process (from state 4 to state 1):**

✓ This process is a reversible adiabatic compression from volume “\(V_4\)” to volume “\(V_1\)”.

✓ No heat is absorbed or released by the gas but a compression work is done on the gas. This means that temperature will increase from the low temperature “\(T_L\)” to the high temperature “\(T_H\)”:

\[
Q_4 = 0
\]

\[
w_4 = C_v (T_H - T_L)
\]

5.1.2 **The engine efficiency**

- The net work done by the system \((w_{\text{net}})\) is:

\[
w_{\text{net}} = w_1 + w_2 + w_3 + w_4
\]

\[
w_{\text{net}} = nR(T_L - T_H) \ln \frac{V_1}{V_2}
\]

- The heat absorbed by the system is:

\[
Q_H = nRT_H \ln \frac{V_2}{V_1}
\]

- The engine efficiency denoted "\(e\)" or "\(\eta\)" is calculated by the ratio of work achieved to the heat absorbed:

\[
\eta = \frac{w_{\text{net}}}{Q_H}
\]
\[ \eta = \frac{nR(T_L - T_H) \ln \frac{V_2}{V_1}}{nRT_H \ln \frac{V_2}{V_1}} \]

\[ \eta = \left(1 - \frac{T_L}{T_H}\right) \times 100 \]

- Idealized engine of maximum efficiency, working in reversible cycle doesn't really exist. All real engines are less efficient than the Carnot Engine because they operate irreversibly (due to friction) and because they complete a cycle in a brief time period (are never in a state of equilibrium).

**Example 5.1**
Knowing that the boiling point of water at \(1 \times 10^5 \) Pa is 100 °C and at \(5 \times 10^6 \) Pa is 295 °C, calculate the efficiency of an engine that operates between a condenser temperature of 40 °C and the boiling point of water at each of these two pressures.

**Solution**
\[ \eta = 1 - \frac{T_L}{T_H} \times 100 \]

<table>
<thead>
<tr>
<th>Pressure (Pa)</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1 \times 10^5)</td>
<td>16.1%</td>
</tr>
<tr>
<td>(5 \times 10^6)</td>
<td>44.9%</td>
</tr>
</tbody>
</table>

**Practice exercise**
Calculate the quantity of heat required to perform a 1000 J of work by an engine that operates between 300K and 400K.

**Example 5.2**
One mole of an ideal gas is used in Carnot cycle. It expands first isothermally at 600K from \(1 \times 10^6\) Pa to \(1 \times 10^5\) Pa; then adiabatically to a minimum temperature equals to 300K; then it is compressed first isothermally at 300 K to \(1 \times 10^6\) Pa, then adiabatically to a maximum temperature of 600 K. Knowing that \(C_{m,p} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}\), calculate \(\Delta U\), \(w\), \(q\), network, and efficiency.

**Solution**

First:
\( \Delta U_1 = 0 \)
\[ w_1 = nRT \ln \frac{P_2}{P_1} = 1 \times 8.314 \times 600 \times \ln \frac{1 \times 10^6}{1 \times 10^5} = -11486 \text{ J} \]
\[ q_1 = -w_1 = +11486 \text{ J} \]

Second:
\( \Delta U_2 = n \times C_{m,v} \Delta T = n \times (C_{m,v} - R) \times \Delta T \)
\[ \Delta U_2 = 1 \times (20.785 - 8.314) \times (300 - 600) = -3741 \text{ J} \]
\[ w_2 = (\Delta U)_2 = -3741 \text{ J} \]

Third:
\( \Delta U_3 = 0 \)
\[ w_3 = nRT \ln \frac{P_2}{P_1} = 1 \times 8.314 \times 300 \times \ln \frac{1 \times 10^6}{1 \times 10^5} = +5743 \text{ J} \]
\[ q_3 = -w_3 = -5743 \text{ J} \]

Fourth: \( q_4 = 0 \)
\( \Delta U_4 = n \times C_{m,v} \Delta T = n \times (C_{m,v} - R) \times \Delta T \)
\[ \Delta U_4 = 1 \times (20.785 - 8.314) \times (600 - 300) = +3741 \text{ J} \]
\[ w_4 = (\Delta U)_4 = +3741 \text{ J} \]

Net:
\( \Delta U = (\Delta U)_1 + (\Delta U)_2 + (\Delta U)_3 + (\Delta U)_4 = 0 \)
\[ w = w_1 + w_2 + w_3 + w_4 = -5743 \text{ J} \]
\[ q = q_1 + q_2 + q_3 + q_4 = +5743 \text{ J} \]
\[ \eta = 1 - \frac{T_L}{T_H} \times 100 = 1 - \frac{300}{600} \times 100 = 50\% \]

OR

\[ \eta = \frac{w_{\text{net}}}{Q_{\text{H}}} = \frac{5743}{11486} = 0.50 \]

**Practice exercise**

One mol of an ideal gas expands at 373 K to twice its initial volume, expands adiabatically to three times its initial volume, compressed at its final temperature to an unspecified volume, and finally compressed adiabatically to its original volume. Knowing that \( C_{\text{v,m}} = 12.471 \, \text{J} \, \text{K}^{-1} \, \text{mol}^{-1} \), calculate \( \Delta U \), \( w \), \( q \), network, and efficiency.

### 5.1.3 The consequences of the Carnot's cycle

Mere glance to the efficiency equation \( (\eta = 1 - \frac{T_L}{T_H} \times 100) \) reveals that:

1. Efficiency depends on the initial and the final temperature not on the nature of the gas.
2. Efficiency can be 100% only if \( T_L = 0 \) K or if \( T_H = \infty \) K. Both choices are impossible.
3. Because it is impossible that \( T_L = 0 \) K and \( T_H = \infty \) K, it is impossible for the efficiency to be unity (100%).
4. Efficiency is always less than unity (less than 100%).
5. It is impossible for heat absorbed to be converted completely to work.
6. Some of the heat absorbed is always wasted doing no work.

### 5.2 Spontaneity: Spontaneous and nonspontaneous processes

- There are many daily observations suggest that changes can be divided into two classes:
  1. A **spontaneous change** which is a change that has a tendency to occur without work having to be done to bring it about. It is a change which has a natural tendency to occur. It is the process that occurs by its own, i.e. without external interferes.
  2. A **nonspontaneous change** is a change that can be brought about only by doing work. It is a change which has no natural tendency to occur. The reverse of any spontaneous process cannot occur by its own but it can be made to occur by doing work: gas can be compressed into a smaller volume by pushing in a piston, the temperature of a cool object can be raised by forcing an electric current through a heater attached to it, and water can be decomposed by the passage of an electric current. However, in each case we need to act in some way on the system to bring about the nonspontaneous change.

- Examples of some spontaneous changes are so many. Below are some:
  - Breaking a glass bottle into pieces upon falling on the floor is a spontaneous process but reforming the glass bottle from its broken pieces is a nonspontaneous process.
  - \( \text{CO}_2 \) formation from burning \( \text{C} \) in \( \text{O}_2 \) is a spontaneous process, but dissociation of \( \text{CO}_2 \) into \( \text{C} \) and \( \text{O}_2 \) is a nonspontaneous process.
  - Flow of water from the top of mountains down to valleys is a spontaneous process, but rising water from valleys up to the top of mountains is a nonspontaneous process.
  - Transfer of heat from a hot object to a cold one is a spontaneous process but transfer of heat from a cold object to a hot one is a nonspontaneous process.
In thermodynamics the term spontaneous has nothing to do with speed. Some spontaneous changes are very fast, such as the precipitation reaction that occurs when solutions of sodium chloride and silver nitrate are mixed. However, some spontaneous changes are so slow that there may be no observable change even after millions of years. For example, although the decomposition of benzene into carbon and hydrogen is spontaneous, it does not occur at a measurable rate under normal conditions, and benzene is a common laboratory commodity with a shelf life of (in principle) millions of years.

Thermodynamics deals with the tendency to change; it is mute on the rate at which that tendency is realized.

It is important to keep in mind that:
1) All natural processes are spontaneous.
2) Occurrence of any process must obey the first law. No energy can be created or destroyed.
3) The first law cannot be violated nor can it predict the direction a process will take. It always assures that, as long as energy is conserved, any process is possible regardless whether it is spontaneous or nonspontaneous.
4) Since the first law does not object the occurrence of the nonspontaneous process for just being nonspontaneous, why then does not the nonspontaneous process occur?

There must be some feature of the world that accounts for the distinction between the two types of change.

The solution to this dilemma is given by the concept of a property of systems named “entropy” which was not known to humans before and was not established before 1857.

5.3 The concept of entropy: A new name of newly known property

5.3.1 The precursory to the second law

Human trials to achieve work on the expense of heat has a remote history. However, the most revolutionary invention did not appear except on the early nineteenth century.

Early heat-powered engines such as the engines of Thomas Savery (1698), Newcomen (1712) and the Cugnot steam tricycle (1769) were converting less than two percent of the input energy into useful work; a great deal of useful energy was dissipated or lost.

Physicists and engineers were working sincerely and hardly to invent a heat engine that convert all the heat it absorbed into a useful work. However, no success was achieved. Simply, work achieved is not equivalent to heat supplied.

In 1824 Carnot developed his cycle which was explained at the beginning of this chapter. Carnot visualized an ideal engine in which any heat converted into work, could be reinstated by reversing the motion of the cycle, a concept subsequently known as thermodynamic reversibility.

Carnot postulated the concept that “some heat is always lost in the conversion into work”. He also discovered that the efficiency of the heat engines is dependent only on the temperatures of the heat reservoirs between which the engine is working, and not on the types of the substance.

This loss of energy remained a puzzle.

Unfortunately, Carnot’s findings were ignored and did not attract the attentions of scientists except after years of his death.
• But we can say that Carnot’s findings were carrying in its bowels the embryo of the second law of thermodynamics, and that Carnot cycle gave the first early insight into this law.
• After his findings were looked at deeply, Rudolf Clausius introduced in the early 1850s the argument that in any irreversible process a small amount of heat is lost across the system boundary. Clausius continued to develop the ideas of lost energy and he finally coined the term entropy.
• The concept of entropy is developed in response to the observations that a certain amount of functional energy released from combustion reactions is always lost and cannot be transformed into useful work.

5.3.2 Order and disorder/randomness
• We discovered from Carnot’s cycle that heat absorbed in a heat engine is converted partially to work. The question now is: what happened to the heat that did not convert to work?
• We discovered from the first law that work done reversibly is higher than that done irreversibly. The question now is: why?
• The figure below shows a gas is a cylinder with a piston. It shows the gas before and after it absorbs heat.
• In 1 the particles are moving randomly and after absorbing heat in 2 the speed and kinetic energy of the particles increase.

Some particles, but not all, collides the piston forcing it to move upward. We say that heat absorbed by the gas lead the gas to achieve work. Other particles just gain higher speed and higher energy and do not participate in doing work. These particles used the heat they absorbed only to increase their random movement and chaos. The result is that the work which is done is less than the heat that is absorbed. This is why, in Carnot’s cycle, not all heat is converted to work; and this is why work done reversibly is higher than that done irreversibly.

5.4 Entropy as a function of disorder and randomness
• Before knowing the importance of randomness, there was no consideration given to anything related to it. So, there was no function for it.
Once randomness was realized during the 19th century, scientists paid more attention to it.

Clausius introduced a function he called “ENTROPY”\(^2\), and chosen the symbol “S” for it.

The most important aspects of entropy can be summarized as follows:

1) Entropy is the thermodynamic function of randomness.
2) The change in the system entropy \(\Delta S_{\text{syst}}\) is given by:

\[
\Delta S_{\text{syst}} = \frac{q_{\text{rev}}}{T}
\]

It is clear from the above equation that:
- \(\Delta S_{\text{syst}}\) increases when heat is absorbed by the system and vice versa.
- The numerical value of \(\Delta S\) increases as \(q\) increases and \(T\) decreases.

1) Because the surroundings are very huge, when compared with the system, we can consider its absorbance or release of heat to be reversible:

\[
\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}
\]

2) Change in the universe entropy is:

\[
\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}
\]

3) Because \(\Delta S\) is calculated by dividing amount of heat, measured by energy unit, by temperature, measured by Kelvin, its unit is J K\(^{-1}\) or kJ K\(^{-1}\).
4) Values of \(\Delta S\) are small when compared to these of \(\Delta U\) or \(\Delta H\) of the same change.
5) Therefore, values of changes in entropy are usually listed using J K\(^{-1}\) rather than kJ K\(^{-1}\).
6) Any change that increases randomness, chaos and disorder will cause an increase in the entropy, and the change in its entropy will be positive. The vice versa is true.
7) If a change, such as decomposition, increases number of substances entropy will increase and the change in entropy will be positive. The vice versa is true.
8) Because entropy (S) is the thermodynamic function of chaos and disorder, and because particles of matter in its solid state is in a much order and a less chaos than when in its liquid state, entropy of matter in its liquid state is greater than in its solid state. Also, because particles of matter in its liquid state is in a much order and a less chaos than when in its gaseous state, entropy of matter in its gaseous state is greater than in its liquid state.
9) According to point 8 above:

\[
S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}
\]

**Example 5.3**

Determine and rationalize if the entropy change will be positive or negative for the following reactions:

---

\(^2\) Entropy is a new word originated from two Greece words that mean "energy in change."
A) \((\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)} \rightarrow \text{Cr}_2\text{O}_3\text{(s)} + 4\text{H}_2\text{O(L)} + \text{CO}_2\text{(g)}\)

B) \(2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}\)

C) \(\text{PCl}_5 \rightarrow \text{PCl}_3 + \text{Cl}_2\text{(g)}\)

**Solution**

**Reaction A**

\((\text{NH}_4)_2\text{Cr}_2\text{O}_7\text{(s)} \rightarrow \text{Cr}_2\text{O}_3\text{(s)} + 4\text{H}_2\text{O(L)} + \text{CO}_2\text{(g)}\)

The reactant side contains only one mole where the product side has six moles produced. Also a gas is produced.

The change in entropy will be positive.

**Reaction B**

\(2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)}\)

There are 3 moles on the reactant side and only 2 on the product side.

The change in entropy will be negative.

**Reaction C**

\(\text{PCl}_5\text{(g)} \rightarrow \text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)}\)

There are more moles on the product side than on the reactant side and a gas is produced.

The change in entropy will be positive.

**Practice exercise**

Determine and rationalize if the entropy change will be positive or negative for the following reactions:

A) \(\text{CaO(s)} + \text{CO}_2\text{(g)} \rightarrow \text{CaCO}_3\text{(s)}\)

B) \(\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow 2\text{HCl(g)}\)

C) \(2\text{AgBr(s)} \rightarrow 2\text{Ag(s)} + \text{Br}_2\text{(g)}\)

**5.5 The Second Law statement**

Statement that defines the second law is not one. There are so many statements. Below are the most used:

1) Any natural processes is spontaneous
2) Heat cannot be transferred from a cold object to a hot object.
3) Entropy of the universe increases and its energy is constant.
4) Any system will change to the most probable position if left alone.
5) The most stable state of a left-alone system is that with highest entropy.
6) The entropy of all objects participating in an irreversible process increases as the process proceeds.
7) Any left-alone system will change slowly or quickly to the most stable state. And no system will change from its equilibrium state unless affected by an external interfere.
8) Entropy is the arrow of time.

**5.6 Calculating ΔS for some specific changes**

**5.6.1 Changes in entropy accompanying reversible processes**

1. Changes in the physical phases of matter at constant temperature and pressure:

\[ \Delta S_{\text{trans}} = \frac{q_{\text{trans}}}{T_{\text{trans}}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} \]
Example 5.4
Calculate $\Delta S^\circ$, in J/K, for the following changes:

A) $\text{H}_2\text{O}(\text{L}, 373 \text{ K}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(\text{g}, 373 \text{ K}, 101325 \text{ Pa})$ \hspace{1cm} $\Delta H = +40.85 \text{ kJ}$

B) If the standard enthalpy of freezing of water equals $-6.008 \text{ kJ/mol}$ and the freezing point of water is $0 \degree\text{C}$, calculate the change in entropy as a result of freezing $39 \text{ g}$ of water.

**Solution**

\[
\Delta S_{\text{trans}} = \frac{q_{\text{trans}}}{T_{\text{trans}}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}}
\]

A)

\[
\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{boiling}}}
\]

\[
\Delta S_{\text{vap}} = \frac{40.85 \text{ kJ} \times 1000 \text{ J}}{373 \text{ K}} = 109.5 \text{ J/K}
\]

B)

\[
\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}
\]

\[
\Delta H_{\text{fus}} = n \times \Delta H_{\text{fus}}^\circ = \frac{44 \text{ g}}{18 \text{ mol}} \times -6.008 \text{ kJ/mol} \times 1000 \text{ J} = -14686.22 \text{ J}
\]

\[
\Delta S_{\text{freez}} = \frac{-14686.22 \text{ J}}{273 \text{ K}} = -53.8 \text{ J/K}
\]

**Practice exercise**

Calculate $\Delta S^\circ$, in J/K, for the following changes:

A) $\text{CH}_3\text{OH}(\text{L}, 337.7 \text{ K}, 1 \text{ atm}) \rightarrow \text{CH}_3\text{OH}(\text{g}, 337.7 \text{ K}, 1 \text{ atm})$ \hspace{1cm} $\Delta H = +38.3 \text{ kJ}$

B) If the standard enthalpy of transition of Sn metal from the crystal structure $\alpha$ to the crystal structure $\beta$ equals $+2.09 \text{ kJ/mol}$ and the transition point is $13\degree\text{C}$, calculate the change in entropy as a result of transition $1.5 \text{ mol}$ of Sn from $\alpha$ structure to $\beta$ structure.

2. Changes in the temperature of a gas at constant pressure:

\[
\Delta S_p = C_p \ln \frac{T_2}{T_1}
\]

3. Changes in the temperature of a gas at constant volume:

\[
\Delta S_v = C_v \ln \frac{T_2}{T_1}
\]

4. Changes in the pressure of a gas at constant temperature:

\[
\Delta S_T = nR \ln \frac{P_1}{P_2}
\]

5. Changes in the volume of a gas at constant temperature:

\[
\Delta S_T = nR \ln \frac{V_2}{V_1}
\]
Example 5.6
The temperature and pressure of an ideal gas are changed from 27 ºC and 101325 Pa to 127 ºC and 135100 Pa. Calculate ∆Sº.

Solution
This is a change in temperature and pressure of the same quantity of a gas at constant volume:

\[ C_p = n \times C_{p,m} = n \times (C_{m,v} + R) = n \times (1.5 \times R + R) = n \times 2.5 \times R \]

\[ C_p = 4.06 \times 10^{-4} \text{ mol} \times 2.5 \times 8.314 \times \frac{1}{\text{mol K}} = 8.44 \times 10^{-3} \text{ J/K} \]

\[ \Delta S_1 = C_p \ln \frac{T_2}{T_1} = 8.44 \times 10^{-3} \text{ J/K} \times \ln \frac{400}{300} = 2.43 \times 10^{-3} \text{ J K}^{-1} \]

\[ \Delta S_2 = nR \ln \frac{P_1}{P_2} = 4.06 \times 10^{-4} \text{ mol} \times 8.314 \times \frac{1}{\text{mol K}} \times \ln \frac{101325}{135100} = 0.972 \times 10^{-4} \text{ J/K} \]

\[ \Sigma \Delta S = \Delta S_1 + \Delta S_2 = (2.43 \times 10^{-3} \text{ J/K}) + (0.972 \times 10^{-4} \text{ J/K}) = 1.458 \times 10^{-3} \text{ J/K} \]

Practice exercise
Knowing that \( C_{v,m} = 12.471 \text{ J/K mol} \), calculate ∆Sº for the following change:

100 cm³ Ar(g, 25 ºC, 101325 Pa) → 125 cm³ Ar(g, 99.5 ºC, 101325 Pa)

Example 5.7
Knowing that \( C_{p,m} = 2.5R \), calculate ∆S and V_2 of the following change:

10 dm³ ideal gas (27 ºC, 1 atm) → 13.33 dm³ dm³ ideal gas (127 ºC, 1 atm)

Solution
This is a change in temperature and volume of the same quantity of a gas at constant pressure:

\[ n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 10 \text{ dm}^3}{0.0821 \text{ atm dm}^3 \text{ mol}^{-1} \text{ K}^{-1} \times 300 \text{ K}} = 0.406 \text{ mol} \]

\[ C_p = n \times C_{p,m} = 0.406 \text{ mol} \times 2.5 \times 8.314 \times \frac{1}{\text{mol K}} = 8.44 \text{ J/K} \]

\[ \Delta S_1 = C_p \ln \frac{T_2}{T_1} = 8.44 \text{ J/K} \times \ln \frac{1333}{127} = 2.43 \text{ J/K} \]

\[ \Delta S_2 = nR \ln \frac{V_2}{V_1} = 0.406 \text{ mol} \times 8.314 \text{ J/mol K} \ln \frac{1333}{127} = 0.970 \text{ J/K} \]

\[ \Sigma \Delta S = \Delta S_1 + \Delta S_2 = + = 3.4 \text{ J/K} \]

Practice exercise
Knowing that \( C_{p,m,\text{ideal gas}} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1} \), calculate ∆S for the following change:

73.89 dm³ ideal gas (27 ºC, 1 atm) → 246.3 dm³ ideal gas (727 ºC, 1 atm)

5.6.2 Changes in entropy accompanying irreversible processes
• If the change happened in an irreversible process, all we need to do is to adapt a path that starts from the initial state of the system and ends at its final state in whatever number of steps, but all steps must be reversible.
• Because the entropy is a state function, the total change in entropy in the reversible path is equal to that in the irreversible path.
• Therefore, we apply the previous equations mentioned for reversible processes to calculate the change in entropy that happened irreversibly.

5.6.3 Changes in entropy at a certain temperature from its value at another temperature
• If ∆S is known at a certain temperature (T₁) it can be calculated at any other temperature (T₂) using the following equation:
\[ \Delta S_2 = \Delta S_1 + \Delta C_p \ln \frac{T_2}{T_1} \]

**Example 5.8**

If \( \Delta S_{\text{dissoc,H}_2\text{O}}^\circ = -44.423 \text{ J/K mol} \) and from the information at 25 °C in the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>H(_2)O(g)</th>
<th>H(_2)(g)</th>
<th>O(_2)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{m,p} / \text{J K}^{-1} \text{ mol}^{-1} )</td>
<td>33.56</td>
<td>28.83</td>
<td>29.12</td>
</tr>
</tbody>
</table>

Calculate the standard entropy of dissociation of one mole of water vapor (\( \Delta S_{\text{dissoc}}^\circ \)) at 68 °C.

**Solution**

\[ \text{H}_2\text{O}(g) \rightarrow \text{H}_2(g) + 0.5\text{O}_2(g) \]

\( \Delta C_p = \Sigma C_p(p) - \Sigma C_p(r) \)

\( \Sigma C_p(p) = (1 \text{ mol} \times 28.83 \text{ J K}^{-1} \text{ mol}^{-1} + 0.5 \text{ mol} \times 29.12 \text{ J K}^{-1} \text{ mol}^{-1}) = 43.39 \text{ J/K} \)

\( \Sigma C_p(r) = 1 \text{ mol} \times 33.56 \text{ J K}^{-1} \text{ mol}^{-1} = 33.56 \text{ J K}^{-1} \)

\( \Delta C_p = 43.39 \text{ J/K} - 33.56 \text{ J K}^{-1} = 9.83 \text{ J/K} \)

\( \Delta S_2^\circ = \Delta S_1^\circ + \Delta C_p \ln \frac{T_2}{T_1} \)

\( \Delta S_{341 \text{K}}^\circ = -44.423 \text{ J/K} + 9.83 \text{ J/K} \times \ln \frac{341 \text{K}}{298 \text{K}} = -43.1 \text{ J/K} \)

**Practice exercise**

If \( \Delta S_{\text{comb,CH}_4}^\circ = -242.9 \text{ J/K mol} \) and from the information at 25 °C in the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>CO(_2)(g)</th>
<th>H(_2)O(L)</th>
<th>CH(_4)(g)</th>
<th>O(_2)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{m,p} / \text{J K}^{-1} \text{ mol}^{-1} )</td>
<td>73.11</td>
<td>75.291</td>
<td>35.309</td>
<td>29.12</td>
</tr>
</tbody>
</table>

Calculate the standard entropy of combusting 48.0 g of methane (\( \Delta S_{\text{comb}}^\circ \)) at 77 °C.
Questions and problems

1. One mole of an ideal gas is used in Carnot cycle. It expands first isothermally at 600K from 1 × 10^6 Pa to 1 × 10^5 Pa; then adiabatically to a minimum temperature equals to 300K; then it is compressed first isothermally at 300 K to 1 × 10^6 Pa, then adiabatically to a maximum temperature opf 600 K. Knowing that C_{m,p} = 20.785 J K^{-1} mol^{-1}, calculate ΔU, w, q, network, and efficiency.

2. Knowing that ΔH_{fusion}, H_2O is 6.008 kJ mol^{-1}, calculate the entropy change as a result of melting (fusing or liquefying) 1 mol of ice at 0 ºC and 101325 Pa. OR: Calculate ΔS° of the following change:
H_2O(s, 0 ºC, 101325 Pa) → H_2O(L, 0 ºC, 101325 Pa) $\Delta H = +6.008$ kJ

3. Calculate ΔS° of the following change:
H_2O(L, 373 K, 101325 Pa) → H_2O(g, 373 K, 101325 Pa) $\Delta H = +40.85$ kJ

4. Knowing that the absolute entropy of 1 mol of a gas at 298 K is 146 J K^{-1} mol^{-1}, and C_{p,m} = 20.9 J K^{-1} mol^{-1}, calculate its value at 500 ºC at the same pressure.

5. In an isolated flask with a negligible heat capacity, a 0.556 mol of solid water (ice) at 0 ºC is added to 1.11 mol of liquid water at 90 ºC. If the enthalpy of fusion of water is 5.98 kJ mol^{-1}, and the molar heat capacity of liquid water is 75.312 J ºC mol^{-1}, calculate the entropy changes of the system and the surroundings.

6. Knowing C_{m,p,H_2O(L)} = 75.312 J K^{-1} mol^{-1}, C_{m,p,H_2O(s)} = 37.2 J K^{-1} mol^{-1}, and $\Delta H_{fusion,H_2O} = 5980$ J mol^{-1} at 0 ºC, calculate the entropy change of the system, the surroundings, and the universe as a result of the following change:
H_2O(L, 263 K, 101325 Pa) → H_2O(s, 263 K, 101325 Pa)

7. Knowing C_{m,p,H_2O(L)} = 75.312 J K^{-1} mol^{-1}, C_{m,p,H_2O(g)} = 33.58 J K^{-1} mol^{-1}, and $\Delta H_{vap,H_2O,100 ºC} = 40660$ J mol^{-1}, calculate $\Delta S_{univ}$, $\Delta S_{sys}$, and $\Delta S_{surr}$ as a result of:
H_2O(L, 298 K, 1.01 × 10^5 Pa) → H_2O(g, 398 K, 5.00 × 10^4 Pa)

8. Two moles of an ideal gas expanded at 298 k to a volume that is 2.5 times its original volume. Calculate $\Delta S_{sys}$, $\Delta S_{surr}$, and $\Delta S_{univ}$ if the expansion is:
A) reversible, B) free, C) irreversible and the heat absorbed is less by 400 J mol^{-1} than that in the reversible expansion in (A).

9. Knowing that C_{m,v,N_2(g)} = 12.471 J K^{-1} mol^{-1}, calculate T_1, V_1, V_2, $\Delta S_{sys}$, $\Delta S_{surr}$, and $\Delta S_{univ}$, of the following adiabatic irreversible change:
0.1 kg N_2(g, 298 K, 30 atm) → 0.1 kg N_2(g, T_2, 10 atm)

10. Knowing that C_{p,m,ideal gas} = 2.5R, calculate $\Delta S$ and V_2 of the following change:
10 dm^3 ideal gas (27 ºC, 1 atm) → V_2 dm^3 ideal gas (127 ºC, 1 atm)

11. If 1 mol of an ideal gas expands isothermally at 27 ºC to three times its original volume, calculate $\Delta S_{sys}$, $\Delta S_{surr}$ if the process is carried out once isothermally and once freely.

12. Knowing that C_{v,m} = 12.471 J K^{-1} mol^{-1}, calculate $\Delta S°$ of the following change:
0.5 dm^3 ideal gas(25 ºC, 1 atm) → 1 dm^3 ideal gas(323 ºC, 1 atm)

13. Knowing that $\Delta H_{f,H_2O(L)} = -286$ kJ mol^{-1}, calculate $\Delta S°_{surr}$ as a result of the formation of 1 mol of water at 25 ºC and 101325 Pa.
6. THE THIRD LAW
6. The Third Law of Thermodynamics
(The Absolute Entropies)

6.1 The dilemma of \( C_p \) at temperatures close to 0 K

- Let us go back to the equation \( \Delta S = C_p \ln \frac{T_2}{T_1} \) which showed how to calculate the change in entropy at constant pressure as the change taking place is only the change in temperature from \( T_1 \) to \( T_2 \) and nothing else.
- In fact, this equation is derived from the following equation:

\[
\Delta S = \int_{T_1}^{T_2} C_p \frac{T_2}{T_1}
\]

- Of course, writing \( \Delta S = C_p \ln \frac{T_2}{T_1} \) is not acceptable unless we have assumed that the value of \( C_p \) in the equation is constant between \( T_1 \) and \( T_2 \) which, in fact, is not.
- Why, then, we assumed that \( C_p \) in the equation is constant between \( T_1 \) and \( T_2 \)? The reason behind this seemingly wrong assumption is that the difference in its values between \( T_1 \) and \( T_2 \) is in fact so small to the extent that allows us to neglect for the sake of an easier way for mathematical calculations.
- Also, it is a crucial point to comprehend that bringing a substance to a low temperature is not easy or possible all the way to the absolute zero temperature.
- For any substance, there is always a minimum temperature below which the substance cannot be cooled further. Consequently, the value of \( C_p \) is unknown below this temperature. This represent a serious impediment because not knowing \( C_p \) means that we cannot determine the value of \( \Delta S \).
- The solution for this deadlock was provided in 1912 by the Dutch-American physicist, physical chemist and Noble prize winner in chemistry Peter Debye.
- Here, we will only take his final and simple equation he ended to.
- To understand his findings, let us name the lowest temperature that can be reached for any substance “Debye temperature” and let us give it the symbol “\( T_D \)”.
- His equation is written as:

\[
\Delta S_{0 \text{ to } T_D} = \frac{C_p T_D}{3}
\]

This equation is read as follows:

At constant pressure, the increase of the entropy of any substance as a result of increasing its temperature from 0 K to the lowest temperature at which we can determine its \( C_p \) is equal to one third its heat capacity, at this constant pressure, at this lowest temperature.

6.2 The absolute value of \( S \) at constant \( P \) at any temperature

- Regardless of the disorder, chaos and how much the value of \( S \) at 0 K, any increase in the value of \( S \) of any substance as a result of its temperature being above 0 K can be determined and known as follows:
  1) If substance temperature increases from 0 K to \( T_D \) at constant \( P \), the increase in its entropy is given by Debye equation:
\[ \Delta S_{0 \text{K to } T_D} = \frac{C_p T_D}{3} \]

2) We already know from the previous chapter that changing the temperature of a substance from \( T_i \) to \( T_f \) at constant pressure changes the entropy by a value given by the following equation:

\[ \Delta S_{T_i \text{ to } T_f} = C_p \ln \frac{T_f}{T_i} \]

(\( C_p \) is heat capacity of the substance in this certain physical phase, and is constant between \( T_i \) and \( T_f \))

3) If the substance undergoes a change in its physical phase at constant pressure and temperature, the change in its entropy is given by the following equation:

\[ \Delta S_{\text{physical change}} = \frac{\Delta H_{\text{physical change}}}{T_{\text{physical change}}} \]

- In addition to whatever value the entropy has at 0 K, the increase in it can be determined with confident using the above three equations.
- Since we become able to know the increment of entropy (S) that is added to whatever value the entropy has at 0 K means that we are just around the corner to know the absolute value of the entropy of any substance at constant pressure at any temperature. The only remaining task ahead of us is knowing the value of its entropy at 0K (\( S_{0 \text{K}} \)) at the same pressure.

6.3 The third law of thermodynamics
- At this stage, we do not know the value of the entropy when \( T = 0 \).
- However, experimental data proves that entropies for all perfectly ordered crystalline materials must be the same at \( T = 0 \).
- According to our understanding of entropy as a measure of disorder, we understand that absence of disorder means that the value of the entropy is zero.
- Now we can state that:
  - When a substance at 0 K is totally ordered in perfect crystals its entropy is zero
  - The above statement is the well-known third law of thermodynamics.

6.4 Residual entropy
- If the solid is totally ordered and perfectly crystallized then its entropy at 0 K is zero:

\[ S_{0 \text{K, perfectly ordered}} = 0 \]

- If the solid is not perfectly ordered or crystallized then its entropy at 0 K is not zero but has a positive value:

\[ S_{0 \text{K, disordered}} \neq 0 \]

- The positive value of the entropy of any substance at 0 K is positive, is called “the residual entropy” and is given the symbol \( S_{res} \). Therefore, in this case:
The value of $S_{\text{res}}$ can be evaluated once we have a good knowledge of the so-called “statistical entropy” which is a part of the “statistical thermodynamics” which is beyond the scope of our discussion.

Examples of the values of residual entropy are:

$S_{\text{res,H}_2\text{O}(s)} = 3.4 \text{ J/K mol}$
$S_{\text{res,CO(s)}} = 5.8 \text{ J/K mol}$

6.5 The third law uses

The statement of the third law strictly denies the existence of total order and the nonexistence of chaos in matter unless the matter satisfies two strict conditions:

First: the matter temperature is 0 K.
Second: the matter is in a total order with no single disorder.

At standard pressure, the entropy of any substance at 0 K is $S^0$ which has a positive value unless the substance is in a perfect order with no single chaos.

At a temperature above 0 K, the entropy of any substance must be more than that of its entropy at 0 K by a value of $\Delta S$.

Therefore, at standard pressure if the temperature is $T$ the entropy at this temperature is $S^T$.

The value of $S^T$ is more than the value $S^0$ by $\Delta S^T$:

$$\Delta S^T = S^T - S^0$$
$$S^T = S^0 + \Delta S^T$$

If the substance is 100% crystallized without any deformation at 0 K, its entropy is zero:

$$S^0 = 0$$
$$S^T = \int_0^T C_p \frac{dT}{T}$$

Therefore, and as a result of knowing that the value of absolute entropy is zero at 0 K when the substance is 100% crystallized without any deformation, third law reveals that:

- The value of entropy at 0 K is called the residual entropy, $S_{\text{res}}$. It represents the remaining chaos that is left over after taking the matter to the lowest possible temperature which is 0K.
- If the substance at 0 K is 100% ordered and has no deformations its absolute entropy will be zero.
- If the substance at 0 K is not 100% ordered and is deformed its absolute entropy will not be zero but it will have a positive value.
- The value of the residual entropy ($S_{\text{res}}$) can be determined by some very complicated calculations that we will not go through.
- The heat capacity of any substance at constant pressure, $C_p$, can be determined at any temperature except below Debye temperature, $T_D$ which is defined as the lowest temperatures at which $C_p$ can be evaluated.
When temperature is equal to $T_D$, heat capacity of any substance at constant pressure, is equal to $C_{p,T_D}$. Debye found out that difference between the entropy of matter at 0 K and its entropy at $T_D$ is:

$$\Delta S_{T_D} = \frac{C_{p,T_D}}{3}$$

1. At standard pressure, the absolute entropy at $T_D$:

$$S_{T_D}^o = S_{res}^o + \frac{C_{p,T_D}}{3}$$

2. If the substance is 100% ordered without any deformation at 0 K, residual entropy is zero ($S_{res}^o = 0$) and:

$$S_{T_D}^o = \frac{C_{p,T_D}}{3}$$

6.6 Calculating the absolute entropy at any temperature

1. The value of the absolute entropy can be calculated at any temperature by the use of the so-called heating (or cooling) curves shown in the figure next page.

2. Heating curves consists of seven stages:

   Stage 1: the stage of the residual entropy ($S_0$), i.e. the value of $S$ at 0K:
   If the substance is 100% ordered with no deformation,
   
   $$S_0 = 0$$
   
   If the substance is not 100% ordered,
   
   $$S_0 = S_{res}$$

   Stage 2: the stage of increasing entropy as a result of increasing temperature from 0 K to $T_D$, ($\Delta S_{0\to T_D}$),
   
   $$\Delta S_{0\to T_D} = \frac{C_{p,T_D}}{3}$$

   Stage 3: the stage of increasing entropy as a result of increasing temperature from $T_D$ to the fusion (melting) point ($\Delta S_{T_D\to T_{fus}}$):
   This depends on the number of crystalline forms the substance has in its solid phase. Below is the case of a substance that only has one solid state, and the case of a substance that has two solid states.
   
   ✓ If the substance has only one solid state when its entropy increases as temperature increases from $T_D$ to $T_{fus}$ by a value equal to $\Delta S_{T_D\to T_{fus}}$;
   
   $$\Delta S_{T_D\to T_{fus}} = C_{p,s} \ln \frac{T_{fus}}{T_D}$$

   ✓ If the substance has two solid states, say $\alpha$ and $\beta$ states its entropy increases, while it is in the $\alpha$ state, as its temperature increases from $T_D$ to the temperature $T_{\alpha\to\beta}$, which is the temperature at which it
starts changing from the α state to the β state. This increase in entropy is \( \Delta S_{T_D \rightarrow T_{\alpha \rightarrow \beta}} \):

\[
\Delta S_{T_D \rightarrow T_{\alpha \rightarrow \beta}} = C_{p,\alpha} \ln \frac{T_{\alpha \rightarrow \beta}}{T_D}
\]

Once the substance starts changing from α, state to β state its temperature \( T_{\alpha \rightarrow \beta} \) becomes constant as long as the substance is changing from α to β. The increase in entropy accompanying this change of state at constant pressure and temperature is \( \Delta S_{\alpha \rightarrow \beta} \):

\[
\Delta S_{\alpha \rightarrow \beta} = \frac{\Delta H_{\alpha \rightarrow \beta}}{T_{\alpha \rightarrow \beta}}
\]

After the substance becomes completely in the β state, its temperature resume increasing from \( T_{\alpha \rightarrow \beta} \) to the fusion temperature, \( T_{\text{fus}} \), which is the temperature at which it starts melting. This increase in temperature increases the entropy by \( \Delta S_{T_{\alpha \rightarrow \beta} \rightarrow T_{\text{fus}}} \):

\[
\Delta S_{T_{\alpha \rightarrow \beta} \rightarrow T_{\text{fus}}} = C_{p,\beta} \ln \frac{T_{\text{fus}}}{T_{\alpha \rightarrow \beta}}
\]

✓ If the solid substance has three, four or more crystalline forms, increase in its entropy follows the same pattern explained above.

Stage 4: the stage of increasing entropy as a result of changing the substance from its solid phase to its liquid phase at its fusion point (\( \Delta S_{\text{fus}} \)):

Once the substance starts melting, its fusion temperature \( T_{\text{fus}} \) becomes constant as long as the substance changes from its solid phase to its liquid phase. The increase in entropy accompanying this change of phase at constant pressure and temperature is \( \Delta S_{\text{fus}} \):

\[
\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}
\]

Stage 5: the increase in entropy as a result of increasing temperature of the liquid substance from its fusion/melting point (\( T_{\text{fus}} \)) to its boiling point (\( T_b \)):

After the substance becomes completely in its liquid phase its temperature resume increasing from \( T_{\text{fus}} \) to its boiling point, \( T_b \). This increase in temperature increases the entropy by \( \Delta S_{T_{\text{fus}} \rightarrow T_b} \):

\[
\Delta S_{T_{\text{fus}} \rightarrow T_b} = C_{p,L} \ln \frac{T_b}{T_{\text{fus}}}
\]

Stage 6: the increase in entropy as a result of changing the substance from its liquid phase to its gaseous phase at its boiling point (\( \Delta S_{\text{vap}} \)):

\[
\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}
\]
Stage 7: the increase in entropy as a result of increasing temperature of the gaseous substance from the boiling point to any temperature above it \(T_{\text{gas}}\). This increase is denoted \(\Delta S_{T_b \rightarrow T_{\text{gas}}}\): 

\[
\Delta S_{T_b \rightarrow T_{\text{gas}}} = C_{p,g} \ln \frac{T_{\text{gas}}}{T_b}
\]

3. Heating curves shown in the following figures is for heating any substance that is initially at the lowest temperature (0 K), and finally at the highest temperature \(T_{\text{gas}}\). However, initial temperature could be any temperature between 0 K and \(T_g\).

**Example 6.1**

A solid substance is found to be in perfect crystals at 0 K. It is heated to a temperature \(T_g\) \((T_g\) is a temperature that is above the boiling point). The substance, in its solid state, has two crystalline forms, the form A is at low temperatures, and the form B is at high temperatures. Write the mathematical equations for all changes that illustrate the values of entropy changes. Its absolute entropy at \(T_g\) \((S_{T_g})\). Also, write the mathematical equation that illustrates the value of its absolute entropy at \(T_g\) \((S_{T_g})\).

**Solution**

1. \(S\) at 0 K: \(S_0 = 0\) (Perfect crystals)
2. From 0 K to \(T_D\): \(\Delta S_1 = \frac{C_{p,T_D}}{3}\)
3. From \(T_D\) to \(T_B \rightarrow A\): \(\Delta S_2 = C_{p,B} \ln \frac{T_B \rightarrow A}{T_D}\)
4. From solid B to solid A at \(T_B \rightarrow A\): \(\Delta S_3 = \frac{\Delta H_{B \rightarrow A}}{T_B \rightarrow A}\)
5. From \(T_B \rightarrow A\) to \(T_{\text{fusion}}\): \(\Delta S_4 = C_{p,A} \ln \frac{T_{\text{fusion}}}{T_B \rightarrow A}\)
6. From solid A to liquid at \(T_{\text{fusion}}\): \(\Delta S_5 = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}\)
7. From \(T_{\text{fusion}}\) to \(T_{\text{boiling}}\): \(\Delta S_6 = C_{p,L} \ln \frac{T_{\text{boiling}}}{T_{\text{fusion}}}\)
8. From liquid to gas at \(T_{\text{boiling}}\): \(\Delta S_7 = \frac{\Delta H_{\text{vaporization}}}{T_{\text{boiling}}}\)
9. From \(T_{\text{boiling}}\) to \(T_g\): \(\Delta S_8 = C_{p,g} \ln \frac{T_g}{T_{\text{boiling}}}\)

\[
\Delta S_{\text{total}} = \Sigma \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8 + \Delta S_9
\]

**Practice exercise**

A solid substance is found not to be in perfect crystals at 0 K. It is heated until it becomes a liquid at \(T_L\) a temperature that is above its melting point \((T_l)\) and below its boiling point \((T_b)\). The substance, in its solid state, has only one crystalline forms. Write the mathematical equation that illustrates the value of its absolute entropy at \(T_g\) \((S_{T_L})\).

---

6.7 Calculating \(\Delta S\) of chemical reactions

1. The advantage gained from the third law, namely knowing the values of the absolute entropies of substances, gave us the opportunity to obtain them at any other condition.
2. Values of the absolute entropy at standard conditions (1 atm and 298 K) are usually listed in thermodynamic tables as \(S^0\) in the unit of Joule/K mol. The table below shows some.
3. As it appeared during the study of thermochemistry, knowing the standard enthalpy of formation of reactants and products enables us to calculate the standard change in enthalpy of any reaction $\Delta H_{\text{rxn}}^\circ$ using the simple and straightforward equation:

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ (\text{products}) - \sum \Delta H_f^\circ (\text{reactants})$$

Also, knowing $S^\circ$ values of reactants and products enables us to calculate the standard change in entropy for any reaction $\Delta S_{\text{rxn}}^\circ$ using the following simple and straightforward equation:

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

<table>
<thead>
<tr>
<th>Substance</th>
<th>$S^\circ$ [J/(mol·K)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>126.2</td>
</tr>
<tr>
<td>H₂</td>
<td>130.7</td>
</tr>
<tr>
<td>Ne</td>
<td>146.3</td>
</tr>
<tr>
<td>Ar</td>
<td>154.8</td>
</tr>
<tr>
<td>Kr</td>
<td>164.1</td>
</tr>
<tr>
<td>Xe</td>
<td>169.7</td>
</tr>
<tr>
<td>H₂O</td>
<td>188.8</td>
</tr>
<tr>
<td>N₂</td>
<td>191.6</td>
</tr>
<tr>
<td>O₂</td>
<td>205.2</td>
</tr>
<tr>
<td>CO₂</td>
<td>213.8</td>
</tr>
<tr>
<td>I₂</td>
<td>260.7</td>
</tr>
<tr>
<td>C₂H₅OH(L)</td>
<td></td>
</tr>
<tr>
<td>C(graphite)</td>
<td></td>
</tr>
<tr>
<td>H₂(g)</td>
<td></td>
</tr>
<tr>
<td>O₂(g)</td>
<td></td>
</tr>
</tbody>
</table>

### Example 6.2

From the information in the table below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>C₂H₅OH(L)</th>
<th>C(graphite)</th>
<th>H₂(g)</th>
<th>O₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ$ / J K⁻¹ mol⁻¹</td>
<td>160.7</td>
<td>5.7</td>
<td>130.684</td>
<td>205.1</td>
</tr>
</tbody>
</table>

Calculate, in the same units, the standard entropy of formation of liquid ethanol ($\Delta H_f^\circ$).

**Solution**

$$2\text{C(graphite)} + 3\text{H}_2(g) + 0.5\text{O}_2(g) \rightarrow \text{C}_2\text{H}_5\text{OH(L)}$$

$$\Delta S^\circ = \sum S^\circ (\text{products}) - \sum S^\circ (\text{reactants})$$

$$\Sigma S^\circ (\text{products}) = 1 \text{ mol} \times 160.7 \text{ J/K mol} = 160.7 \text{ J/K}$$

$$\Sigma S^\circ (\text{reactants}) = (2 \text{ mol} \times 5.7 \text{ J/K mol} + 3 \text{ mol} \times 130.684 \text{ J/K mol} + 0.5 \text{ mol} \times 205.138 \text{ J/K mol}) = 506.002 \text{ J/K}$$

$$-345 \text{ J/K}$$

$$\Delta S^\circ = 160.7 \text{ J/K} - 506.002 \text{ J/K} = -345.302 \text{ J/K}$$

### Practice exercise

From the information in the table below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>H₂O(g)</th>
<th>H₂(g)</th>
<th>O₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ$ / J K⁻¹ mol⁻¹</td>
<td>188.83</td>
<td>130.684</td>
<td>205.1</td>
</tr>
</tbody>
</table>

Calculate, in the same units, the standard entropy of dissociation of water vapor ($\Delta H_{\text{dissoc}}^\circ$).
QUESTIONs AND PROBLEMS

1. A solid substance is found to be in perfect crystals at 0 K. It is heated until it becomes a gas at \( T_g \), a temperature that is above and below its boiling point (\( T_b \)). The substance, in its solid state, has two crystalline forms, the form A is at low temperatures, and the form B is at high temperatures. Write the mathematical equation that illustrates the value of its absolute entropy at \( T_g \) (\( S_{T_g} \)).

2. A solid substance is found not to be in perfect crystals at 0 K. It is heated until it becomes a liquid at \( T_L \), a temperature that is above its melting point (\( T_f \)) and below its boiling point (\( T_b \)). The substance, in its solid state, has only one crystalline forms. Write the mathematical equation that illustrate the value of its absolute entropy at \( T_L \) (\( S_{T_L} \)).

3. Knowing that \( S^\circ \), in J K\(^{-1}\) mol\(^{-1}\), of \( \text{C}_2\text{H}_5\text{OH}(\text{L}) = 160.7 \), \( \text{C} \text{(graphite)} = 5.7 \), \( \text{H}_2(\text{g}) = 130.684 \), \( \text{O}_2(\text{g}) = 205.1 \), calculate, in the same units, the standard entropy of formation of liquid ethanol (\( \Delta H_{f}^\circ \)).

4. At standard pressure, solid \( \text{N}_2 \) exist in \( \alpha \) crystalline form below 35.61 K, and in \( \beta \) crystalline form between 35.61 K and its melting point, 63.14 K. From the following information at standard pressure, calculate its standard absolute entropy at 25 ºC:
\[ S_0^\circ = 0 \]

It changes from \( \alpha \) to \( \beta \) at 35.51 K.
\[ \Delta H_{\alpha \rightarrow \beta}^\circ = 228.9 \text{ kJ mol}^{-1} \]
\[ C_{p,m,\beta} = 40.822 \text{ kJ mol}^{-1} \]
\[ T_{fus} = 63.14 \text{ K} \]
\[ \Delta H_{fus}^\circ = 720.9 \text{ kJ mol}^{-1} \]
\[ C_{p,L} = 56.318 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ T_{b} = 77.32 \text{ K} \]
\[ \Delta H_{vap}^\circ = 5.535 \text{ kJ mol}^{-1} \]
\[ C_{p,g} = 29.055 \text{ J K}^{-1} \text{ mol}^{-1} \]

5. From the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \text{H}_2\text{O}(\text{g}) )</th>
<th>( \text{H}_2(\text{g}) )</th>
<th>( \text{O}_2(\text{g}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( S^\circ / \text{J K}^{-1} \text{ mol}^{-1} )</td>
<td>188.83</td>
<td>130.684</td>
<td>205.1</td>
</tr>
<tr>
<td>( C_{m,\beta} / \text{J K}^{-1} \text{ mol}^{-1} )</td>
<td>33.56</td>
<td>28.83</td>
<td>29.12</td>
</tr>
</tbody>
</table>

Calculate the standard entropy of dissociation of water vapor at 68 ºC (\( \Delta H_{dissociation}^\circ \)).
7. THE FREE ENERGY
7. THE FREE ENERGY
(THE GIBBS AND THE HELMHOLTZ FREE ENERGIES)

7.1 Some history
- The term “affinity” was used by chemist since probably the thirteenth century meaning the force that makes a chemical reaction occurs. However, this term had no definite definition.
- The term “maximum work”, was proposed by the French chemist Marcellin Berthelot in 1875 to mean that all chemical changes occurring without intervention of external energy tend to produce materials which liberate heat.
- In 1865, the German physicist Rudolf Clausius showed that the heat used to transform the system from one state to the next cannot be used to do external work. Clausius defined this transformation heat as $q$:

$$q = T \Delta S$$

- In 1873, Willard Gibbs introduced the preliminary outline of the principles of predicting or estimating the tendencies of various natural processes to occur. In 1876, Gibbs introduced the term “chemical potential”. This was the firm establishment that takes into account chemical reactions and states of bodies that are chemically different from each other.
- In 1882, after the arguments introduced by Clausius and Gibbs, the German scientist Hermann von Helmholtz stated that “affinity” is not the heat given out in the formation of a compound but rather it is the largest quantity of work which can be gained when the reaction is carried out in a reversible manner.
- The maximum work is thus regarded as the decrease in the free, or available, energy of the system, and the free energy is either Gibbs free energy (G) at constant temperature and pressure, or Helmholtz free energy (A) at constant temperature and volume.
- The heat given out is a measure of the decrease in the total energy of the system (internal energy). Thus, Gibbs energy or Helmholtz energy is the amount of energy “free” for work under the given conditions.
- The term “affinity” did not resign completely and the term “free energy” did not finally take over until 1923 when the book of Lewis and Randall “Thermodynamics and the Free Energy of Chemical Reactions” was published.

7.2 The concept of free energy
- Energy is usually defined as the ability to do work; this ability is called now “the free energy”.
- The thermodynamic free energy is the amount of work that a thermodynamic system performs.
- The total energy of the system is its internal energy (U).
- Free energy is the portion of U that is available to perform thermodynamic work. In other words, free energy is the work that is achieved by thermal energy.
- Because the first law states that energy is always conserved, it is evident that free energy is the kind of energy that can perform work as the second law states.
- Free energy is subject to irreversible loss in the course of this work which is achieved by thermal energy.
• As mentioned before, this free energy is the internal energy of a system (U) minus the amount of energy that cannot be used to perform work. And this unusable energy is given by the entropy of the system (S) multiplied by the temperature of the system (S × T) and it is a thermodynamic state function.

7.3 The Gibbs free energy

• One of the problems with entropy calculations is that we have to work out two entropy changes, the change in the system and the change in the surroundings, and then consider the sign of their sum.

• It is the achievement of the great American theoretician J. W. Gibbs (1839–1903), who discovered how to combine the two calculations into one.

• The total entropy change that accompanies a process is:

\[
\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}
\]

\(\Delta S_{\text{sys}}\) is the entropy change for the system

\(\Delta S_{\text{sur}}\) is the entropy change for the surroundings

\(\Delta S_{\text{total}} > 0\) for a spontaneous change

• As it was discussed in chapter 5, if the process occurs at constant pressure and temperature, we can use the following equation to express the change in entropy of the surroundings in terms of the enthalpy change of the system, \(\Delta H_{\text{sys}}\):

\[
\Delta S_{\text{sur}} = -\frac{\Delta H_{\text{sys}}}{T}
\]

• When the resulting expression is inserted into this one, we obtain at constant temperature and pressure:

\[
\Delta S_{\text{total}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}
\]

• The great advantage of this formula is that it expresses the total entropy change of the system and its surroundings in terms of properties of the system alone.

• The only restriction is that the changes must be at constant pressure and temperature.

• The Gibbs energy, G, is defined as:

\[
G = H - TS
\]

• The Gibbs energy is commonly referred to as the “free energy” and also as the “Gibbs free energy”.

• Because H, T, and S are state functions, G is a state function too.

• At constant temperature and pressure, the change in Gibbs energy of the system, \(\Delta G_{\text{sys}}\), arises from changes in enthalpy and entropy:

\[
\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}
\]

(T and P are constant)

Because:

\[
\Delta S_{\text{total}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}
\]
We find that:

\[ \Delta S_{\text{sys}} = \Delta S_{\text{total}} + \frac{\Delta H_{\text{sys}}}{T} \]

\[ \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \times (\Delta S_{\text{total}} + \frac{\Delta H_{\text{sys}}}{T}) \]

\[ \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T \Delta S_{\text{total}} + T \times \frac{\Delta H_{\text{sys}}}{T} \]

\[ \Delta G = -T \Delta S_{\text{total}} \text{ (T and P are constant)} \]

- We see that at constant temperature and pressure, the change in Gibbs energy of a system is proportional to the overall change in entropy of the system plus its surroundings.

### 7.4 Total entropy and free energy as spontaneity indicators

- The difference in sign between \( \Delta G_{\text{sys}} \) and \( \Delta S_{\text{total}} \) implies that the condition for a process being spontaneous changes from \( \Delta S_{\text{total}} > 0 \) in terms of the total entropy (which is universally true) to \( \Delta G_{\text{sys}} < 0 \) in terms of the Gibbs energy (under the condition that processes are occurring at constant temperature and pressure).
- That is, in a spontaneous change at constant temperature and pressure, the Gibbs energy decreases.
- The figure below shows that a spontaneous change causes increase in the entropy of the universe and an increase in the Gibbs free energy of the system if the change is at constant pressure and temperature.

- It may seem more natural to think of a system as falling to a lower value of some property. However, it must never be forgotten that to say that a system tends to fall to lower Gibbs energy is only a modified way of saying that a system and its surroundings jointly tend towards a greater total entropy.
- The only criterion of spontaneous change is the total entropy of the system and its surroundings; the Gibbs energy merely contrives a way of expressing that total change in terms of the properties of the system alone and is valid only for processes that occur at constant temperature and pressure.
• Every chemical reaction that is spontaneous under conditions of constant temperature and pressure, including those that drive the processes of growth, learning, and reproduction, are reactions that change in the direction of lower Gibbs energy, or—another way of expressing the same thing—result in the overall entropy of the system and its surroundings becoming greater.

• A second feature of the Gibbs energy is that the value of $\Delta G$ for a process gives the maximum nonexpansion work that can be extracted from the process at constant temperature and pressure.

• By nonexpansion work, $w'$, we mean any work other than that arising from the expansion of the system. It may include electrical work, if the process takes place inside an electrochemical or biological cell, or other kinds of mechanical work, such as the winding of a spring or the contraction of a muscle.

• To demonstrate this property, we need to combine the First and Second Laws, and we find at constant temperature and pressure:

$$\Delta G_{sys} = w'_{max}$$

• To illustrate this important finding, let us look at the Experimental results which show that for the formation of 1 mol H$_2$O(L) at 25°C and 1 bar, $\Delta H = -286$ kJ and $\Delta G = -237$ kJ.

✓ The two values of $\Delta H$ and $\Delta G$ mean that up to 237 kJ of nonexpansion work can be extracted from the reaction between H$_2$(g) and O$_2$(g) to produce 1 mol of H$_2$O(L) at 25°C.

✓ If the reaction takes place in a fuel cell (a device for using a chemical reaction to produce an electric current, like those used on the space shuttle) then up to 237 kJ of electrical energy can be generated for each mole of H$_2$O produced.

✓ This energy is enough to keep a 60 W light bulb shining for about 1.1 h.

✓ If no attempt is made to extract any energy as work, then 286 kJ (in general, $\Delta H$) of energy will be produced as heat.

✓ If some of the energy released is used to do work, then up to 237 kJ (in general, $\Delta G$) of nonexpansion work can be obtained.

Example 7.1
A small bird has a mass of 30 g is to fly to a branch 10 m above the ground. What is the minimum mass of glucose that is consumed? $\Delta G$ of the oxidation of 1.0 mol C$_6$H$_{12}$O$_6$(s) to carbon dioxide and water vapor at 25°C is $-2828$ kJ.

Solution

Work = the nonexpansion work to be done “$w’” = mgh

Where “m” is the mass, “h” is the height and “g” is the acceleration of free fall.

\[ w' = (30 \times 10^{-3} \text{ kg}) \times (9.81 \text{ m s}^{-2}) \times (10 \text{ m}) \]

\[ w' = 2.943 \text{ kg m}^2\text{s}^{-2} = 2.943 \text{ J} \]

This nonexpansion work, can be identified with $\Delta G$.

2828 $\times$ $10^3$ J is released by consuming 1 mole of glucose

2.943 J is released by consuming n mole of glucose

\[ n = \frac{2.943 \text{ J} \times 1 \text{ mol}}{2828000 \text{ J}} = 1.0407 \times 10^{-6} \text{ mol} \]

m = n $\times$ M = 1.0407 $\times$ $10^{-6}$ mol $\times$ 180 g/mol

m = 1.9 $\times$ $10^{-4}$ g = 0.19 mg

That is, the bird must consume at least 0.19 mg of glucose for the mechanical effort (and more if it thinks about it).
**Practice exercise**
A hard-working human brain, perhaps one that is grappling with physical chemistry, operates at about 25 W (1 W = 1 J s\(^{-1}\)). What mass of glucose must be consumed to sustain that power output for an hour?

- The great importance of the Gibbs energy in chemistry is that if we know it, then we know the maximum nonexpansion work that we can obtain by doing the reaction.
- In some cases, the nonexpansion work is extracted in different ways. For example:
  ✓ The reactions in an electrochemical cell to produce electrical energy.
  ✓ The reaction used to build other molecules, as in the case of biological cells, where the Gibbs energy available from the hydrolysis of ATP (adenosine triphosphate) to ADP (adenosine diphosphate) is used to build proteins from amino acids, to power muscular contraction, and to drive the neuronal circuits in our brains.

- Some insight into the physical significance of G itself comes from its definition as \( H - TS \).
- The enthalpy is a measure of the energy that can be obtained from the system as heat.
- The term TS is a measure of the quantity of energy stored in the random motion of the molecules making up the sample.
- Work, as we have seen, is energy transferred in an orderly way, so we cannot expect to obtain work from the energy stored randomly.
- The difference between the total stored energy and the energy stored randomly, i.e. “\( H - TS \)”, is available for doing work, and we recognize that difference as the Gibbs energy.
- In other words, the Gibbs energy is the energy stored in the orderly motion and arrangement of the molecules in the system.

### 7.5 The Helmholtz free energy
- The previous discussion on the Gibbs free energy (\( G \)) also applies on the Helmholtz free energy (\( A \)).
- The only difference between the Gibbs free energy (\( G \)) and Helmholtz free energy (\( A \)) is that “\( G \)” is the free energy of the system at constant pressure and temperature and “\( A \)” is the free energy of the system at constant volume and temperature.
- Therefore, while “\( G \)” is the maximum nonexpansion work that can be extracted from the process at constant temperature and pressure, “\( A \)” is the maximum nonexpansion work that can be extracted from the process at constant temperature and volume.

\[
\Delta A_{sys} = \Delta U_{sys} - T\Delta S_{sys} \quad (T \text{ and } V \text{ are constant})
\]

### 7.6 Comparison between Gibbs and the Helmholtz free energies
- Carefully, let us first inspect the following table:
### HELMHOLTZ FREE ENERGY

<table>
<thead>
<tr>
<th>HELMHOLTZ FREE ENERGY</th>
<th>GIBBS FREE ENERGY</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $A = U - TS$</td>
<td>$G = H - TS$</td>
</tr>
<tr>
<td>2. $\Delta A = \Delta U - T\Delta S$</td>
<td>$\Delta G = \Delta H - T\Delta S$</td>
</tr>
<tr>
<td>3. $dA = dU - SdT - TdS$</td>
<td>$dG = dh - SdT - TdS$</td>
</tr>
<tr>
<td>$dA = dU - SdT - dq_{rev}$</td>
<td>$dG = dh - SdT - dq_{rev}$</td>
</tr>
<tr>
<td>$dA = -SdT + dU + dw$</td>
<td>$dG = -SdT + dU + PdV + VdP + dw$</td>
</tr>
<tr>
<td>$dA = -SdT - PdV$</td>
<td>$dG = -SdT + PdV$</td>
</tr>
</tbody>
</table>

### 7.7 Spontaneity and free energy

- Knowing whether a system would undergo a process spontaneously or not is a vital issue to chemists.
- It is well known that systems seek the lowest possible level of energy and the highest possible level of entropy.
- This tempts us to judge a process that causes a decrease in energy or an increase in entropy to be spontaneous.
- However, it is well known that there are many spontaneous cases that involve an increase in energy and a decrease in entropy. For example, vaporization of seawater involves an increase in energy yet it is a spontaneous process; and plants growing involve a decrease in entropy yet it is spontaneous.
- Free energy is the solution to this dilemma.
- If we look at the equation that relates free energy to both internal energy (or enthalpy) and entropy, namely “$\Delta A = \Delta U - T\Delta S$” and “$\Delta G = \Delta H - T\Delta S$”, We can clearly see how both changes in energy, in terms of $\Delta U$ or $\Delta H$, and entropy, $\Delta S$, synergize in these equations to restrict spontaneity to these processes that insures only negative values for $\Delta A$ or $\Delta G$. The reason behind this is that “spontaneity means changing the system to a more favorable state of equilibrium which cannot be reached without the expenditure of energy as work to overcome obstacles hindering fulfillment of the more favorable state of equilibrium.”
- This kind of work is on the expense of the free energy the system possesses.
- The signs of the change in $G$ (or $A$) and $S$ determines whether the process is spontaneous, nonspontaneous, or at equilibrium:
  - When $\Delta U$ or $\Delta H$ is positive and $\Delta S$ is negative the process will always be nonspontaneous.
  - When $\Delta U$ or $\Delta H$ is negative and $\Delta S$ is positive the process will always be spontaneous.
  - When both $\Delta U$ or $\Delta H$ and $\Delta S$ are positive the process will only be spontaneous at high temperatures.
✓ When both $\Delta U$ or $\Delta H$ and $\Delta S$ are negative the process will only be spontaneous at low temperatures.

- The following table clarifies this so important and so simple criterion:

<table>
<thead>
<tr>
<th>$\Delta U$ or $\Delta H$ SIGN</th>
<th>$\Delta S$ SIGN</th>
<th>$\Delta A$ or $\Delta G$ SIGN</th>
<th>TYPE OF PROCESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>+</td>
<td>+</td>
<td>+</td>
<td>NONSPONTANEOUS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>EQUILIBRIUM</td>
</tr>
<tr>
<td>+</td>
<td>–</td>
<td>–</td>
<td>SPONTANEOUS</td>
</tr>
<tr>
<td>–</td>
<td>+</td>
<td>+</td>
<td>NONSPONTANEOUS</td>
</tr>
<tr>
<td>–</td>
<td>–</td>
<td>+</td>
<td>NONSPONTANEOUS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>EQUILIBRIUM</td>
</tr>
</tbody>
</table>

**Example 7.2**

From the information in the table below, calculate $\Delta G$ of the following reaction:

$$3O_2(g) \rightarrow 2O_3(g)$$

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$/kJ mol$^{-1}$</th>
<th>O$_3$(g)</th>
<th>O$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>142.7</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

**Solution**

$$\Delta H_{rxn}^\circ = \Sigma \Delta H_{t,products}^\circ - \Sigma \Delta H_{t,reactants}^\circ$$

$$\Delta H_{rxn}^\circ = (2 \text{ mol} \times 142.7 \text{ kJ mol}^{-1}) - (2 \text{ mol} \times 0)$$

$$\Delta H_{rxn}^\circ = 285.4 \text{ kJ}$$

$$\Delta S_{rxn}^\circ = \Sigma S_{products}^\circ - \Sigma S_{reactants}^\circ$$

$$\Delta S_{rxn}^\circ = \Sigma 2 \text{ mol} \times 238.93 \text{ J K}^{-1} \text{ mol}^{-1} - \Sigma 3 \text{ mol} \times 205.138 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\Delta S_{rxn}^\circ = -137.554 \text{ J K}^{-1}$$

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

$$\Delta G_{rxn}^\circ = 285.4 \text{ kJ} - 298 \text{ K} \times -137.554 \text{ J K}^{-1} \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$

$$\Delta G_{rxn}^\circ = 326.39 \text{ kJ}$$

**Practice exercise**

From the information in the table below, calculate $\Delta G$ of the following reaction:

$$C_4H_{10}(g) + 6.5O_2(g) \rightarrow 4CO_2(g) + 5H_2O(L)$$

<table>
<thead>
<tr>
<th>$\Delta H_f^\circ$/kJ mol$^{-1}$</th>
<th>$\Delta G_f^\circ$/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_4H_{10}(g)$</td>
<td>310.23</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>213.74</td>
</tr>
<tr>
<td>H$_2$O(L)</td>
<td>69.91</td>
</tr>
</tbody>
</table>

**7.8 Fugacity, activity, and standard state of matter**

On page 31, chapter 1 we discussed in detail “the standard state, the standard temperature and pressure (STP), and the standard conditions” here we resume
discussion of the standard state of substances on the light of free energy.

7.8.1 Fugacity
• We know from section 7.5 that \(\frac{\partial G}{\partial P}\)_T = + V. Let us apply this equation to the perfect (ideal) gas leads:

\[
\begin{align*}
\left(\frac{\partial G}{\partial P}\right)_T &= + V \\
\Delta G &= \int_1^2 V dP \\
V &= \frac{nRT}{P} \\
\Delta G &= \int_1^2 nRT \frac{dP}{P} \\
\Delta G &= nRT \ln \frac{P_2}{P_1}
\end{align*}
\]

• Last equation is only correct for the perfect (ideal) gases where \(V = \frac{nRT}{P}\) but not on the real (nonideal gases) where \(V \neq \frac{nRT}{P}\). Therefore, for nonideal gases:

\[
\Delta G \neq nRT \ln \frac{P_2}{P_1}
\]

• To solve this problem, “fugacity” symbolized “f” was introduced in 1901 by the American chemist Gilbert Lewis, and two years later was affirmed to mean “scaping tendency” in his book with Merle Randall “thermodynamics and the Free Energy of Chemical Substances”.

• The word “fugacity” is derived from the Latin “fugere” which means “to flee”.

• Fugacity carries the unit of pressure. It contains what could be called the correction factor that allows it to replace pressure in the ideal gas law.

• Fugacity of a gas is related to its pressure is by the following equation

\[
f = \gamma_f P
\]

\(\gamma_f\) is the fugacity coefficient

• For perfect and for real gases:

\[
\begin{align*}
\Delta G &= nRT \ln \frac{f_2}{f_1} \\
\Delta G &= nRT \ln \frac{\gamma_f \times P_2}{\gamma_f \times P_1}
\end{align*}
\]

✓ For perfect gases, \(\gamma = 100\% = 1\) (100%) and \(f = P\). Therefore:

\[
\Delta G = nRT \ln \frac{f_2}{f_1} = nRT \ln \frac{P_2}{P_1}
\]

✓ For real gases, \(\gamma < 1\) and \(f = \gamma_f P\), therefore \(f < P\). Therefore:

\[
\Delta G = nRT \ln \frac{f_2}{f_1} = nRT \ln \frac{\gamma_f \times P_2}{\gamma_f \times P_1}
\]
7.8.2 Activity

- For gases, we know that:
  \[ \Delta G = G_2 - G_1 = nRT \ln \frac{f_2}{f_1} \]

- If the system’s initial state is its standard state, where its free energy is \( G^\circ \), and it changes to a final state, where its free energy is \( G \), then:
  \[ G - G^\circ = nRT \ln \frac{f}{f^\circ} \]
  \[ G = G^\circ + RT \ln (\frac{f}{f^\circ})^n \]

Where \( \frac{f}{f^\circ} \) is called activity and symbolized \( \alpha \):

\[ \alpha = \frac{f}{f^\circ} \]

\[ G = G^\circ + RT \ln (\alpha)^n \]

- If the system is at its standard state, its free energy \( G \) is \( (G^\circ) \):

\[ G = G^\circ \]

Therefore:

\[ RT \ln (\alpha)^n = 0 \]

- \( RT \ln (\alpha)^n = 0 \) means that \( \alpha = 1 \) and substance is at its standard state.
- The conclusion is that when \( RT \ln (\alpha)^n = 0 \) means that \( \alpha = 1 \)

7.8.3 Standard state of substances

- From the previous discussion above, we conclude that the thermodynamic definition of "standard state" is as follows:

**THE STANDARD STATE OF ANY SUBSTANCE IS ITS STATE WHEN ITS ACTIVITY IS EQUAL TO UNITY**

- The value of activity is related to concentration (molarity, \( C \); molality, \( m \); and mole fraction \( X \)) as follows:

\[ \alpha = \gamma_c \, C = \gamma_m \, m = \gamma_x \, X \]

where \( \gamma_c, \gamma_m, \) and \( \gamma_x \) are the activity’s coefficients in terms of molarity, molality, and mole fraction.

- When the system is solute in a solvent at infinite dilution or closed to infinite dilution, no interactions between system’s particles exist, or they are negligible, and its activity’s coefficient becomes equal, or so close to unity, which leads its activity to be equal to its concentration, or so close to it:
When concentration approaches zero, $\gamma$ approaches 1, and $\alpha$ approaches concentration.

- The question now is: could a substance activity be equal to unity? The answer is yes and it differs from a substance to another. This is illustrated as follows:

1) **WHEN THE SUBSTANCE IS A PURE GASE:**
   If we have a gas, it will be at its standard state when its activity is equal to unity. And making its activity equal to unity depends on whether the gas is ideal or nonideal.
   ✓ **If the pure gas is ideal:**
     
     $\alpha = 1$ when $f = 1 \text{ atm}$
     
     And because:
     
     $f = \gamma_g \ P$
     
     We find that:
     
     $f = 1 \text{ atm}$ when $p = 1 \text{ atm}$
     
     And because $\gamma_{ideal \ gas} = 1$ we conclude that:
     
     The ideal gas is in its standard state when $\alpha = 1$ which occurs when $f = P = 1 \text{ atm}$

✓ **If the pure gas is real (nonideal):**

     $a = 1$ when $f = 1 \text{ atm}$
     
     And because:
     
     $f = \gamma_g \ P$
     
     we find that:
     
     $f = 1 \text{ atm}$ when its $P > 1 \text{ atm}$
     
     And because:
     
     $\gamma_g < 1$
     
     we conclude that:
     
     The real gas is in its standard state when $\alpha = 1$ which occurs when $f = 1 \text{ atm}$ which occurs when $P > 1 \text{ atm}$

The value of a real gas pressure that makes its activity equal to unity depends on how far it is from ideality. As gas is less deviated from ideality its pressure becomes closer to its fugacity. Generally speaking, and because
we usually deal with gases at moderate pressures and temperatures, we approximate the value of its fugacity coefficient at 1 atm pressure to be equal to unity. Therefore:

The real gas is in its standard state when \( \alpha = 1 \) which occurs when \( f = P = 1 \) atm

2) **WHEN THE SUBSTANCE IS A PURE LIQUID:**
If we have a liquid, the effect of pressure on its properties is small to an extent to be neglected. This means that its particles are 100% active as long as the pressures are moderate. This allows us to generalize the case:

Any pure liquid becomes in its standard state when \( \alpha = 1 \) which occurs when \( P = 1 \) atm

3) **WHEN THE SUBSTANCE IS A PURE SOLID:**
Many solids can exist in more than one crystalline form. This means that its particles will be more active when it is in its most stable crystalline form. Because the effect of pressure, as long as it is moderate, on solids’ properties is small to an extent to be neglected, we can generalize the case for any pure solid in its most stable crystalline form:

Any pure solid in its most stable crystal form becomes in its standard state when \( \alpha = 1 \) which occurs when \( P = 1 \) atm

4) **WHEN THE SUBSTANCE IS A SOLUTE IN A SOLVENT:**
Because:

\[
\alpha = \gamma_c \ C = \gamma_m \ m = \gamma_s \ X
\]

and in order to give the same value of activity, the values of \( \gamma_c, \gamma_m, \) and \( \gamma_s \) differ. It is found that activity of a solution particles are almost 100% at concentration equal to unity. Therefore, for any solutions:

Any solute in a solvent becomes in its standard state when \( \alpha = 1 \) which occurs when molality = 1 mol kg\(^{-1}\)

7.9 **Standard free energy of formation**
- It was pointed out on page 98 in chapter 4 that the reaction which produces a substance from its elements in their standard state is called the standard formation reaction. And the standard change in enthalpy of any reaction can be calculated from the standard enthalpies of formations of reactants and products according to:

\[
\Delta H_{\text{rxn}}^{\circ} = \Sigma \Delta H_f^{\circ}(\text{products}) - \Sigma \Delta H_f^{\circ}(\text{reactants})
\]

- Also, the standard change in free energy of any reaction is calculated from the standard free energies of formations of reactants and products according to:
\[ \Delta G_{\text{rxn}}^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants}) \]

- As the standard enthalpies of formations of substances are listed in thermodynamics tables, the standard free energies of formations are listed too. An example of such tables is presented here.

<table>
<thead>
<tr>
<th>compound</th>
<th>( \Delta G_f^\circ ) (kJ/mol)</th>
<th>compound</th>
<th>( \Delta G_f^\circ ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr(s)</td>
<td>−96.90</td>
<td>MgSO_4(s)</td>
<td>−1170.6</td>
</tr>
<tr>
<td>AgCl(s)</td>
<td>−109.8</td>
<td>MnO(s)</td>
<td>−362.9</td>
</tr>
<tr>
<td>AgI(s)</td>
<td>−66.19</td>
<td>MnO_2(s)</td>
<td>−465.2</td>
</tr>
<tr>
<td>Ag_2O(s)</td>
<td>−30.6</td>
<td>NaCl(s)</td>
<td>−393.17</td>
</tr>
<tr>
<td>Ag_2S(s)</td>
<td>−11.21</td>
<td>NaF(s)</td>
<td>−546.3</td>
</tr>
<tr>
<td>Al_2O_3(s)</td>
<td>−1582.3</td>
<td>NaOH(s)</td>
<td>−419.2</td>
</tr>
<tr>
<td>BaCl_2(s)</td>
<td>−806.7</td>
<td>NH_3(g)</td>
<td>−26.57</td>
</tr>
<tr>
<td>BaCO_3(s)</td>
<td>−1134.4</td>
<td>CuO(s)</td>
<td>−129.7</td>
</tr>
<tr>
<td>BaO(s)</td>
<td>−520.4</td>
<td>Cu_2O(s)</td>
<td>−146.0</td>
</tr>
<tr>
<td>BaSO_4(s)</td>
<td>−1362.2</td>
<td>CuSO_4(s)</td>
<td>−661.8</td>
</tr>
<tr>
<td>CaCl_2(s)</td>
<td>−748.8</td>
<td>Fe_2O_3(s)</td>
<td>−742.2</td>
</tr>
<tr>
<td>CaCO_3</td>
<td>−1129.1</td>
<td>Fe_3O_4(s)</td>
<td>−1015.4</td>
</tr>
<tr>
<td>CaO(s)</td>
<td>−603.3</td>
<td>HBr(g)</td>
<td>−53.45</td>
</tr>
<tr>
<td>Ca(OH)_2(s)</td>
<td>−897.5</td>
<td>HCl(g)</td>
<td>−95.30</td>
</tr>
<tr>
<td>CaSO_4(s)</td>
<td>−1309.1</td>
<td>HI(g)</td>
<td>+1.70</td>
</tr>
<tr>
<td>CCl_4(L)</td>
<td>−65.21</td>
<td>HNO_3(L)</td>
<td>−80.71</td>
</tr>
<tr>
<td>CH_4(g)</td>
<td>−50.70</td>
<td>H_2O(g)</td>
<td>−228.61</td>
</tr>
<tr>
<td>CH_3OH(L)</td>
<td>−161.96</td>
<td>NH_3Cl(s)</td>
<td>−202.87</td>
</tr>
<tr>
<td>CO(g)</td>
<td>−137.17</td>
<td>NH_3NO_3(s)</td>
<td>−183.87</td>
</tr>
<tr>
<td>CO_2(g)</td>
<td>−394.39</td>
<td>NO(g)</td>
<td>+86.55</td>
</tr>
<tr>
<td>H_2O(L)</td>
<td>−237.14</td>
<td>NO_2(g)</td>
<td>+51.31</td>
</tr>
<tr>
<td>H_2O_2(L)</td>
<td>−120.42</td>
<td>NiO(s)</td>
<td>−123.56</td>
</tr>
<tr>
<td>H_2S(g)</td>
<td>−33.4</td>
<td>PbBr_2(s)</td>
<td>−330.70</td>
</tr>
<tr>
<td>H_2SO_4(L)</td>
<td>−689.93</td>
<td>PbCl_2(s)</td>
<td>−314.05</td>
</tr>
<tr>
<td>HgO(s)</td>
<td>−58.49</td>
<td>PbO(s)</td>
<td>−187.89</td>
</tr>
<tr>
<td>HgS(s)</td>
<td>−50.6</td>
<td>PbO_2(s)</td>
<td>−217.33</td>
</tr>
<tr>
<td>KBr(s)</td>
<td>−380.7</td>
<td>PCl_3(g)</td>
<td>−267.8</td>
</tr>
<tr>
<td>KCl(s)</td>
<td>−408.5</td>
<td>PCl_5(g)</td>
<td>−272.3</td>
</tr>
<tr>
<td>KClO_3(s)</td>
<td>−296.31</td>
<td>SiO_2(s)</td>
<td>−856.64</td>
</tr>
<tr>
<td>KF(s)</td>
<td>−537.8</td>
<td>SnO(s)</td>
<td>−256.8</td>
</tr>
<tr>
<td>MgCl_2(s)</td>
<td>−591.8</td>
<td>SnO_2(s)</td>
<td>−519.6</td>
</tr>
<tr>
<td>MgCO_3(s)</td>
<td>−1012.1</td>
<td>SO_2(g)</td>
<td>−300.13</td>
</tr>
<tr>
<td>MgO(s)</td>
<td>−596.3</td>
<td>So_3(g)</td>
<td>−370.4</td>
</tr>
<tr>
<td>Mg(OH)_2(s)</td>
<td>−769.47</td>
<td>ZnO(s)</td>
<td>−318.3</td>
</tr>
</tbody>
</table>

- The values of the standard Gibbs energies of formation \( \Delta G_f^\circ \) of compounds are very useful to judge the stability of a compound compared to the stability of its elements when they are in their reference states.
- The values of the standard Gibbs energies of formation \( \Delta G_f^\circ \) of elements when they are in their reference states are zero. On the other hand, the values of the
standard Gibbs energies of formation $\Delta G_f^\circ$ of compounds are either positive or negative.

- We can look to the values of the standard Gibbs energies of formation $\Delta G_f^\circ$ as an analog of the values of altitudes. The figure below shows this analogy:

Let us consider the standard Gibbs energies of formation $\Delta G_f^\circ$ of elements as the “sea level” of stability.
- The standard Gibbs energies of formation $\Delta G_f^\circ$ of compounds will be either above or below this sea level.
- If the standard Gibbs energy of formation is positive and the compound is above 'sea level', and has a spontaneous tendency to sink towards thermodynamic sea level and decompose into the elements. That is, $K < 1$ for their formation reaction.
- We say that a compound with $\Delta G_f^\circ > 0$ is thermodynamically unstable with respect to its elements or that it is an endergonic compound.
- Ozone, for which $\Delta G_f^\circ = +163 \text{ kJ mol}^{-1}$, has a spontaneous tendency to decompose into oxygen under standard conditions at 25°C. More precisely, the equilibrium constant for the reaction $\text{O}_2(g) \rightleftharpoons \text{O}_3(g)$ is less than 1 (much less in fact, for $K = 2.7 \times 10^{-29}$).
- However, although ozone is thermodynamically unstable, it can survive if the reactions that convert it into oxygen are slow. That is the case in the upper atmosphere, and the $\text{O}_3$ molecules in the ozone layer survive for long periods.
- Benzene ($\Delta G_f^\circ = +124 \text{ kJ mol}^{-1}$) is also thermodynamically unstable with respect to its elements ($K = 1.8 \times 10^{-22}$). However, the fact that bottles of benzene are everyday laboratory commodities also reminds us of the important point that spontaneity is a thermodynamic tendency that might not be realized at a significant rate in practice.

- Another useful point of the standard Gibbs energies of formation ($\Delta G_f^\circ$) is that there is no point in searching for direct syntheses of a thermodynamically unstable compound from its elements (under standard conditions, at the temperature to which the data apply), because the reaction does not occur in the required direction: the reverse reaction, decomposition, is spontaneous.
- Endergonic compounds must be synthesized by alternative routes or under conditions for which their Gibbs energy of formation is negative and they lie beneath thermodynamic sea level.
- Compounds below the thermodynamic sea level with $\Delta G_f^\circ < 0$ and $K > 1$ (for their formation reactions) are said to be thermodynamically stable with respect to their elements or are called exergonic compounds.
- An example is the exergonic compound ethane, with $\Delta G_f^\circ = -33 \text{ kJ mol}^{-1}$: the negative sign shows that the formation of ethane gas is spontaneous in the sense that $K > 1$ (in fact, $K = 7.1 \times 10^5$ at 25°C).

### Example
From the information in the table below, calculate $\Delta G_{\text{rxn}}^\circ$ of the following reaction:

$$2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g)$$

<table>
<thead>
<tr>
<th></th>
<th>CO$_2$(g)</th>
<th>CO(g)</th>
<th>O$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_f^\circ$/kJ mol$^{-1}$</td>
<td>$-394$</td>
<td>$-137$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

**Solution**

$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_{f,\text{products}}^\circ - \sum \Delta G_{f,\text{reactants}}^\circ$$

$$\Delta G_{\text{rxn}}^\circ = (2 \text{ mol} \times -394 \text{ kJ mol}^{-1}) - (2 \text{ mol} \times -137 + 1 \text{ mol} \times 0)$$

$$\Delta G_{\text{rxn}}^\circ = -514 \text{ kJ}$$

### Practice exercise
From the information in the table below, calculate $\Delta G_{\text{rxn}}^\circ$ of the following reaction:

$$\text{CH}_3\text{COOH}(L) + \text{C}_2\text{H}_5\text{OH}(L) \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5(L) + \text{H}_2\text{O}(L)$$

<table>
<thead>
<tr>
<th></th>
<th>\text{H}_3\text{COOH}(L)</th>
<th>\text{C}_2\text{H}_5\text{OH}(L)</th>
<th>\text{CH}_3\text{COOC}_2\text{H}_5(L)</th>
<th>\text{H}_2\text{O}(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_f^\circ$/kJ mol$^{-1}$</td>
<td>$-389.9$</td>
<td>$-174.78$</td>
<td>$-332.7$</td>
<td>$-237.13$</td>
</tr>
</tbody>
</table>

### Example
From the information in the table below, calculate $\Delta G^\circ$ of the following reaction:

$$4\text{NH}_3(g) + 5\text{O}_2(g) \rightleftharpoons 4\text{NO}(g) + 6\text{H}_2\text{O}(g)$$

<table>
<thead>
<tr>
<th></th>
<th>NO(g)</th>
<th>H$_2$O(g)</th>
<th>NH$_3$(g)</th>
<th>O$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_f^\circ$/kJ mol$^{-1}$</td>
<td>$+186.55$</td>
<td>$-228.57$</td>
<td>$-16.45$</td>
<td>$0$</td>
</tr>
</tbody>
</table>

**Solution**

$$\Delta G_{\text{rxn}}^\circ = \sum \Delta G_{f,\text{products}}^\circ - \sum \Delta G_{f,\text{reactants}}^\circ$$

$$\Delta G_{\text{rxn}}^\circ = (4 \text{ mol} \times 186.55 \text{ kJ mol}^{-1} + 6 \times -228.57) - (4 \text{ mol} \times -16.45 + 5 \text{ mol} \times 0)$$

$$\Delta G_{\text{rxn}}^\circ = -559.42 \text{ kJ}$$

### Practice exercise
From the information in the table below, calculate $\Delta G_{\text{rxn}}^\circ$ of the following reaction:

$$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$$

<table>
<thead>
<tr>
<th></th>
<th>CaCO$_3$(s)</th>
<th>CaO(s)</th>
<th>CO$_2$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_f^\circ$/kJ mol$^{-1}$</td>
<td>$-1128.8$</td>
<td>$-604.3$</td>
<td>$-394.36$</td>
</tr>
</tbody>
</table>
QUESTIONS AND PROBLEMS

1. Calculate $\Delta G$ as a result of a reversible compression of 4 mol of an ideal gas at 300 K from $2.02 \times 10^5$ Pa to $4.04 \times 10^5$ Pa.

2. Calculate $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta A$, and $\Delta G$ as a result of a reversible expansion of 1 mol of an ideal gas at 300 K from $2 \text{ dm}^3$ to $20 \text{ dm}^3$.

3. Calculate $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S_{\text{sys}}$, $\Delta S_{\text{surr}}$, $\Delta S_{\text{univ}}$, $\Delta A$, and $\Delta G$ as a result of a reversible expansion of 1 mol of an ideal gas against vacuum at 300 K from $1 \times 10^6$ Pa to $1 \times 10^5$ Pa.

4. Calculate $q$, $w$, $\Delta U$, $\Delta H$, $\Delta S$, $\Delta A$, and $\Delta G$ as a result of vaporization of 1 mol of toluene at its boiling point, 384 K. $\Delta H_{\text{vap}}$ (toluene) = 33.42 kJ mol$^{-1}$.

5. Calculate $\Delta A$ and $\Delta G$ of the following change: $\text{H}_2\text{O(L, 1 atm, 100 ºC)} \rightarrow \text{H}_2\text{O(g, 1 atm, 100 ºC)}$.

6. Knowing that $C_{\text{m,p,H}_2\text{O(L)}} = 75.42 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{\text{m,p,H}_2\text{O(s)}} = 37.2 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{\text{fusion,H}_2\text{O,273 K}} = 5980 \text{ J mol}^{-1}$, calculate $\Delta G$ of the following change: $\text{H}_2\text{O(L, 300 K, 1.01 \times 10^5 Pa)} \rightarrow \text{H}_2\text{O(s, 300 K, 1.01 \times 10^5 Pa)}$.

7. If the constant pressure molar heat capacity of liquid water is $75.4 \text{ J K}^{-1} \text{ mol}^{-1}$ and of gaseous water is $33.2 \text{ J K}^{-1} \text{ mol}^{-1}$, and the molar standard enthalpy of water vaporization is $40.85 \text{ kJ mol}^{-1}$, calculate $\Delta G$ of the following change: $\text{H}_2\text{O(L, 300 K, 263 K, 101325 Pa)} \rightarrow \text{H}_2\text{O(s, 263 K, 101325 Pa)}$.

8. From the table below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>H$_2$(g)</th>
<th>Cl$_2$(g)</th>
<th>HCl(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE / kJ mol$^{-1}$</td>
<td>435</td>
<td>240</td>
<td>430</td>
</tr>
<tr>
<td>S / J K$^{-1}$ mol$^{-1}$</td>
<td>130.59</td>
<td>222.96</td>
<td>186.68</td>
</tr>
</tbody>
</table>

calculate, in kJ, the change in Gibbs free energy of the following reaction: $\text{H}_2(g) + \text{Cl}_2(g) \rightarrow 2\text{HCl(g)}$.

9. From the table below:

<table>
<thead>
<tr>
<th>Substance</th>
<th>NH$_4$NO$_2$(s)</th>
<th>H$_2$(g)</th>
<th>H$_2$O(g)</th>
<th>N$_2$H$_4$(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f$ / kJ mol$^{-1}$</td>
<td>-365</td>
<td>0</td>
<td>-242</td>
<td>50</td>
</tr>
<tr>
<td>$S^\circ / J K^{-1}$ mol$^{-1}$</td>
<td>150</td>
<td>130</td>
<td>189</td>
<td>120</td>
</tr>
</tbody>
</table>

calculate, in kJ K$^{-1}$, the change in Gibbs free energy of the following reaction: $\text{NH}_4\text{NO}_2(s) + 3\text{H}_2(g) \rightarrow 3\text{H}_2\text{O(g)} + \text{N}_2\text{H}_4(g)$.

10. Knowing that $\Delta U = -2880 \text{ kJ}$ and $\Delta S = 182.4 \text{ J K}^{-1}$ for the following reaction: $\text{C}_6\text{H}_12\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O(g)}$ calculate $\Delta A$, $\Delta G$, the maximum work can be done, and the useful work. Calculate the difference between $\Delta A$ and $\Delta G$, and what does it represent.

11. Knowing that: $\Delta U = 2.88 \text{ kJ}$ and $\Delta S = 182.4 \text{ J K}^{-1}$ for the following reaction: malate $\rightarrow$ fumarate $\Delta G = 3 \text{ kJ}$

fumarate $\rightarrow$ aspirate $\Delta G = -15.5 \text{ kJ}$

calculate $\Delta G$ of the following change:

malate $\rightarrow$ aspirate $\Delta G = ?$

12. Knowing that: $\text{C}_6\text{H}_12\text{O}_6(s) \rightarrow \text{C}_6\text{H}_12\text{O}_6(aq, 10 \text{ m})$ $\Delta G = 0$

and from the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$\text{C}_6\text{H}_12\text{O}_6$(s)</th>
<th>CO$_2$(g)</th>
<th>H$_2$O(L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_f$ / kJ mol$^{-1}$</td>
<td>-913</td>
<td>-395</td>
<td>-237</td>
</tr>
</tbody>
</table>

calculate, in kJ mol$^{-1}$, the change in Gibbs free energy as a result of glucose oxidation in our bodies:

$\text{C}_6\text{H}_12\text{O}_6(aq, 0.1 \text{ m}) + 6\text{O}_2(g, 0.2 \text{ atm}) \rightarrow 6\text{CO}_2(g, 0.0003 \text{ atm}) + 6\text{H}_2\text{O(L)}$.
13. Calculate the difference between ∆A and ∆G of the following change at 300 K:

\[ \text{H}_2(g, 1.01 \times 10^5) + 0.5\text{O}_2(g, 1.01 \times 10^5) \rightarrow \text{H}_2\text{O}(L, 1.01 \times 10^5) \]

14. Using the values of ∆S° and ∆H° calculate ∆H° of the following reaction:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]

15. In a particular biological reaction taking place in the body at 37°C, the change in enthalpy was −135 kJ mol⁻¹ and the change in entropy was −136 J K⁻¹ mol⁻¹.
   (a) Calculate the change in Gibbs energy.
   (b) Is the reaction spontaneous?
   (c) Calculate the total change in entropy of the system and the surroundings.

16. The change in Gibbs energy that accompanies the oxidation of C₆H₁₂O₆(s) to carbon dioxide and water vapor at 25°C is −2828 kJ mol⁻¹. How much glucose does a person of mass 65 kg need to consume to climb through 10 m?

17. The formation of glutamine from glutamate and ammonium ions requires 14.2 kJ mol⁻¹ of energy input. It is driven by the hydrolysis of ATP to ADP mediated by the enzyme glutamine synthetase.
   (a) Given that the change in Gibbs energy for the hydrolysis of ATP corresponds to ∆G = −31 kJ mol⁻¹ under the conditions prevailing in a typical cell, can the hydrolysis drive the formation of glutamine?
   (b) How many moles of ATP must be hydrolyzed to form 1 mol of glutamine?

18. The hydrolysis of acetyl phosphate has ∆G = −42 kJ mol⁻¹ under typical biological conditions. If acetyl phosphate were to be synthesized by coupling to the hydrolysis of ATP, what is the minimum number of ATP molecules that would need to be involved?

19. Suppose that the radius of a typical cell is 10 mm and that inside it 106 ATP molecules are hydrolyzed each second. What is the power density of the cell in watts per cubic meter (1 W = 1 J s⁻¹). A computer battery delivers about 15 W and has a volume of 100 cm³. Which has the greater power density, the cell or the battery?
8. THERMODYNAMIC EQUILIBRIUM: CHEMICAL EQUILIBRIA
8. THERMODYNAMIC EQUILIBRIUM: CHEMICAL EQUILIBRIA

8.1 The concept of thermodynamic equilibrium

- Chemical thermodynamics predicts whether reactants have a spontaneous tendency to change into products, to predict the composition of the mixture at equilibrium, and to predict how that composition will be modified by changing the conditions.
- Although reactions in industry are rarely allowed to reach equilibrium, knowing whether equilibrium lies in favor of reactants or products under certain conditions is a good indication of the feasibility of a process.
- On page 30 of chapter 1, we introduced the definition of the chemical thermodynamic equilibrium. It was mentioned that any system cannot be considered in a thermodynamic equilibrium unless it satisfies thermal, mechanical, and chemical equilibriums simultaneously.
- The word equilibrium means a state of balance. In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system.
- A system that is in equilibrium experiences no changes when it is isolated from its surroundings. The opposite of equilibrium systems is nonequilibrium systems that are instantaneously off balance.

8.2 Thermodynamic background

- The only thermodynamic criterion for spontaneous change at any condition is $\Delta S_{\text{univ}} < 0$.
- The thermodynamic criterion for spontaneous change at constant temperature and pressure is $\Delta G_{\text{sys}} < 0$.
- The principal idea is that, at constant temperature and pressure, a reaction mixture tends to adjust its composition until its Gibbs energy is a minimum.
- There are cases in which the mixture at equilibrium contains almost no reactants or almost no products. And there are cases in which the mixture at equilibrium contains a considerable amount of both reactants and products. The question is “to what extent would a reaction proceed?”
- This can be clarified using the following figure.
✓ The line (a) shows that in some cases, the mixture at equilibrium contains a very little amount of the products which means that some very little amount reactants convert into products before G has reached its minimum value. The reaction ‘does not go’. Almost no products are formed.
✓ The line (c) shows that in some cases, the mixture at equilibrium contains a very large amount of the products which means that very large amount reactants convert into products before G has reached its minimum value. The reaction ‘goes’. Almost no reactants are left.
✓ The line (c) shows that in some cases the mixture at equilibrium contains substantial amounts of both reactants and products as G has reached its minimum value. The reaction ‘goes both ways’. This is the reversible reactions where G reaches its minimum when the amounts of reactants and products become constant.

8.3 Criteria of thermodynamic equilibrium

- From the first law and at constant temperature:

\[ dU = TdS - PdV - VdP \]

- If in addition to keeping T constant we keep S, U, V, or P constant, we can conclude that:
  
  A) At constant T and S:
  
  \[ (\Delta U)_{T,S} = 0 \]
  
  The system is in an equilibrium if \( \Delta U = 0 \) at constant T and S.

  B) At constant T and U:
  
  \[ (\Delta S)_{T,U} = 0 \]
  
  The system is in an equilibrium if \( \Delta S = 0 \) at constant T and U.

  C) At constant T and V:
  
  \[ (\Delta A)_{T,V} = 0 \]
  
  The system is in an equilibrium if \( \Delta A = 0 \) at constant T and V.

  D) At constant T and P:
  
  \[ (\Delta G)_{T,P} = 0 \]
  
  The system is in an equilibrium if \( \Delta G = 0 \) at constant T and P.

- Any of the above four criteria is good to be used to judge whether a system is at chemical thermodynamic equilibrium or not.
- However, because our daily life and our scientific and industrial activities are mostly accomplished at constant pressure; and because P is easier to control and to keep constant than U, S, and V, it is more convenient to take change in G at constant T and P as the indicator of the existence and establishment of chemical thermodynamic equilibrium.

- We should notice that:
Since \( G = H - TS \), \( G \) takes into account \( S \).
Since \( H = U + PV \), \( G \), also, takes into account \( U \) and \( V \).
It is clear that \( G \) takes into account all of \( T, P, V, U, \) and \( S \).

### 8.4 The reaction Gibbs energy: Direction of change

- To keep our ideas in focus, we consider two important reactions.
  1) The first is the reaction taking place in the aqueous environment of the cell which is the isomerism of glucose-6-phosphate (1, G6P) to fructose-6-phosphate (2, F6P), which is an early step in the anaerobic breakdown of glucose:

\[
G6P(aq) \rightleftharpoons F6P(aq)
\]

In this reaction, suppose that in a short interval while the reaction is in progress, the amount of G6P changes by \(-\Delta n\):

\[
G6P(aq) \rightleftharpoons F6P(aq)
\]

As a result of this change in amount, the contribution of G6P to the total Gibbs energy of the system changes by \(-\Delta G_{m,G6P} \times \Delta n\), where \(\Delta G_{m,G6P}\) is the partial molar Gibbs energy \((-\mu_{G6P} \times \Delta n\), which is the chemical potential of G6P in the reaction mixture). In the same interval, the amount of F6P changes by \(+\Delta n\), so its contribution to the total Gibbs energy changes by \(+\Delta G_{m,F6P} \times \Delta n\), where \(\Delta G_{m,F6P}\) is the partial molar Gibbs energy \((+\mu_{F6P} \times \Delta n\), which is the chemical potential of F6P in the reaction mixture).

Provided \(\Delta n\) is small enough to leave the composition virtually unchanged, the net change in Gibbs energy of the system is

\[
\Delta G = \mu_{F6P} \times \Delta n - \mu_{G6P} \times \Delta n
\]

\[
\frac{\Delta G}{\Delta n} = \mu_{F6P} - \mu_{G6P}
\]

\[
\Delta G_{\text{reaction}} = \mu_{F6P} - \mu_{G6P}
\]

The following figure shows that \(\Delta G_{\text{reaction}}\) (\(\Delta G\)) is the slope of the graph of \(G\) plotted against the changing composition of the system.
2) The second is the synthesis of ammonia, which is of crucial importance for industry and agriculture:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \]

If the amount of \( \text{N}_2 \) changes by \( -\Delta n \), the amount of \( \text{H}_2 \) will change by \( -3\Delta n \) and the amount of \( \text{NH}_3 \) will change by \( +2\Delta n \).

The total Gibbs energy of the mixture

\[
\Delta G = \mu_{\text{NH}_3} \times 2\Delta n - \mu_{\text{N}_2} \times \Delta n - \mu_{\text{H}_2} \times 3\Delta n
\]

Where \( \mu \) is the chemical potential (the partial molar Gibbs energy) of each substance in the reaction mixture.

The Gibbs energy of this reaction is:

\[
\Delta G_{\text{reaction}} = 2\mu_{\text{NH}_3} - (\mu_{\text{N}_2} + 3\mu_{\text{H}_2})
\]

- For the general symbolic reaction:

\[ a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D} \]

The Gibbs energy is:

\[
\Delta G_{\text{reaction}} = (c\mu_{\text{C}} + d\mu_{\text{D}}) - (a\mu_{\text{A}} + b\mu_{\text{B}})
\]

- The chemical potential of a substance depends on the composition of the mixture in which it is present and is high when its concentration or partial pressure is high.
- Keeping in mind that \( \Delta G_{\text{reaction}} \) is the slope of \( G \) plotted against composition, the following figure shows how \( \Delta G_{\text{reaction}} \) changes as the composition changes:

- When the mixture is rich in the reactants A and B and because \( \mu_{\text{A}} \) and \( \mu_{\text{B}} \) are then high, \( \Delta rG < 0 \) and the slope of \( G \) is negative (down from left to right).
- When the mixture is rich in the products C and D and because \( \mu_{\text{C}} \) and \( \mu_{\text{D}} \) are then high, \( \Delta rG > 0 \) and the slope of \( G \) is positive (up from left to right).
✓ At compositions corresponding to $\Delta G_{\text{reaction}} < 0$ the reaction tends to form more products.

✓ At compositions corresponding to $\Delta G_{\text{reaction}} > 0$, the reverse reaction is spontaneous, and the products tend to decompose into reactants.

✓ Where $\Delta G_{\text{reaction}} = 0$ (at the minimum of the graph where the slope is zero), the reaction has no tendency to form either products or reactants. In other words, the reaction is at equilibrium. That is, the criterion for chemical equilibrium at constant temperature and pressure is $\Delta G_{\text{reaction}} = 0$.

• In summary, at constant $T$ and $P$:
  ✓ If $G$ decreases, $\Delta G$ is negative, then the reaction from left to right is spontaneous.
  ✓ If $G$ increases, $\Delta G$ is positive, then the reaction from right to left is spontaneous.
  ✓ If $G$ doesn't change ($G_A = G_B$), $\Delta G$ is zero, then the reaction in both directions is spontaneous.

8.5 Free energy and equilibrium: The vant’ Hoff isotherm

• We know that:

$$\Delta G = G_B - G_A = nRT \ln \frac{\alpha_B}{\alpha_A}$$

$$G_A = G_A^\circ + RT \ln \alpha_A^n$$

$$G_B = G_B^\circ + RT \ln \alpha_B^n$$

$$\Delta G = G_B - G_A = (G_B^\circ + RT \ln \alpha_B^n) - (G_A^\circ + RT \ln \alpha_A^n)$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{\alpha_B^n}{\alpha_A^n}$$

• Generally, if the reaction is:

$$aA + bB + \cdots \rightleftharpoons cC + dD + \cdots$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{\alpha_C^c \alpha_D^d \cdots}{\alpha_A^a \alpha_B^b \cdots}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{\Pi(\alpha_{\text{PRODUCTS}})^n_p}{\Pi(\alpha_{\text{reactants}})^n_r}$$

Where $\Pi(\alpha_{\text{PRODUCTS}})^n_p$ and $\Pi(\alpha_{\text{reactants}})^n_r$ are "the multiplication of activities of products and reactants with each raised to its coefficient in the chemical equation".

$$\frac{\Pi(\alpha_{\text{PRODUCTS}})^n_p}{\Pi(\alpha_{\text{reactants}})^n_r} = Q$$

where $Q$ is called "the reaction quotient". Therefore:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

This equation is one of the very important equations in thermodynamics and is called vant' Hoff isotherm.

From vant' Hoff isotherm, if the reaction is at equilibrium:
\[ \Delta G = 0, \text{ and } Q = K_e \]

where \( K_e \) is the equilibrium constant. Therefore, at equilibrium:

\[ \Delta G^\circ = - RT \ln K_e \]

From this equation and vant' Hoff isotherm:

\[ \Delta G = \Delta G^\circ + RT \ln \frac{Q}{K_e} \]

**Example**

From the following table calculate \( \Delta G^\circ \) and \( K \) of the reaction:

<table>
<thead>
<tr>
<th>Substance</th>
<th>C(graphite)</th>
<th>H_2(g)</th>
<th>CH_4(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G_f^\circ ) / kJ mol(^{-1})</td>
<td>0</td>
<td>0</td>
<td>-74.83</td>
</tr>
<tr>
<td>( S / J K^{-1} ) mol(^{-1})</td>
<td>5.68</td>
<td>130.59</td>
<td>186.19</td>
</tr>
</tbody>
</table>

**Solution**

The reaction is the standard formation of CH_4(g). therefore, its \( \Delta H^\circ = -74 \) kJ

\[ \Delta S^\circ = \Sigma S^\circ (p) - \Sigma S^\circ (r) \]

\[ \Sigma S^\circ (p) = 1 \text{ mol } \times 186.19 \frac{J}{\text{mol K}} = 186.19 \frac{J}{K} \]

\[ \Sigma S^\circ (r) = 1 \text{ mol } \times 5.68 \frac{J}{\text{mol K}} + 2 \text{ mol } \times 130.59 \frac{J}{\text{mol K}} = 266.86 \frac{J}{\text{mol K}} \]

\[ \Delta S^\circ = 186.19 \frac{J}{\text{mol K}} - 266.86 \frac{J}{\text{mol K}} = -80.67 \frac{J}{\text{mol K}} \]

\[ \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ = (-74 \frac{kJ}{mol}) - (298 \text{ K } \times -0.08067 \frac{kJ}{mol K}) = -49.96 \frac{kJ}{mol} \]

\[ \ln K = \frac{\Delta G^\circ}{RT} = - \frac{-49.96 \frac{kJ}{mol} \times 1000 \frac{J}{kJ}}{8.314 \frac{J}{mol K} \times 298 \text{ K}} = 20.5 \]

\[ K = 8 \times 10^8 \]

**Practice exercise**

From the following table at 25 °C:

<table>
<thead>
<tr>
<th>Substance</th>
<th>H_2(g)</th>
<th>CO(g)</th>
<th>H_2O(g)</th>
<th>CO_2(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta G_f^\circ ) / kJ mol(^{-1})</td>
<td>0</td>
<td>-137.27</td>
<td>-228.59</td>
<td>-394.38</td>
</tr>
<tr>
<td>( \Delta H_f^\circ ) / kJ mol(^{-1})</td>
<td>0</td>
<td>-110.52</td>
<td>-241.83</td>
<td>-392.51</td>
</tr>
</tbody>
</table>

calculate \( K_p \) of the following reaction at 25 °C and 800 °C:

\[ \text{CO(g)} + \text{H}_2\text{O(g)} \rightarrow \text{H}_2(g) + \text{CO}_2(g) \]

**Example**

Write the reaction quotient for the esterification reaction:

\[ \text{CH}_3\text{COOH(L)} + \text{C}_2\text{H}_5\text{OH(L)} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(L) + \text{H}_2\text{O(L)} \]

**Solution**

\[ Q = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5]}{[\text{CH}_3\text{COOH}] \times [\text{C}_2\text{H}_5\text{OH}]} \]

**Practice exercise**

Write the reaction quotient for the combustion of dimethyl ether: reaction:

\[ \text{CH}_3\text{OCH}_3(L) + 3\text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g) + 3\text{H}_2\text{O(L)} \]

**Example**

Calculate the equilibrium constant for the following reaction at 25 °C:
\[ H_2(g) + I_2(s) \rightleftharpoons 2HI(g) \quad \Delta G^\circ = 3.40 \text{ kJ mol}^{-1} \]

**Solution**
\[ \Delta G^\circ = -RT \ln K \]
\[ 3.4 \text{ kJ} = -8.314 \times \frac{1}{\text{K mol}} \times 298 \times \ln K \]
\[ \ln K = -1.37 \]
\[ K = 0.25 \]

**Practice exercise**
Calculate \( \Delta G^\circ \) for the following reaction at 25 °C:
\[ 2\text{NO(g) + O}_2(g) \rightleftharpoons 2\text{NO}_2(g) \quad K = 4.38 \times 10^{-13} \]

**Example**
Calculate \( \Delta G^\circ \), in kJ, for the following reaction at 25 °C:
\[ \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \quad K = 1.58 \times 10^{-9} \]

**Solution**
\[ \Delta G^\circ = -RT \ln K = -8.314 \times \frac{1}{\text{K mol}} \times 298 \times \ln 1.58 \times 10^{-9} = 5.02 \times 10^4 \text{ J} \]
\[ \Delta G^\circ = 5.02 \times 10^4 \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 50.2 \text{ kJ} \]

**Practice exercise**
Calculate the equilibrium constant for the following reaction at 25 °C:
\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta G^\circ = -32.90 \text{ kJ mol}^{-1} \]

- We conclude from the equation “\( \Delta G^\circ = -RT \ln K_b \)” that the magnitude of the equilibrium constant is a good indication of the feasibility of a reaction.
- Broadly speaking:
  - If \( K \gg 1 \) (\( K > 10^3 \) and \( \Delta G_{\text{reaction}} < -17 \text{ kJ at 25°C} \)), then the reaction has a strong tendency to form products. So, we can conclude that the reaction is thermodynamically feasible (\( \Delta G_{\text{reaction}} < 0 \)). Reactions of this type are called **exergonic**
  - If \( K << 1 \) (\( K < 10^{-3} \) and \( \Delta G > +17 \text{ kJ at 25°C} \)), then the equilibrium composition will consist of largely unchanged reactants. So, we can conclude that the reaction is not thermodynamically feasible (\( \Delta G_{\text{reaction}} > 0 \)). Reactions of this type are called **endergonic**
  - If \( K \) is comparable to 1 (between \( 10^{-3} \) and \( 10^3 \)), then significant amounts of both reactants and products will be present at equilibrium.
- We also know the following equation:
\[ \Delta G_{\text{reaction}} = \Delta H_{\text{reaction}} - T\Delta S_{\text{reaction}} \]
This equation tells us the conditions of having a positive or a negative \( \Delta G_{\text{reaction}} \):
1) If \( \Delta H_{\text{reaction}} < 0 \) and \( \Delta S_{\text{reaction}} > 0 \) then \( \Delta G_{\text{reaction}} < 0 \) and \( K > 1 \) at all temperatures.
2) If \( \Delta H_{\text{reaction}} < 0 \) and \( \Delta S_{\text{reaction}} < 0 \) then \( \Delta G_{\text{reaction}} < 0 \) and \( K > 1 \) at only low temperatures.
3) If \( \Delta H_{\text{reaction}} > 0 \) and \( \Delta S_{\text{reaction}} < 0 \) then \( \Delta G_{\text{reaction}} < 0 \) and \( K > 1 \) at only high temperatures.
4) If \( \Delta H_{\text{reaction}} > 0 \) and \( \Delta S_{\text{reaction}} < 0 \) then \( \Delta G_{\text{reaction}} > 0 \) and \( K < 1 \) at all temperatures.
8.6 Expressing equilibrium constant
The equilibrium constant \( K_e \) could be expressed in several terms as follows:

1. If expressed in terms of activities it will be denoted as \( K_\alpha \), where:
   \[
   K_\alpha = \frac{\Pi \text{products activities}^n(p)}{\Pi \text{reactants activities}^n(r)}
   \]

2. If expressed in terms of molarities it will be denoted as \( K_c \), where:
   \[
   K_c = \frac{\Pi \text{products molarities}^n(p)}{\Pi \text{reactants molarities}^n(r)}
   \]

3. If expressed in terms of pressures it will be denoted as \( K_p \), where:
   \[
   K_p = \frac{\Pi \text{products pressures}^n(p)}{\Pi \text{reactants pressures}^n(r)}
   \]

4. If expressed in terms of mole fractions it will be denoted as \( K_x \), where:
   \[
   K_x = \frac{\Pi \text{products mole fractions}^n(p)}{\Pi \text{reactants mole fractions}^n(r)}
   \]

8.7 Relationship between \( K_c \) and \( K_p \)
- When the system in equilibrium involves gases, its equilibrium constant could be expressed in terms of rather their concentrations or their pressures. For example:

\[
\text{aA}(g) + \text{bB}(g) \rightarrow \text{cC}(g) + \text{dD}(g) + \cdots
\]

\[
K_c = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}
\]

\[
K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}
\]

- Because the ideal gas law relates pressure to concentration as follows:

\[
P = \frac{n}{V} RT = \text{CRT}
\]

Where \( C \) is the molarity. The relation between \( K_c \) and \( K_p \) is:

\[
K_p = K_c (RT)^{\Delta n_g}
\]

Here, \( \Delta n_g \) is the difference between number of moles of of gases produced and reacted:

\[
\Delta n_g = \Sigma n_g(\text{products}) - \Sigma n_g(\text{products})
\]

Example 8.2
Knowing that \( \Delta G_f^\circ \), in kJ mol\(^{-1}\) of ethane is \(-32.89\) and of ethylene is \(68.12\), calculate \( \Delta G^\circ \) and \( K_p \) of the hydrogenation of 1 mol of ethylene.

Solution
C₂H₄(g) + H₂(g) ⇌ C₂H₆(g)

ΔG° = ΣΔG°ᵣ(µ) - ΣΔG°ᶠ(µ)

ΔG° = [(-32.89 kJ mol⁻¹)] - [(-68.12 kJ mol⁻¹) + 0] = - 101.1 kJ mol⁻¹

ln Kₚ = \frac{ΔG°}{RT} = \frac{-101100 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 40.77

Kₚ = 5 \times 10^{17}

**Practice exercise**

Calculate ΔG° of the following change:

N₂(g) + 3H₂(g) ⇌ 2NH₃(g)

Kₚ, 673 K = 1.64 \times 10^{-4}

---

### 8.8 Factors affecting equilibrium

The response of equilibrium to conditions obeys a famous principle known as LeChatelier’s principle, which can be stated in many ways that give the same idea. One of these statements states that *if a chemical system at equilibrium experiences a change in temperature, concentration, and pressure, then the equilibrium shifts to counteract the imposed change and a new equilibrium is established.*

#### 8.8.1 Effect of changing temperature

Another vant’ Hoff equation is expressed as:

\[
\frac{d \ln K}{d \frac{1}{T}} = - \frac{\Delta H^\circ}{R}
\]

This equation reveals that if ΔH° is independent of temperature, K for endothermic reactions will increase as temperature increases, and vice versa. This result can be clarified by an example such as the following:

\[
\text{Ag}_2\text{CO}_3(s) \rightleftharpoons \text{Ag}_2\text{O}(s) + \text{CO}_2(g) \quad \Delta H^\circ = +80 \text{ kJ}
\]

Because the forward reaction favors absorbing heat, as temperature increases the amounts of products will increase on the expenses of reactants amounts, which consequently increases the value of the equilibrium constant. If the reaction is written in opposite way as:

\[
\text{Ag}_2\text{O}(s) + \text{CO}_2(g) = \text{Ag}_2\text{CO}_3 (s) \quad \Delta H^\circ = -80 \text{ kJ}
\]

the equilibrium constant will decrease as temperature increases.

If, at a certain temperature (T₁), we know the value of the equilibrium constant (K₁), then if the reaction is carried out at another temperature (T₂) the value of the equilibrium constant (K₂) can be calculated using the following equation:

\[
\ln \frac{K₂}{K₁} = \frac{\Delta H^°}{R} (\frac{T₂ - T₁}{T₁ \times T₂})
\]

where ΔH°, the standard enthalpy of the reaction, is considered to have the same value over the range from T₁ to T₂.
Example 8.3
Calculate $\Delta H^\circ$ of a reaction if raising its temperature from 25 °C to 35 °C doubles the value of its equilibrium constant.

Solution

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R \left( \frac{T_2 - T_1}{T_1 \times T_2} \right)}$$

$$\ln 2 \times \frac{K_1}{K_1} = \frac{\Delta H^\circ}{8.314 \left( \frac{308 - 298}{308 \times 298} \right)}$$

$$\ln 2 = \frac{\Delta H^\circ}{8.314 \times \frac{308 \times 298}{308 K \times 298 K}}$$

$$\Delta H^\circ = 52882.28 \text{ J} = 52.88 \text{ kJ}$$

Practice exercise

Calculate $\Delta G^\circ$ and $\Delta S^\circ$ of a reaction at 1200 K if its equilibrium at 1225 K constant is $3.28 \times 10^{-3}$ and its $\Delta H^\circ$ is 216.7 kJ.

8.8.2 Effect of changing concentration

Let’s take the following reaction at equilibrium:

$$3\text{H}_2 + \text{N}_2(g) = 2\text{NH}_3(g)$$

According to Le Chatelier’s principle increasing the concentration of any substance in the equilibrium mixture will force the reaction to proceed faster in the direction that decreases the concentration of this component. We say the reaction shifts toward that direction. This change is in the equilibrium position only. And because temperature did not change, the equilibrium constant will remain the same.

8.8.3 Effect of changing pressure

Let’s again take the same reaction at equilibrium:

$$3\text{H}_2 + \text{N}_2(g) = 2\text{NH}_3(g)$$

Changing the pressure means that the volume of the vessel that contains the reaction mixture is either decreased, and consequently the total pressure of the system increases, or the vessel volume is increased, and consequently the total pressure of the system decreases. According to LeChateliers principle decreasing the vessel volume (increasing the pressure) will force the reaction to proceed faster in the direction that decreases the number of moles of gases, which means in our example that it will shift faster to the right. This change is in the equilibrium position. And because $T$ did not change, the equilibrium constant will remain the same. Sometimes number moles of gases on the left and the right sides of the equation are equal as in the following examples:

$$\text{H}_2(g) + \text{I}_2(g) = 2\text{HI}_2(g)$$

$$\text{C}(s) + \text{O}_2(g) = \text{CO}_2(g)$$

In such cases changing the vessel volume (i.e. changing the pressure) will not shift the equilibrium toward any direction. And again, because $T$ did not change, the equilibrium constant will remain the same.
**8.8.4 Effect of adding a catalyst**

The diagram below shows the reaction path from left to right and from right to left with and without a catalyst. It appears that catalyst decreases the activation energy in the two-opposite direction by the same value.

Arrhenius equation states for the reaction in the two opposite directions that:

\[
\ln k(\text{forward}) = \ln A(\text{forward}) - \frac{E_a(\text{forward})}{RT}
\]

\[
\ln k(\text{reverse}) = \ln A(\text{reverse}) - \frac{E_a(\text{reverse})}{RT}
\]

Because \(A, R,\) and \(T\) are constant. And because \(E_a\) decreased in both directions by the same value, the increase in \(\ln k\), and consequently the increase in the reaction rate in both directions will be equal. As a result, the presence of a catalyst has no effect in equilibrium position or constant.

**8.9 Equations' stoichiometry and equilibrium**

- Any chemical reaction equation such as:

\[
2\text{H}_2\text{S}(g) + \text{CH}_4(g) \rightleftharpoons 4\text{H}_2(g) + \text{CS}_2(g) \quad K_{p1} = 3.31 \times 10^{-4}
\]

can be manipulated in different ways as follows:

A) If we multiply the equation by any number such as 2 or \(\frac{1}{2}\), we can calculate the equilibrium constant of the resulting equation by raising the equilibrium constant of the original equation to a power that equals the same number it was multiplied by. The following are examples for such manipulations:

✓ If the above equation is for multiplied by 2:

\[
4\text{H}_2\text{S}(g) + 2\text{CH}_4(g) \rightleftharpoons 8\text{H}_2(g) + 2\text{CS}_2(g) \quad K_{p2} = ?
\]

the equilibrium constant can be calculated as follows:

\[
K_{p2} = (K_{p1})^2 = (3.31 \times 10^{-4})^2 = 1.1 \times 10^{-7}
\]
If the above equation is for multiplied by 0.5:

\[
\text{H}_2\text{S}(g) + \frac{1}{2}\text{CH}_4(g) = 2\text{H}_2(g) + \frac{1}{2}\text{CS}_2(g) \quad K_{p3} = ?
\]

\[
K_{p3} = (K_{p1})^{0.5} = (3.31 \times 10^{-4})^{0.5} = 1.82 \times 10^{-2}
\]

B) If we reverse the equation, we can calculate the equilibrium constant of the resulting equation by inversing the equilibrium constant of the first. The following is an example for such manipulation:

\[
4\text{H}_2(g) + \text{CS}_2(g) = 2\text{H}_2\text{S}(g) + \text{CH}_4(g) \quad K_{p4} = ?
\]

\[
K_{p4} = \frac{1}{K_{p1}} = \frac{1}{3.31 \times 10^{-4}} = 3.02 \times 10^{3}
\]

C) If we multiply the equation by any number and reverse it, we can calculate its by raising the equilibrium constant of the first to a power that equals the same number followed by inversing the resulting number. The following is an example for such manipulation:

\[
8\text{H}_2(g) + 2\text{CS}_2(g) = 4\text{H}_2\text{S}(g) + 2\text{CH}_4(g) \quad K_{p5} = ?
\]

\[
K_{p5} = \left(\frac{1}{K_{p1}}\right)^2 = \left(\frac{1}{3.31 \times 10^{-4}}\right)^2 = 9.127 \times 10^6
\]
QUESTIONS AND PROBLEMS

1. From the following table:

<table>
<thead>
<tr>
<th>Substance</th>
<th>C(graphite)</th>
<th>H(_2)(g)</th>
<th>CH(_4)(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta G_f^\circ) / kJ mol(^{-1})</td>
<td>0</td>
<td>0</td>
<td>-74.83</td>
</tr>
<tr>
<td>(S^\circ) / J K(^{-1}) mol(^{-1})</td>
<td>5.68</td>
<td>130.59</td>
<td>186.19</td>
</tr>
</tbody>
</table>

calculate \(\Delta G^\circ\) and K of the reaction:

\[ \text{C(graphite) + 2H}_2(g) \rightarrow \text{CH}_4(g) \]

2. Calculate \(\Delta G^\circ\) of the following change:

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \text{K}_{p,673 K} = 1.64 \times 10^{-4} \]

3. Knowing that \(\Delta G_f^\circ\), in kJ mol\(^{-1}\) of ethane is -32.89 and of ethylene is 68.12, calculate \(\Delta G^\circ\) and \(K_p\) of the hydrogenation of 1 mol of ethylene.

4. From the following table at 25 °C:

<table>
<thead>
<tr>
<th>Substance</th>
<th>H(_2)(g)</th>
<th>CO(g)</th>
<th>H(_2)O(g)</th>
<th>CO(_2)(g)</th>
</tr>
</thead>
<tbody>
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<td>(\Delta G_f^\circ) / kJ mol(^{-1})</td>
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<td>0</td>
<td>-110.52</td>
<td>-241.83</td>
<td>-392.51</td>
</tr>
</tbody>
</table>

calculate \(K_p\) of the following reaction at 25 °C and 800 °C:

\[ \text{CO(g) + H}_2\text{O(g) \rightleftharpoons H}_2\text{(g) + CO}_2\text{(g)} \]

5. Calculate \(\Delta H^\circ\) of a reaction if raising its temperature from 25 °C to 35 °C doubles the value of its equilibrium constant.

6. Calculate \(\Delta G^\circ\) and \(\Delta S^\circ\) of a reaction at 1200 K if its equilibrium constant is 3.28 \times 10^{-3} at 1225 K and its \(\Delta H^\circ\) is 216.7 kJ.

7. Knowing that \(\Delta G_f^\circ\) of NH\(_3\)(g) is -16.6 / kJ mol\(^{-1}\), calculate the equilibrium constant of the following reaction:

\[ 2\text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3\text{H}_2(g) \]
9. THERMODYNAMIC EQUILIBRIUM: PHYSICAL EQUILIBRIA OF PURE SUBSTANCES
9. THERMODYNAMIC EQUILIBRIUM: 
PHYSICAL EQUILIBRIA OF PURE SUBSTANCES

9.1 The physical system and the physical change

- We say that we have a physical system when a substance (or more than one substance) exists without any chemical reaction taking place.
- Many physical changes were explained in chapter 4, pages 79 - 94.
- Boiling, freezing, and the conversion of graphite to diamond are examples of phase transitions, or changes of phase without change of chemical composition.
- Many phase changes are common everyday phenomena and their description is an important part of physical chemistry.
- Examples of physical changes is the change of a solid into a liquid, as in the melting of ice, a liquid into a vapor, as in the vaporization of water in our lungs, or a solid phase changes into another solid phase, as in the conversion of graphite into diamond under high pressure, or the conversion of one phase of iron into another as it is heated in the process of steelmaking.
- Any physical system could be in one or more than one physical states (phases), namely gas, liquid, and solid. If the properties of a physical system are fixed and do not experience any forces that change them, we say that the system is in a physical equilibrium.
- Therefore, physical equilibrium can exist between several phases of one component, between several components in one phase, or between several components in several phases.
- For simplicity we will limit our discussion here only to physical equilibrium between several phases of one component.
- The Gibbs energy, \( G = H - TS \), of a substance will be at center stage in all that follows. We need to know how its value depends on the pressure and temperature.

9.2 The condition of stability

- in the discussion of phase transitions of a pure substance, we need to establish the importance of the molar Gibbs energy, \( G_m \), which represents the Gibbs energy of only one mole of the substance:

\[
G_m = \frac{G}{n}
\]

- The molar Gibbs energy, which is an intensive property, depends on the phase of the substance. For instance, the molar Gibbs energy of liquid water is in general different from that of water vapor at the same temperature and pressure.
- When an amount "n" of the substance changes from phase 1 (for instance, liquid), with molar Gibbs energy \( G_{m(1)} \) to phase 2 (for instance, vapor) with molar Gibbs energy \( G_{m(2)} \), the change in Gibbs energy is:

\[
\Delta G = nG_{m(2)} - nG_{m(1)} = n\{G_{m(2)} - G_{m(1)}\}
\]

- Because a spontaneous change at constant temperature and pressure is accompanied by a negative value of \( \Delta G \), this expression shows that a change from
phase 1 to phase 2 is spontaneous if the molar Gibbs energy of phase 2 is lower than that of phase 1.

A SUBSTANCE HAS A SPONTANEOUS TENDENCY TO CHANGE INTO THE PHASE WITH THE LOWEST MOLAR GIBBS ENERGY.

- If at a certain temperature and pressure the solid phase of a substance has a lower molar Gibbs energy than its liquid phase, then the solid phase is thermodynamically more stable and the liquid will (or at least has a tendency to) freeze but if the opposite is true, the liquid phase is thermodynamically more stable and the solid will melt.
- For example, at 1 atm, ice has a lower molar Gibbs energy than liquid water when the temperature is below 0°C, and under these conditions water converts spontaneously into ice.

Example

At 298 K, the Gibbs energy of transition from metallic white tin (α-Sn) to nonmetallic grey tin (β-Sn) is + 0.13 kJ mol⁻¹. Is α-Sn or β-Sn considered the reference state of tin at this temperature?

Solution

The reference state of an element is its most stable form under the prevailing conditions.

\[
\alpha\text{-Sn} \rightarrow \beta\text{-Sn} \quad \Delta G = + 0.13 \text{ kJ mol}^{-1}
\]

Because \( \Delta G \) has a positive value this change is nonspontaneous. Therefore α-Sn is the reference state of tin at this temperature.

9.3 The variation of Gibbs energy with pressure and temperature

9.3.1 The variation of Gibbs energy with pressure

- To discuss how all phase transitions depend on the pressure, we need to know how the molar Gibbs energy varies with pressure.
- The following equation shows that at constant temperature the change in the pressure of one mole of a substance by Δ\( P \) leads to a change in the molar Gibbs energy by \( \Delta G_m \):

\[
\Delta G_m = V_m \Delta P
\]

\( V_m \) is the molar volume of the substance and always has a positive value

- This expression is valid when \( V_m \) is constant in the pressure range of interest.
- The equation \( \Delta G_m = V_m \Delta P \) tells us:
  - First: Because \( V_m \) is positive, the molar Gibbs energy increases (\( \Delta G_m > 0 \)) when the pressure increases (\( \Delta p > 0 \)).
  - Second: For a given change in pressure, the resulting change in molar Gibbs energy is greatest for substances with large molar volumes.
  - Third: Because \( V_m \) of a gas is much larger than that of a condensed phase (a liquid or a solid), the dependence of \( G_m \) on \( P \) is much greater for a gas than for a condensed phase.
- For most substances (water is an important exception), \( V_m \) of the liquid phase is greater than that of the solid phase.
- The following figure shows how \( G_m \) for a substance changes with \( P \) and which state (gas, liquid, solid) is more stable at a certain case.
✓ The figure shows three lines for the three states.
✓ Each line has two colored portions, one is orange and the other is green.
✓ The green portion of each line represents the region where the molar Gibbs energy of a particular phase (solid, liquid or gas) is least.

Now we can look at the three lines to understand the differences between the three phases:

1) **The line representing the solid state** has its green portion at the right. This indicates that at these high pressures, the molar Gibbs energy of the substance is low which means that at these high pressures the substance is more stable when it is a solid rather than when it is a liquid or a gas.

2) **The line representing the liquid state** has its green portion in the middle. This indicates that at these medium pressures, the molar Gibbs energy of the substance is low which means that at these medium pressures the substance is more stable when it is a liquid rather than when it is a solid or a gas.

3) **The line representing the gaseous state** has its green portion at the left. This indicates that at these low pressures, the molar Gibbs energy of the substance is low which means that at these low pressures the substance is more stable when it is a gas rather than when it is a liquid or a solid.

✓ The slope of the graph is greater for a liquid than for a solid.
✓ When we increase P on a substance, $G_m$ of its gas phase rises above that of the liquid, then $G_m$ of the liquid rises above that of the solid.
✓ As pressure increases the gaseous substance condenses to a liquid, and then further increase can result in the formation of a solid.

- The equation $\Delta G_m = V_m \Delta P$ can be looked at as follows. (i and f means initial and final):

  $$(G_{m,f} - G_{m,i}) = V_m (P_f - P_i)$$
  $$G_{m,f} = G_{m,i} + V_m (P_f - P_i)$$

✓ This equation shows that increasing the pressure from $P_i$ to $P_f$ causes an increase in the molar Gibbs energy by a value that is equal to $V_m \times (P_f - P_i)$. 

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If the substance is in its solid or liquid state, and because $V_{m, \text{liquid}}$ and $V_{m, \text{solid}}$ are so small, the dependence of $G_m$ on pressure is very weak especially for the typical ranges of pressure normally of interest to us.

If the substance is in its gaseous state, and because $V_{m, \text{gas}}$ are so large, the dependence of $G_m$ on pressure is very strong even at the typical ranges of pressure normally of interest to us.

Because for one mole of a gas $PV = RT$, the significant dependence of $G_m$ on the pressure when the substance is in its gaseous state is found to obey the following equation:

$$G_{m, P_f} = G_{m, P_i} + RT \ln \frac{P_f}{P_i}$$

The following figure shows the relation between $G_m$ of a perfect gas and the pressure.

The figure shows that increasing the pressure on the gas increases $G_m$ logarithmically.

The curve becomes more flattered as volume becomes smaller (pressures becomes higher). This means that effect of pressure on $G_m$ becomes less at high pressures.

### 9.3.2 The variation of Gibbs energy with temperature

- To discuss how phase transition depend on the temperature, we need to know how the molar Gibbs energy varies with temperature.
- The following equation shows that at constant pressure the change in the temperature of one mole of a substance by a small amount “$\Delta T$” leads to a change in the molar Gibbs energy by $\Delta G_m$:

$$\Delta G_m = -S_m \Delta T$$

$S_m$ is the molar entropy of the substance and it always has a positive value.

$$\Delta G_m = G_{m, T_f} - G_{m, T_i}$$

$$\Delta T = T_f - T_i$$
• This equation is valid when $S_m$ is constant in the temperature range of interest.
• Because $S_m$ is positive increasing temperature makes $\Delta G_m$ negative. This means that increasing temperature decreases $G_m$.
• For a given $\Delta T$ the change in molar Gibbs energy ($\Delta G_m$) is proportional to the molar entropy ($S_m$).
• $S_{m,\text{gas}}$, $S_{m,\text{liquid}}$ and $S_{m,\text{solid}}$ are the molar entropy of the substance in its three phases.
• The value of $S_{m,\text{gas}}$ is tremendously greater than the value of $S_{m,\text{solid}}$ and $S_{m,\text{liquid}}$.
• The value of $S_{m,\text{liquid}}$ is greater than the value of $S_{m,\text{solid}}$ but the difference here is not as much as that between $S_{m,\text{gas}}$ and $S_{m,\text{solid}}$, or even $S_{m,\text{liquid}}$.
• Because $S_{m,\text{gas}}$, $\gg$ $S_{m,\text{solid}}$ and $S_{m,\text{gas}}$, $\gg$ $S_{m,\text{liquid}}$, decreasing temperature makes a significant drop in the value of $S_m$ when the substance is gaseous compared with that drop if the substance was a solid or a liquid.
• Again, the value of $S_m$ of any substance in its liquid phase is higher than that when the substance is in its solid phase. Therefore, decreasing temperature makes the drop in the value of $S_m$ when the substance is liquid more than when it is a solid.
• The following figure shows how $G_m$ for a substance changes with $T$ and which state (gas, liquid, solid) is more stable at a certain case.
  ✓ The figure shows three lines for the three states.
  ✓ Each line has two colored portions, one is orange and the other is green.
  ✓ The green portion of each line represents the region where the molar Gibbs energy of a particular phase (solid, liquid or gas) is least.

Now we can look at the three lines to understand the differences between the three phases:

4) **The line representing the solid state** has its green portion at the left. This indicates that at these low temperatures, the molar Gibbs energy of the
substance is low which means that at these low temperatures the substance is more stable when it is a solid rather than when it is a liquid or a gas.

5) **The line representing the liquid state** has its green portion in the middle. This indicates that at these medium temperatures, the molar Gibbs energy of the substance is low which means that at these medium temperatures the substance is more stable when it is a liquid rather than when it is a solid or a gas.

6) **The line representing the gaseous state** has its green portion at the right. This indicates that at these high temperatures, the molar Gibbs energy of the substance is low which means that at these low temperatures the substance is more stable when it is a gas rather than when it is a liquid or a solid.

- The **transition temperature**, $T_{trs}$, between two phases, such as between liquid and solid is the temperature, at a given pressure, at which the molar Gibbs energies of the two phases are equal.
- Above the solid–liquid transition temperature the liquid phase is thermodynamically more stable; below it, the solid phase is more stable. For example, at 1 atm, the transition temperature for ice and liquid water is 0°C and that for grey and white tin is 13°C.
- At the transition temperature itself, the molar Gibbs energies of the two phases are identical and there is no tendency for either phase to change into the other. At this temperature, therefore, the two phases are in equilibrium.
- At 1 atm, ice and liquid water are in equilibrium at 0°C and the two allotropes of tin are in equilibrium at 13°C.
- To simplify the above discussion, suppose the component we have is X, which is existing in equilibrium between two of its phases (A) and (B) at the same T and P:

$$X(A) = X(B)$$

$X(A)$ and $X(B)$ being in equilibrium at the same T and P means that their Gibbs free energies are equal:

$$G_{X(A)} = G_{X(B)}$$

This means that any change in the free energy of one state will be accompanied with an equal change in the free energy of the other state, and any change in T must be accompanied by a correspondent change in P:

$$dG_{X(A)} = dG_{X(B)}$$

9.4 The Clapeyron equation

- Clapeyron went on derivation ending up to an equation known as **Clapeyron equation**. Clapeyron equation can be written in different identical forms.
  - First form is:

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T\Delta V}$$

  This form helps to calculate the change in pressure per 1 temperature degree.
  - Second form is:
\[ \frac{\Delta T}{\Delta P} = \frac{T \Delta V}{\Delta H} \]

This one helps to calculate the change in temperature per 1 pressure unit.
✓ Third form is:
\[ \frac{\Delta V}{\Delta T} = \frac{\Delta H}{T \Delta P} \]

This one helps to calculate the change in volume per 1 temperature degree.
✓ Fourth form is:
\[ \frac{\Delta T}{\Delta V} = \frac{\Delta P}{\Delta H} \]

This one helps to calculate the change in temperature per 1 volume unit.

**Example 9.1**
Knowing that at 100 °C and 1 atm the molar volume of H₂O(L) is 0.019 dm³ mol⁻¹, the molar volume of H₂O(g) is 30.199 dm³ mol⁻¹, and the molar enthalpy of vaporization of water is 40.82 kJ mol⁻¹, calculate the change in water boiling point accompanying the change in pressure by 1 mmHg.

**Solution**
\[
\frac{dT}{dP} = 1 \text{ Pa} \times 1 \text{ m}^3 = 1 \text{ J}
\]
\[
\frac{\Delta T}{\Delta P} = \frac{T \Delta V}{\Delta H} = \frac{373 \text{ K} \times (30.199 - 0.019) \text{ dm}³ \times 10^{-3} \text{ m}^3 \text{ mol}^{-1} \times 10^{-3} \text{ m}^3 \text{ dm}^{-1}}{40.82 \text{ kJ} \text{ mol}^{-1} \times 10^{-3} \text{ J} \text{ kJ}^{-1}} = 2.76 \times 10^{-4} \text{ K Pa}^{-1} = 0.037 \text{ K mmHg}^{-1}
\]

Regarding units we should remember that 1 Pa × 1 m³ = 1 J.
Changing the pressure by 1 mmHg changes boiling point by 0.037 K.

**Practice exercise**
Knowing for benzene (C₆H₆) that its normal solidification (freezing) point is 5 °C, molar volume when liquid is 87.282 cm³ mol⁻¹, molar volume when solid is 82.68 cm³ mol⁻¹, and standard molar enthalpy of solidification is − 9.984 kJ mol⁻¹, calculate the change in pressure needed to change its boiling point by 1 °C.

**Example 9.2**
Knowing for H₂O that its freezing point is 273 K, molar volume when liquid is 18.0036 cm³ mol⁻¹, molar volume when solid is 19.6335 cm³ mol⁻¹, and its standard molar enthalpy of freezing is − 6.03 kJ mol⁻¹, calculate the change in its freezing point accompanying the change in pressure by 1 atm.

**Solution**
\[
\frac{dT}{dP} = \frac{\Delta T}{\Delta P} = \frac{273 \text{ K} \times (18.0036 - 19.6335) \text{ cm}³ \text{ mol}^{-1} \times 10^{-6} \text{ m}^3 \text{ cm}^{-1}}{-6.03 \text{ kJ} \text{ mol}^{-1} \times 10^{-3} \text{ J} \text{ kJ}^{-1}} = + 0.0738 \times 10^{-8} \text{ Km}^3 \text{ Pa}^{-1}
\]
\[
\frac{dT}{dP} = + 0.0738 \times 10^{-8} \text{ K Pa}^{-1} = -0.0738 \times 10^{-8} \text{ K Pa}^{-1} = + 0.0738 \times 10^{-8} \frac{K}{\text{Pa} \times 1 \text{ atm} \times 101325 \text{ Pa}}
\]

Changing the pressure by 1 atm changes freezing point by 0.00748 K.

**Practice exercise**
Knowing for solid sulfur (S₈) that its molar volume when it is in monoclinic form is
more than what it is in rhombic form by 3.226 cm³/mol, transition point from monoclinic form to rhombic form at 1 atm is 95.4 °C, and its standard molar enthalpy of this transition is 3.04 kJ/mol, calculate the change in its transition point accompanying the change in pressure by 1 atm.

9.5 Special cases of Clapeyron equation
- Clapeyron equation can be modified to the following equation:

\[ \Delta P = P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1} \]

A) Vaporization process:
When a substance vaporizes from its liquid state to its gaseous state, its volume in its gaseous state becomes much larger than in its liquid state to the extent that it is very acceptable to neglect the liquid volume. Accordingly:

\[ \Delta V = V_g - V_L \approx V_g \]

To appreciate this, remember that the volume of one mole of liquid water at 1 atm and 0 °C is 18 cm³ which is equal to 0.018 L, while that of one mole of water vapor at the same conditions is 22400 cm³ which is equal to 22.4 L, the difference between these two values:

\[ \Delta V = V_g - V_L = 22.4 - 0.018 = 22.383 \text{ L} \]

It's clear that:

\[ 22.383 \text{ L} \approx 22.4 \text{ L} \]

Accordingly, and in the case of vaporization the equation:

\[ \Delta P = \frac{\Delta H_{vap}}{\Delta V} \frac{\Delta T}{T} \]

can be written as follows:

\[ \Delta P = \frac{\Delta H_{vap}}{V_g} \frac{\Delta T}{T} \]

Because:

\[ V = \frac{nRT}{P} \]

Clausius went further on derivation from Clapeyron equation to get the following equation known as Clausius-Clapeyron equation:

\[ \ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left( \frac{T_2 - T_1}{T_1 \times T_2} \right) \]

Example 9.3
From the following table for decane:
Calculate: A) $\Delta H_{\text{vap}}$  
B) $\Delta S_{\text{vap}}$ at 100 °C

**Solution**

$$ \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{RT} \left( \frac{T_2 - T_1}{T_1 T_2} \right) $$

$$ \ln \frac{40}{10} = \frac{\Delta H_{\text{vap}}}{8.314 \text{kJ mol}^{-1} \text{K}^{-1}} \left( \frac{328.7 \text{K} - 423.6 \text{K}}{423.6 \text{K} \times 328.7 \text{K}} \right) $$

$\Delta H_{\text{vap}} = 16919 \text{J mol}^{-1} = 16.92 \text{kJ mol}^{-1}$

$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{16919}{373 \text{K} \times 328.7 \text{K}} = 45.33 \text{J K}^{-1} \text{mol}^{-1}$

**Practice exercise**

Knowing that $\Delta H_{\text{vap, ethanol}} = 38.7 \text{kJ mol}^{-1}$, and $t_{\text{boiling, ethanol}} = 78.4 ^\circ \text{C}$, calculate the pressure at which ethanol boils at 25 °C.

**Example 9.4**

Knowing that $\Delta H_{\text{vap, ethanol}} = 38.7 \text{kJ mol}^{-1}$, and $t_{\text{boiling, ethanol}} = 78.4 ^\circ \text{C}$, calculate the pressure at which ethanol boils at 25 °C.

**Solution**

$$ \ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{RT} \left( \frac{T_2 - T_1}{T_1 T_2} \right) $$

$$ \ln \frac{1}{\frac{1}{10}} = \frac{38700}{8.314 \text{kJ mol}^{-1} \text{K}^{-1}} \left( \frac{298 - 351.4}{351.4 \times 298} \right) $$

$P_2 = 0.09313 \text{ atm} = 70.78 \text{ mmHg} = 9436 \text{ Pa}$

**Practice exercise**

From the following information of an organic compound:

- $T_{\text{freezing}} = 80 ^\circ \text{C}$
- $P_{\text{vap, liquid, 85.95 °C}} = 10 \text{ mmHg}$
- $P_{\text{vap, liquid, 119.45 °C}} = 40 \text{ mmHg}$
- $P_{\text{vap, solid, 52.6 °C}} = 1 \text{ mmHg}$
- triple point is 80 °C and 1 atm

A) Calculate:

B) $\Delta H_{\text{vap}}$

C) $t_{\text{biling}}$

D) $\Delta S_{\text{vap}}$ at $T_{\text{biling}}$

E) $P_{\text{vap}}$ at $T_{\text{solidification}}$

F) $\Delta H_{\text{sublimation}}$

G) $\Delta H_{\text{solidification}}$

H) Temperature at which $P_{\text{vap}}$ of the solid compound is $1 \times 10^{-5}$ mmHg.

**B) Fusion (melting) process**

When a substance fuses (melts) from its solid state to its liquid state:

$$ \Delta V = V_L - V_s \quad \Delta P = \frac{\Delta H_{\text{fus}}}{V_L - V_g} \frac{\Delta T}{T} $$

For most substances, $\Delta V$ is positive, and for some little substances is negative. Accordingly, increasing pressure mostly increases temperature.

**C) Sublimation process**
When a substance sublimes from its liquid state to its gaseous state:

\[ \Delta V = V_g - V_s \approx V_g \]

\[ \Delta P = \frac{\Delta H_{\text{sub}}}{V_g} \frac{\Delta T}{T} \]
QUESTIONS AND PROBLEMS

1. Knowing that:

\[ A(g) \rightleftharpoons B(g) \]

\[ K_{p, 300 \text{ K}} = 0.1 \]

A) Calculate \( \Delta G^\circ \).
B) Calculate \( \Delta G \) when \( P_A = 20 \text{ atm} \) and \( P_B = 1 \text{ atm} \).
C) Calculate the value of \( P_B \) at which \( A \) can't change to \( B \).

2. If the constant pressure-molar heat capacity of liquid water is 75.4 J K\(^{-1}\) mol\(^{-1}\) and of gaseous water is 33.2 J K\(^{-1}\) mol\(^{-1}\), and the molar standard enthalpy of vaporization of water is 40.85 kJ mol\(^{-1}\), calculate \( \Delta H, \Delta S, \) and \( \Delta G \) of the following change:

\[ \text{H}_2\text{O}(L, 300 \text{ K}, 1.01 \times 10^5 \text{ Pa}) \rightarrow \text{H}_2\text{O}(g, 300 \text{ K}, 1.01 \times 10^4 \text{ Pa}) \]

3. Calculate \( \Delta G \) as a result of doubling the pressure of 4 mol of an ideal gas at 300 K.

4. Calculate \( q, w, \Delta U, \Delta S, \Delta A, \) and \( \Delta G \) as a result of changing the volume of 1 mol of an ideal gas to 10 times its original volume.

5. Knowing that at 100°C and 1 atm the molar volume of \( \text{H}_2\text{O}(L) \) is 0.019 dm\(^3\) mol\(^{-1}\), the molar volume of \( \text{H}_2\text{O}(g) \) is 30.199 dm\(^3\) mol\(^{-1}\), and the molar enthalpy of vaporization of water is 40.82 kJ mol\(^{-1}\), calculate the change in water boiling point accompanying the change in pressure by 1 mmHg.

6. Knowing for benzene (\( \text{C}_6\text{H}_6 \)) that its normal solidification (freezing) point is 5°C, molar volume when liquid is 87.282 cm\(^3\) mol\(^{-1}\), molar volume when solid is 82.68 cm\(^3\) mol\(^{-1}\), and standard molar enthalpy of solidification is 9,984 kJ mol\(^{-1}\), calculate the change in pressure needed to change its boiling point by 1°C.

7. Knowing for \( \text{H}_2\text{O} \) that its molar volume when liquid is 18.0036 cm\(^3\) mol\(^{-1}\), molar volume when solid is 19.6335 cm\(^3\) mol\(^{-1}\), and its standard molar enthalpy of solidification is 6.03 kJ mol\(^{-1}\), calculate the change in its solidification point accompanying the change in pressure by 1 atm.

8. Knowing for sulfur that its molar volume when it is in monoclinic solid form is more than when it is in rhombic solid form by 0.0126 cm\(^3\) g\(^{-1}\), transition point from monoclinic form to rhombic form at 1 atm is 95.5°C, and its standard molar enthalpy of transition from monoclinic form to rhombic form is 13.4 J g\(^{-1}\), calculate the change in its transition point accompanying the change in pressure by 1 atm.

9. From the following table:

<table>
<thead>
<tr>
<th>( P_{\text{vap}} ) / torr</th>
<th>10</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t ) / °C</td>
<td>55.7</td>
<td>150.6</td>
</tr>
</tbody>
</table>

calculate \( \Delta H_{\text{vap}} \) and \( \Delta S_{\text{vap}} \) of decane at 100°C and at its normal boiling point.

10. Knowing that \( \Delta H_{\text{vap, ethanol}} = 38.7 \text{ kJ mol}^{-1} \), and \( T_{\text{boiling, ethanol}} = 78.4 \degree \text{C} \), calculate the pressure at which ethanol boils at 25°C.

11. From the following information of an organic compound:

| \( t_{\text{solidification}} \) = 80 °C |
| \( P_{\text{liquid, vap, 85.8 \degree C}} \) = 10 mmHg |
| \( P_{\text{liquid, vap, 119.3 \degree C}} \) = 40 mmHg |
| \( P_{\text{solid, vap, 52.6 \degree C}} \) = 1 mmHg |
| triple point = 80 °C and 1 atm |

Calculate:

A) \( \Delta H_{\text{vap}} \)
B) \( T_{\text{boiling}} \)
C) \( \Delta S_{\text{vap}} \) at \( T_{\text{boiling}} \)
D) \( P_{\text{vap}} \) at \( T_{\text{solidification}} \)
E) $\Delta H_{\text{sublimation}}$
F) $\Delta H_{\text{solidification}}$
G) temperature at which $P_{\text{vap}}$ of the solid compound is $1 \times 10^{-5}$ mmHg.

12. Knowing that $\Delta H_{\text{vap,water}} = 42.3$ kJ mol$^{-1}$, calculate the pressure at which water boils at 25 ºC.