



**COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT
DR. AHMAD AL-OWAIS**

**CHEM 232 AND CHEM 233
LECTURES IN
CHEMICAL THERMODYNAMICS**

**462
ACADEMIC YEAR 1446 (2024/2025)**

PERSONAL INFORMATION

اسم الطالب باللغة العربية →→	
STUDENT UNIVERCIY NUMBER →→→→→	
MOBILE NUMBER →	
FIRST MIDTERM EXAM →→→→→→→→→ (15 grades)	
SECONDMIDTERM EXAM →→→→→→→→→ (15 grades)	
FINAL EXAM →→→→→ (40 grades)	
LECTURER →→→→→	د. أحمد العويس CHEMISTRY DEPARTMENT OFFICE: 2A15 COLLEGE OF SCIENCES BUILDING: 5

- **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 in general**
- **Thermodynamics development came as 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**
- **During the years from 1854 to 1858 the word “*thermo-dynamic*” developed to be “*thermo-dynamics*” by the Scottish physicist William Thomson (Lord Kelvin) in his paper titled "An Account of Carnot's Theory of the Motive Power of Heat". Also, he put the first definition of thermodynamics: "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"**
- **Since then, “thermodynamics” has become an essential science in many fields, including physics, chemistry, engineering, and biology**

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1. DEFINITIONS AND BASIC CONCEPTS



1. DEFINITIONS AND BASIC CONCEPTS

1.1 Energy

- Traditionally, energy is defined as “the capacity to do work:
- Although the "calory", abbreviated "cal", is a very common energy unit, and probably is the most common unit we use in our daily, the SI unit of energy is the “kg m² s⁻²” which is named “Joule” and abbreviated “J”:

$$1 \text{ J} = 1 \text{ kg m}^2 \text{ s}^{-2} = = 4.184 \text{ J}$$

Example 1.1

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”
$$E_k = \frac{1}{2} m v^2$$
 - ✓ 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
- 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

1.2 Work

- When an object is moved through a distance “d” against an opposing force “F”, we say that work “w” is done:

$$w = F \times d$$

- The SI unit of work is the energy unit. Historically, energy is defined by work not the opposite
- To raise a body of mass 1.0 kg on the surface of the Earth through a vertical distance of 1.0 m requires us to do the following amount of work:

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

$$\text{Work} = (9.8 \text{ N}) \times (1.0 \text{ m}) = 9.8 \text{ N m} = 9.8 \text{ J}$$

- **Types of work**

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

- ✓ **Electric work, w_{electric} :**

It is calculated using the following equation:

$$w_{\text{electric}} = - n F E$$

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

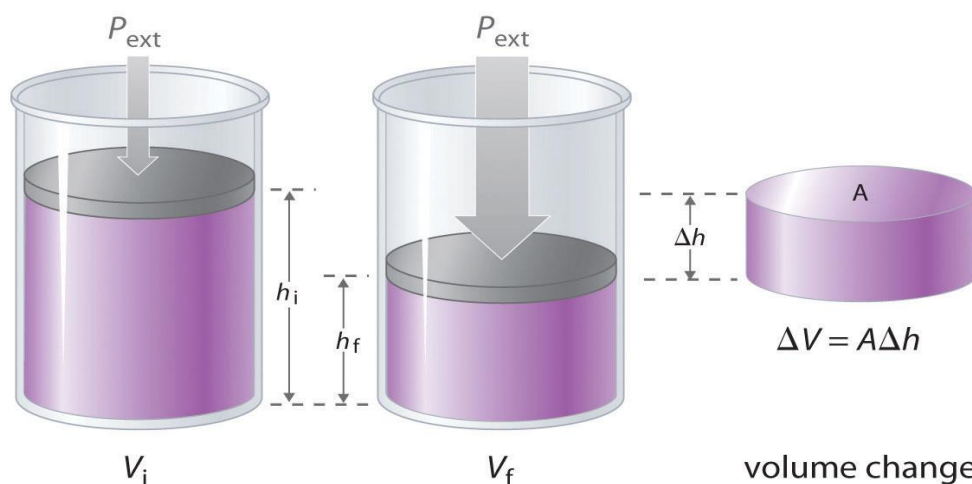
- ✓ **PV work, w_{pv} :**

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, 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 ΔV.



This compression is due to a work done on the system. This type of work is calculated by the following well-known equation:

$$\begin{aligned} \mathbf{P} &= \frac{\mathbf{F}}{\mathbf{A}} \\ \mathbf{F} &= \mathbf{P} \times \mathbf{A} \\ \mathbf{w}_{\text{PV}} &= \mathbf{F} \times \Delta \mathbf{h} \\ \mathbf{w}_{\text{PV}} &= \mathbf{P} \times \mathbf{A} \times \Delta \mathbf{h} \\ \mathbf{w}_{\text{PV}} &= \mathbf{P} \times \Delta \mathbf{V} \end{aligned}$$

Because the convention gives the work done **on** the system a **positive** sign and the work done **by** the system a **negative** sign, a negative sign, “-“, must be introduced to the previous equation:

$$\mathbf{w}_{\text{PV}} = - \mathbf{P}_{\text{ext}} \times \Delta \mathbf{V}$$

Using the **Pa** unit for **P** and **m³** unit for **V** produces work in **J** unit.

Example 1.2

The pressure above the piston of a cylinder 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 °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?

1.3 Heat

- ✓ Heat is not a property of the system

- ✓ Heat is not a type of energy that is contained or possessed by the system
- ✓ Yes, we usually say that the system absorbs or releases heat; and the degree of hotness (temperature) of the system increases or decrease, but, we never think or say that "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. When it comes to heat we find ourselves as lost in a desert
- ✓ About temperature. "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 to the other with the lower degree of hotness". **THIS FLOW OF ENERGY IS HEAT**

THE DEFINITION OF 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
- ✓ Heat is not a property of the system

1.4 Temperature

- *Temperature* is a measure of the degree of hotness or coldness of the body
- Although the unit for temperature that is used in all countries is either in degrees of Celsius unit "°C" or degrees of Fahrenheit unit "°F", the SI unit for temperature is Kelvin "K". (**we do not put the symbol of degree "°" when using Kelvin unit**)
- Temperature is mostly measured on either the Celsius scale or the Kelvin scale.
 - ✓ **On the Celsius scale**, the temperature is expressed in degrees Celsius "°C", its symbol is "t", the freezing point of water at 1 atm is 0°C and the boiling point of water at 1 atm is 100°C
 - ✓ **On the Kelvin scale**, the temperature is expressed in Kelvin "K", (note that the degree sign is not used for this unit), the freezing point of water at 1 atm is 273.15 K and the boiling point of water at 1 atm is 373.15 K
- **Temperature and kinetic energy**
 - ✓ Increase or decrease in the temperature of the system depends solely on the kinetic energy of the system's particles
 - ✓ 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 (temperatures) become in contact with each other, energy will flow as heat 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

1.5 The kinetic molecular model of gases

- The **kinetic model of gases** consists of the following five assumptions:
 - 1) A gas consists of particles 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 volume of the particles 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
- The molecules move with many different speeds and in random directions, both the speed and the direction change when they collide with each other or the the walls
 - The 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 assumption that the molecules do not interact unless they are in contact implies that the potential energy of the molecules 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 of all the molecules. This means that the faster the molecules travel the greater their kinetic energy and the greater the its total energy
 - The speeds of molecules are not the same at any certain instant, also the speed of any molecule is not constant but changes continuously. Therefore, the speed of any molecule is expressed as the square root of the mean value of the squares of the speeds of the molecules “c” which is called “**the root-mean-square speed**” and abbreviated as “**rms speed**” of the molecules. The rms speed is given by the following equation:

$$c = \sqrt{\frac{3RT}{M}}$$

Where M is the molar mass. The conclusions from this equation are:

- 1) rms speed “c” is proportional to \sqrt{T}
 - 2) rms speed “c” is proportional to $\sqrt{\frac{1}{M}}$
 - 3) rms speed “c” is the same for gases with M at the same T
- **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:

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

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

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

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

- ✓ Because $n = \frac{N}{N_A}$ where N is the number of molecules and N_A is Avogadro’s number, the equation:

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

k (sometimes k_B) is a constant called Boltzmann constant:

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

Therefore,

$$\text{Kinetic energy} = \frac{3}{2} \times k \times N \times T$$

$$\text{Kinetic energy} = \frac{3}{2} \times n \times R \times T = \frac{3}{2} \times k \times N \times T$$

✓ The conclusions 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
- 4) This simply means that kinetic energy does not depend on the type of the gas
- 5) The speed of the gaseous molecules does depend on the type of the gas
- 6) The kinetic energy of *n moles* of a gas, ke_n , is:

$$ke_n = \frac{3}{2} \times n \times R \times T$$

- 7) The kinetic energy of *only one moles* of a gas, $KE_{\text{one mole}}$, is given by the equation

$$KE_{\text{one mole}} = \frac{3}{2} \times R \times T$$

- 8) The kinetic energy of *N molecules* of a gas, ke_N , is given by the equation

$$ke_N = \frac{3}{2} \times N \times k \times T$$

- 9) The kinetic energy of *only one molecule* of a gas, $KE_{\text{one molecule}}$, is called the molecular kinetic energy and is given by the equation

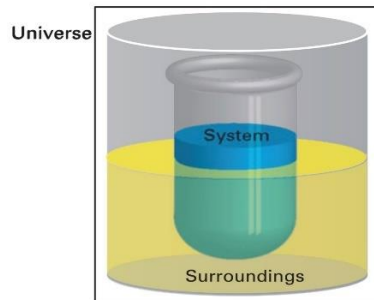
$$KE_{\text{one molecule}} = \frac{3}{2} \times k \times T$$

- 10) The values of ke_n and ke_N are equal:

$$\frac{3}{2} \times n \times R \times T = \frac{3}{2} \times N \times k \times T$$

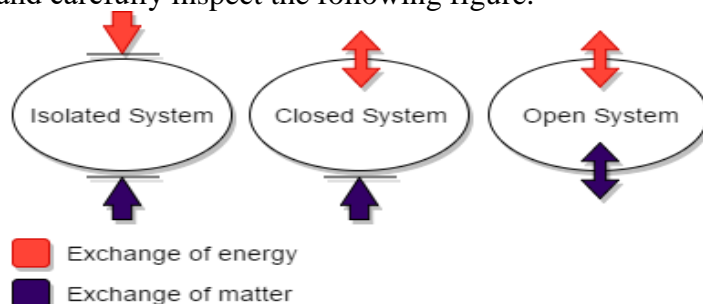
1.6 The system, the surroundings, the boundaries and the universe

✓ 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 (walls)** of the system act to separate the system from its surroundings
 - ✓ Boundaries may be notional or real
 - ✓ Boundaries delimit a finite volume
 - ✓ Boundaries may be made of wood, glass, steel, or any other material
 - ✓ Boundaries may and may not allow exchange of matter, energy or both with its surroundings

- ❖ **The diathermic boundaries or walls** allows heat to flow through and the process is called "*diathermic process*"
- ❖ **The adiabatic boundaries or walls** does not allow heat to flow through and the process is called "*adiabatic process*".
- **The universe:** In thermodynamics, the universe is the system, its surroundings and its boundaries. If the system is a 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.



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

2) The closed system

A closed system is a system in which matter cannot be transferred in or out of its boundaries

3) The isolated system

An isolated system is a system in which matter and energy remains constant within the system, and no energy or matter transfer takes place across the boundaries

1.7 Specific heat capacity, heat capacity and quantity of heat

• Specific heat capacity (C_s)

- ✓ Specific heat capacity (Specific heat), C_s , 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)
- ✓ $m = 1 \text{ g}$ and $\Delta T = 1 \text{ }^\circ\text{C}$

Values of specific heat capacity of some substances are:

Substance	$C_s / \text{J g}^{-1} \text{ }^\circ\text{C}^{-1}$
Au(s)	0.129
Cu(s)	0.385
Fe(s)	0.444
C(diamond)	0.502
C(graphite)	0.720
Al(s)	0.900
H ₂ O(L)	4.184

• 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 by only 1 °C (or 1 Kelvin)
- ✓ $m = \text{any mass other than } 1 \text{ g}$, $\Delta T = 1 \text{ }^\circ\text{C}$
 $C = m \times C_s$

• 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 by any number of Celsius degrees (or Kelvin)
- ✓ m = any mass other than 1 g, ΔT any value other than 1 °C.

$$q = C \times \Delta T = m \times C_s \times \Delta T$$

Example 1.3

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

$$q = m \times C_s \times (T_2 - T_1)$$

$$q = 250 \text{ g} \times 4.184 \frac{\text{J}}{\text{g} \text{ °C}} \times (56 - 20) \text{ °C} = 37656 \text{ J}$$

Practice exercise

If 1.5 kg of copper 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: 125 °C)

Example 1.4

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

$$q = m \times C_s \times (T_2 - T_1)$$

$$3257.4 \text{ J} = 150 \text{ g} \times 2.44 \frac{\text{J}}{\text{g} \text{ °C}} \times (T_2 - 22)$$

$$T_2 = 30.9 \text{ °C}$$

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) of this substance.

(Answer: $C_s = 4.17 \times 10^{-3} \text{ J g}^{-1} \text{ °C}^{-1}$)

1.8 Heat capacity of ideal gases at constant volume (C_v), and at constant pressure (C_p)

- The kinetic energy of the ideal gas depends on its amount and its temperature
- Kinetic energy of 1 mole of the ideal gas is the molar kinetic energy ($KE_{\text{one mole}}$):

$$KE_{\text{one mole}} = \frac{3}{2} \times R \times T = 12.471 \frac{\text{J}}{\text{mol K}} \times T$$

- If the initial temperature is T_i and the final temperature, T_f , is $T_i + 1$. Therefore,

$$KE_{\text{one mol,initial}} = 12.471 \frac{\text{J}}{\text{K}} \times T_i$$

$$KE_{\text{one mol,final}} = 12.471 \frac{\text{J}}{\text{K}} \times (T_i + 1 \text{ K})$$

$$KE_{\text{final}} = \left\{ 12.471 \frac{\text{J}}{\text{K}} \times T_i \right\} + 12.471 \text{ J}$$

$$KE_{\text{one mol,final}} = KE_{\text{one mol,initial}} + 12.471 \text{ J}$$

- 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
- "How can we increase the kinetic energy of one mole of an ideal gas by 12.471 J?"
"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)**

$$V_{\text{final}} = V_{\text{initial}}$$

$$\Delta V = V_{\text{final}} - V_{\text{initial}} = 0$$

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

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

Increasing the temperature of one mole of an ideal gas by only one degree Celsius can be achieved by increasing its kinetic energy by 12.471 J, which can be done by supplying it with 12.471 J of heat while keeping its volume unchanged.

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:

$$C_{v,m} = 1.5 \times R = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

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

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

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

✓ **Second: supplying heat at constant pressure (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 Celsius 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:

$$C_{p,m} = 1.5 \times R + w$$

$$w = n \times R \times \Delta T = 1 \text{ mol} \times R \times 1 \text{ K} = R$$

$$C_{p,m} = 1.5 \times R + R$$

$$C_{p,m} = 2.5 \times R = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$$

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

$$C_p = n \times C_{m,p}$$

$$C_p = n \times 2.5 \times R = n \times 20.785 \text{ J K}^{-1}$$

✓ **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:

$$C_p - C_v = (n \times C_{p,m}) - (n \times C_{v,m})$$

$$C_p - C_v = n (2.5 \times R - 1.5 \times R)$$

$$C_p - C_v = n \times R = n \times 8.314 \text{ J K}^{-1}$$

If the gas amount is one mole:

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

✓ **Fourth: The ratio of C_p to C_v**

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

$$\gamma = \frac{C_p}{C_v} = \frac{n \times C_{p,m}}{n \times C_{v,m}} = \frac{C_{p,m}}{C_{v,m}}$$

$$\gamma = \frac{20.785}{12.471}$$

$$\gamma = 1.67$$

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

$$q_v = C_{m,v} \times n \times (T_2 - T_1) = C_v \times (T_2 - T_1)$$

$$q_p = C_{m,p} \times n \times (T_2 - T_1) = C_p \times (T_2 - T_1)$$

Example 1.5
 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 281 K at constant pressure. ($C_{m,v} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$).

Solution
 $C_{p,m} = C_{v,m} + R$
 $C_{p,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$
 $n = \frac{m}{M} = \frac{56 \text{ g}}{32 \frac{\text{g}}{\text{mol}}} = 1.75 \text{ mol}$
 $C_p = n \times C_{p,m} = 1.75 \text{ mol} \times 20.785 \text{ J K}^{-1} \text{ mol}^{-1} = 36.37 \text{ J K}^{-1}$
 $q_p = C_p \times (T_2 - T_1) = 36.37 \text{ J K}^{-1} \times (281 - 298) \text{ K}$
 $q_p = -618 \text{ J} = -6.18 \times 10^{-1} \text{ kJ}$

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: $q_v = 436.485 \text{ J}$)

1.9 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, ke , 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.

Some extensive properties			Some intensive properties		
Name	Symbol	SI units	Name	Symbol	SI units
Volume	V	m ³	Specific volume	V _m	m ³
Mass	m	kg	Density	d	kg m ³
Internal energy	U	J	Specific internal energy	U _m	J
Entropy	S	J K ⁻¹	Entropy	S _m	J kg ⁻¹ K ⁻¹
Enthalpy	H	J	Specific enthalpy	H _m	J kg ⁻¹
Gibbs free energy	G	J	Specific Gibbs free energy	G _m	J kg ⁻¹
Heat capacity	C	J K ⁻¹	Specific heat capacity	C _s	J kg ⁻¹ K ⁻¹

1.10 The state of the system and the path of changing the its state

(THIS SUBJECT WILL BE DISCUSSED AGAIN ON PAGE 94)

- **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 changes any of its properties, then we confidently can 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 the control over the rest of the system properties in the sense that if any of them changes the rest of the properties follow it and also change. These properties are called the “predominating properties”
 - ✓ If we are able to specify the “predominating properties”, then we can be sure that we are able control the system
 - ✓ Scientific knowledge and experiences reveal that there are three properties have proving that 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
 - ✓ 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, 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 at a set of values of properties of the system that must be specified to reproduce the system
- **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 its initial state to its final 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

1.11 The state functions and the path functions

- To understand the precise meaning of the state functions and the path functions let us imagine the following case:
 - ✓ Both you and your friend 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 revealed that path X was tasteful because of its views was orchards and gardens and path Y 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 were 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

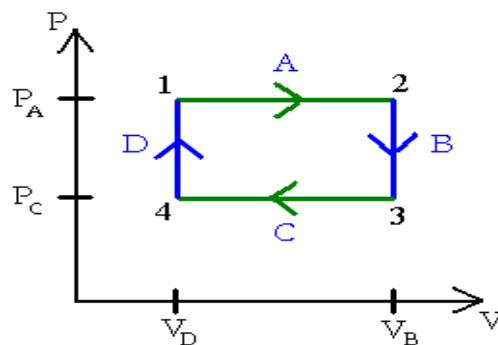
1.12 Processes and types of processes

- A process is the operation which changes the state of a system. The change in the state of a system means that a certain process had been carried out on it
- When a process is carried out on a system, we should know how it was done

- There are 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 initial temperatures. 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 temperatures 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 $\Delta V = 0$

1.13 Cyclic processes

- First, 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

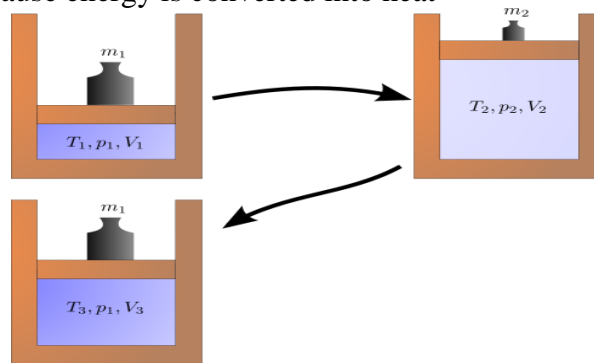


- ✓ At the beginning the gas was at state number 1. the gas pressure and volume were P_A and V_D
 - Step A changes the gas from state number 1 to state number 2
At the state 2, the gas pressure remained P_A but its volume changed to V_B .
 - Step B changes the gas from state number 2 to state number 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

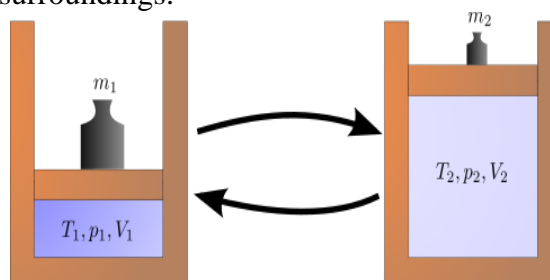
- At the end of the cyclic process all of the state functions of the system have the same values they had at the beginning of the cycle

1.14 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 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 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 below, 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 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

1.15 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

1.16 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

Element	Reference state
Arsenic	grey arsenic
Bromine	liquid
Carbon	graphite
Hydrogen	gas
Iodine	solid
Mercury	liquid
Nitrogen	gas
Oxygen	gas
Phosphorus	white phosphorus
Sulfur	rhombic sulfur
Tin	white tin, α -tin

- ✓ 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 state 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 ($25\text{ }^{\circ}\text{C} = 298.15\text{ K}$)
- ✓ 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 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 $25\text{ }^{\circ}\text{C}$ 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 $0\text{ }^{\circ}\text{C}$ (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

1.17 The internal energy

- The internal energy, denoted "U", 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.

- It has two major components, the internal kinetic energy " U_{kin} " and the internal potential energy " U_{pot} ":

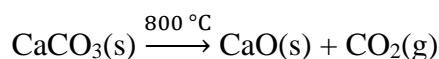
$$U = U_{\text{kin}} + U_{\text{pot}}$$

- ✓ The internal kinetic energy is due to all kind of motions of the system's particles. As a part of the internal energy of the system, it is the energy behind its temperature. This energy is often referred to as the **thermal energy** of a system, which makes it easy to relate to the human feelings of hotness and coldness
- ✓ The internal potential energy 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**
- Not knowing the value of internal energy is not an obstacle in thermodynamics, because its concern is not the absolute value of 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

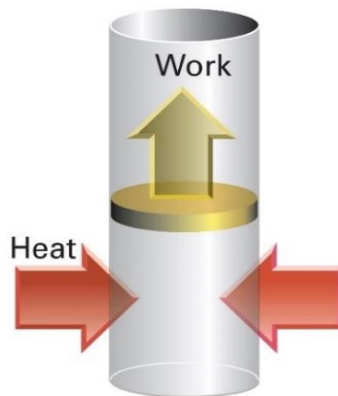
1.18 The enthalpy and the change in enthalpy

The word "enthalpy", is derived from the Greek origins. "en-" meaning "within" and "thalpein" meaning "to heat". Therefore, enthalpy means "heat inside", "or "heat content". The enthalpy of the system increases if it undergoes an endothermic process by absorbing energy as heat from the surroundings; while it decreases if it undergoes an exothermic process by releasing energy as heat to the surroundings.

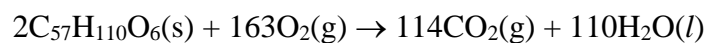
- Much of chemistry and biology, happen in vessels that are open to the atmosphere and subjected to constant pressure, not constrained to constant volume container
- When a change takes place in a system open to the atmosphere, the volume of the system changes. For example, the thermal decomposition of 1.0 mole $\text{CaCO}_3(\text{s})$ at 1 bar and $800\text{ }^\circ\text{C}$ increases the volume to nearly 90 dm^3 on account of the carbon dioxide gas produced:



- To create this large volume for the carbon dioxide, the surrounding atmosphere must be pushed back
- That is, the system must perform expansion work. The following 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 heat supplied 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 our bodies. The overall reaction is



- ✓ In this exothermic reaction there is a net *decrease* in volume equivalent to the elimination of 49 mole (163 mol – 114 mol = 49 mol) of gas molecules for every 2 moles of tristearin molecules that react.
- ✓ The decrease in volume at 25 °C is about 600 cm³ for the consumption of 1 g of fat
- ✓ Because the volume of the system decreases, the atmosphere does work **on** the system. This means that energy is transferred to the system
- ✓ Some of the energy of the surroundings 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 taking 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 is 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 expression “H = U + PV” applies to any system or individual substance: we should not be misled by the ‘PV’ term into thinking that this equation applies only to gases
- 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:

$$H_m = U_m + PV_m$$

- If the system is one mole of a perfect gas, we can write:

$$H_m = U_m + RT$$

- At 298.15 K, $R \times T = 2.5 \frac{\text{kJ}}{\text{mol}}$. Therefore, the molar enthalpy of a perfect gas, at 298.15 K, is greater than its molar internal energy by $2.5 \frac{\text{kJ}}{\text{mol}}$:

$$H_m = U_m + 2.5 \frac{\text{kJ}}{\text{mol}} \quad (\text{At } 298.15 \text{ K})$$

- 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 $2.5 \frac{\text{J}}{\text{mol}}$ more than its molar internal energy, so the numerical difference is negligible
- A change in enthalpy comes from a change in the internal energy and a change in the product of $P \times V$:

$$\Delta H = \Delta U + \Delta(PV)$$

Where $\Delta(PV) = P_{\text{final}} \times V_{\text{final}} - P_{\text{initial}} \times V_{\text{initial}}$

- If the change takes place at constant P, the second term on the right simplifies to:

$$\Delta(PV) = P V_{\text{final}} - P V_{\text{initial}} = P(V_{\text{final}} - V_{\text{initial}}) = P \Delta V$$

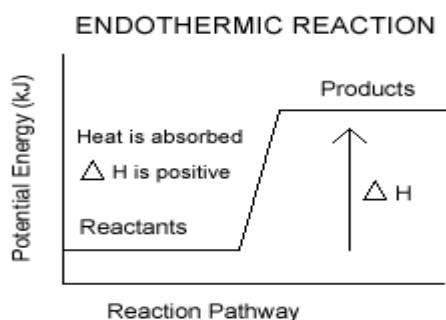
$$\Delta H = \Delta U + P\Delta V$$

- The change in enthalpy of a system is the heat it gains or loses if pressure is constant and no nonexpansion work is done:

$$\Delta H = q_p \quad (\text{constant pressure, no nonexpansion work})$$

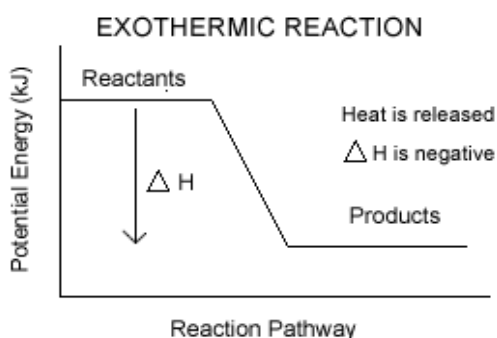
This equation allows us to identify the energy transferred as heat to the system or from it as the change in the enthalpy of the system

- **We should never forget that heat transferred to the system does not actually “exist” in the system: heat is a mean of transferring energy**
- If the change in the state of the system makes ΔH positive the change is described as an endothermic change, endothermic process or endothermic reaction
- If the change in the state of the system makes ΔH negative the change is described as an exothermic change, exothermic process or exothermic reaction



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


1.19 The four laws of thermodynamics

- The thermodynamics main and pronounced feature is its four laws. Namely,
 - 1) The zeroth law (born in 1939)
 - 2) The first law (born in 1850)
 - 3) The second law (born in 1857)
 - 4) The third law (born in 1912)


- 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 became too late for changing the numerical arrangement
 - ✓ The last-born law is named: "**THE ZEROTH LAW**"
 - ✓ The answer of the question: why this law is not named "**THE FOURTH LAW**" is because it is much more basic law than any of the other three laws 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:
$$\text{C}_2\text{H}_2(\text{g}) + 2.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g}) + 2\text{CO}_2(\text{g}) \quad \Delta H = -1255.5 \text{ kJ}$$
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 ($p=1.7 \text{ atm}$, $V=1.56 \text{ L}$) 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 25° to 60°. ($C_{s,\text{Cu}} = 0.39 \text{ J g}^{-1} \text{ K}$).
12. 216 J of energy is required to raise the temperature of aluminum from 15° to 35°C. Calculate the mass of aluminum. ($C_{s,\text{Al}} = 0.9 \text{ J g}^{-1} \text{ °C}^{-1}$).
13. A 1.0 kg sample of metal with a specific heat of 0.50 kJ/Kg °C is heated to 100.0C 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

- *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
- Although temperature and heat have a close relation, they are two different concepts. A lot of us confuse temperature with heat. Heat is a way of transferring energy; temperature is a property that determines the direction of heat flow
- The SI unit for temperature is Kelvin (K)

Example 2.1

A gas having a temperature of 21 °C, what is its temperature in K unit?

Solution

$$\text{Temperature in K} = (\text{Temperature in } ^\circ\text{C} + 273.15 \text{ } ^\circ\text{C}) \times \frac{1 \text{ K}}{1 \text{ } ^\circ\text{C}}$$

$$\text{Temperature in K} = (21 \text{ } ^\circ\text{C} + 273.15 \text{ } ^\circ\text{C}) \times \frac{1 \text{ K}}{1 \text{ } ^\circ\text{C}} = 294 \text{ K}$$

Practice exercise

A gas having a temperature of 315 K, what is its temperature in °C unit?

Example 2.2

Express the body temperature, 37°C, in kelvins.

Solution

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

$$T \text{ (in kelvin)} = 37 \text{ } ^\circ\text{C} + 273.15 = 310.15 \text{ K}$$

Practice exercise

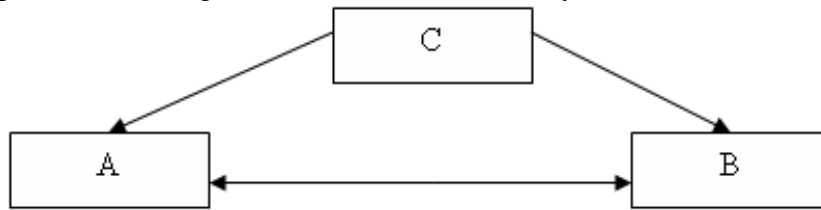
A gas having a temperature of 50 °C, what is its temperature in K unit?

- Temperature is the central property of any system
- 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
- 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.
- **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 property 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

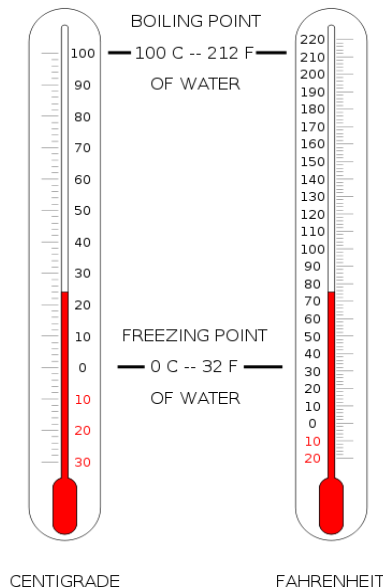
If the systems A and B are in a thermal equilibrium with the system C, then the system A is in thermal equilibrium with the system B.

- 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

- 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. Accordingly the freezing and the boiling temperatures of water are 32 °F and 212 °F respectively. This scale is obsolete except in a few countries
 - ✓ In 1742, the Swedish astronomer Andres Celsius invented his 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 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 $-273.15\text{ }^{\circ}\text{C}$. The idea of this scale was given 150 years before Kelvin was born. **Boyle** 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 equals to $-273.15\text{ }^{\circ}\text{C}$ 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
- The most common systems that satisfy this strict condition are:

- 1) The perfect (ideal) gas with its volume
 - 2) The mercury element with its volume
 - 3) The platinum element with its electric resistance
- The most common is the mercury thermometer:
 - ✓ 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 is put in contact with water that is in a state of freezing (the state of a dynamic equilibrium between the liquid and the solid states). The temperature of this system is the freezing and, at the same time, the melting temperatures 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 (the state of a dynamic equilibrium between the liquid and the gaseous states). The temperature of this system is the boiling and, at the same time, the condensation temperatures 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 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 2.3

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

$$\text{Temperature} = a + b \times \text{resistance in ohm}$$

If $a = -1303.6 \text{ } ^\circ\text{C}$ and $b = 70.43 \text{ } \Omega^{-1} \text{ } ^\circ\text{C}$, calculate the temperature at which its resistance equals $33.1 \text{ } \Omega$.

Solution

$$\text{Temperature} = a + b \times \text{resistance in ohm}$$

$$t = -1303.6 \text{ } ^\circ\text{C} + 70.43 \text{ } \Omega^{-1} \text{ } ^\circ\text{C} \times 33.1 \text{ } \Omega$$

$$t = 1027.6 \text{ } ^\circ\text{C}$$

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 $24.82 \text{ } \Omega$ at $444.6 \text{ } ^\circ\text{C}$ and $33.6 \text{ } \Omega$ at $1063.0 \text{ } ^\circ\text{C}$, Calculate the temperature at which its resistance equals $28.6 \text{ } \Omega$.

Example 2.4

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 2.5

Define the boiling point.

Solution

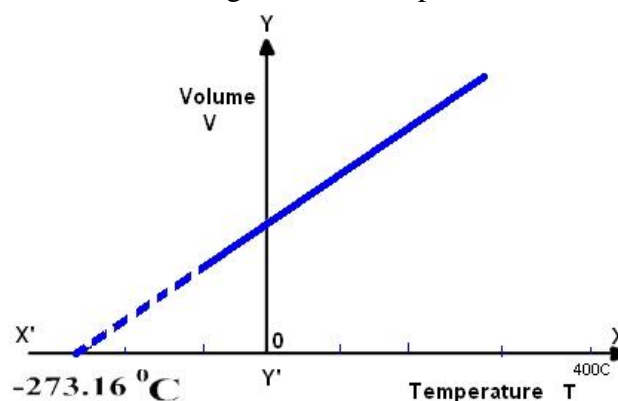
The boiling point is the temperature at which a substance exists in its liquid and gaseous states in thermodynamic equilibrium at a specified vapor pressure.

Practice exercise

Define the freezing point.

2.5 The thermodynamic temperature

- Thermodynamic temperature is the absolute measure of temperature
- 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 becomes zero. The temperature at this point in the Celsius scale is $-273.15\text{ }^{\circ}\text{C}$ 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 $-273.15\text{ }^{\circ}\text{C}$ since the triple point of water is at $0.01\text{ }^{\circ}\text{C}$ ($= 273.16\text{ K}$) and 4.5881 torr ($= 0.006037\text{ atm} = 0.6117\text{ kPa}$).
- 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 $24.82\ \Omega$ at $444.6\ ^\circ\text{C}$ and $33.6\ \Omega$ at $1063.0\ ^\circ\text{C}$. 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:
 - $-65.5\ ^\circ\text{C}$ to K
 - $65.5\ \text{K}$ to $^\circ\text{C}$
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

- People struggled for centuries to create energy from nothing, for they believed that if they could create energy, then they could produce work endlessly. Without exception, these efforts failed
- We now recognize that:

energy can be neither created nor destroyed but merely converted from one form into another or moved from a place to another place

This statement is “**the law of conservation of energy**”

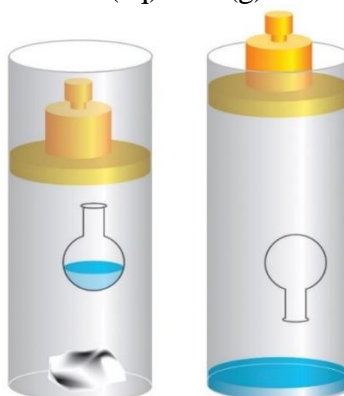
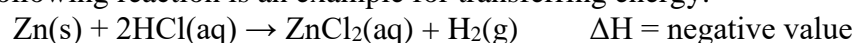
- **The first law of thermodynamics** is a manifestation of the law of conservation of energy. Its mathematical expression states that the change in the internal energy of a system (ΔU) equals the heat absorbed or released by the system (q) plus the work done on or by the system (w):

$$\Delta U = q + w$$

- Regarding heat (**q**):
 - ✓ If the system absorbs **q**: U increases and **q** is positive
 - ✓ If the system releases **q**, U decreases and **q** is negative
- Regarding work (**w**):
 - ✓ If the surroundings do work on the system: U increases and **w** is positive
 - ✓ If the system does work on surroundings: U decreases and **w** is negative.

$\Delta U = q + w$		
SIGN OF q	SIGN OF w	SIGN OF ΔU
+	+	+
+	-	either + or -
-	+	either + or -
-	-	-

- We learned from chapter 1 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 $w \neq 0$
- The following reaction is an example for transferring energy:



The above figure shows on the left a piece of Zn on the bottom of the cylinder and a flask containing a solution of HCl. It shows on the right the flask inverted and the reaction between Zn and HCl has produced H_2 which pushed the piston upward against the surroundings

- ✓ The system did work on the surroundings

- ✓ The system lost heat
- One very important type of work in chemistry is the work of expansion or of compression of gases, this is the work done when a system expands against an external pressure or compressed under the influence of the external pressure
- When a system expands through a volume ΔV against a constant external pressure P_{ex} the work done is given by the following equation:

$$w = - P_{\text{ex}} \Delta V$$
- According to $w = - P_{\text{ex}} \Delta V$, the *external* pressure determines how much work a system does when it expands through a given volume:
 - ✓ the greater P_{ex} , 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 $\text{CO}_2(\text{g})$ at 25°C and 100 kPa. *Hint.* The increase in volume will be 2.48 dm^3 .

Solution

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

$$\Delta V = V_{\text{CO}_2} = 2.48 \text{ dm}^3 \times \frac{1 \text{ m}^3}{1000 \text{ dm}^3} = 0.0248 \text{ m}^3$$

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

- The equation “ $w = - P_{\text{ex}} \Delta V$ ” shows us that to get the least expansion work from a system the external pressure should be minimized to zero; and to get the maximum work system the external pressure has to be at its maximum value
- 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***

The system that remains in mechanical equilibrium with its surroundings at all stages of the expansion does maximum expansion work

- If 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***
- We can summarize this discussion in one of the following choices:
 - ✓ A system does maximum expansion work when the external pressure is equal to that of the system at every stage of the expansion ($P_{\text{ex}} = P$)
 - ✓ 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 “ $w = - P_{\text{ex}} \Delta V$ ” by P_{gas} (the pressure of the gas in the cylinder) because, as the piston moves out, the pressure inside the system decreases

- To make sure the entire process occurs reversibly, we have to adjust the external pressure to match the changing internal pressure
- Suppose that the expansion is isothermal, from the equation “ $w = - P_{\text{ex}} \Delta V$ ”, the work of isothermal reversible expansion of a perfect gas from an initial volume V_{initial} to a final volume V_{final} at a constant temperature T is:

$$w = - nRT \ln \frac{V_{\text{final}}}{V_{\text{initial}}} = nRT \ln \frac{V_{\text{initial}}}{V_{\text{final}}}$$

n is the amount (number of moles) of the gas molecules in the system

- This equation means:
 - (1) **In an expansion ($V_2 > V_1$):** $\frac{V_2}{V_1} > 1$ and $\ln \frac{V_2}{V_1} > 1$. Therefore, w is negative. That is what we should expect: energy *leaves* the system as it does expansion work
 - (2) **For a given change in volume, we get more work the higher the temperature of the confined gas:** At high temperatures, the pressure of the gas is high, so we have to use a high external pressure to match the internal pressure at each stage

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

$$w = - nRT \ln \frac{V_2}{V_1}$$

$$w = - 1 \text{ mol} \times 8.314 \frac{\text{J}}{\text{K mol}} \times 298 \text{ K} \ln \frac{2 \text{ dm}^3}{1 \text{ dm}^3}$$

$$w = 1717 \text{ J} = 1.72 \text{ kJ}$$

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

- Internal energy is a state function and is independent of the path by which that state was reached
- 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, and if we change the temperature and then the pressure, but ensure that the two final values are the same as in the beginning, then the internal energy becomes exactly the same as before
- 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 outside. Therefore, the internal energy of an isolated system cannot change. That is,

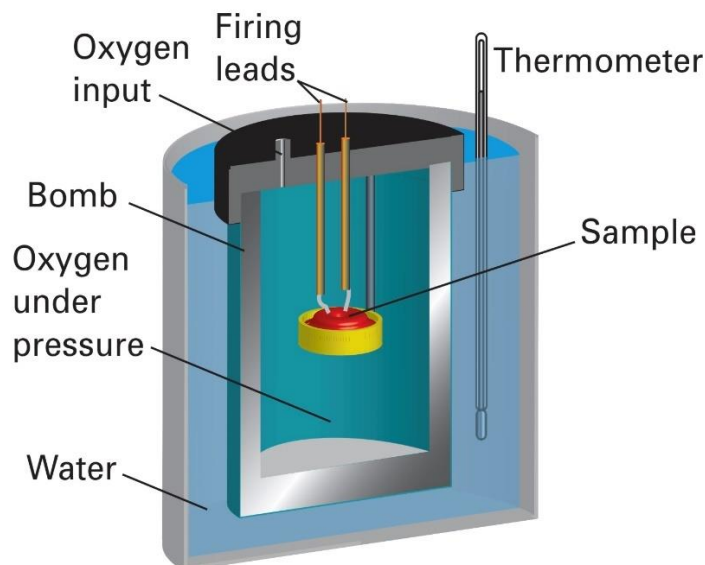
The internal energy of an isolated system is constant

- ✓ This statement is another statement for the first law of thermodynamics. It is closely related to the statement law of the law of conservation of energy but it allows for transfers of energy as heat as well as by doing work
- ✓ The definition of ΔU 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
- ✓ If we carry out a reaction in a container of constant volume, the system can do no expansion work and if no other kind of work (such as electrical work) is done, $w = 0$ and ΔU will be equal to the heat absorbed or released

$$\Delta U = q_v$$

- ✓ 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 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



- ✓ 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 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:

$$w = -P \times \Delta V = -R \times T \times \Delta n_g$$

- ✓ If the change is in the value of T , then:

$$w = -P \times \Delta V = -n \times R \times \Delta T$$

- We already know 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 $w \neq 0$

✓ ΔU at constant volume

$$\Delta U = q + w$$

$$\Delta U = q_v + 0$$

$$\Delta U = q_v$$

✓ ΔU at constant pressure

$$\Delta U = q + w$$

$$\Delta U = q_p + w$$

$$\Delta U = q_p + (-P \times \Delta V) = q_p + (-R \times T \times \Delta n_g) = q_p + (-n \times R \times \Delta T)$$

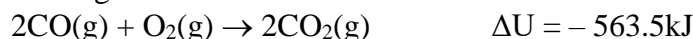
This means that the heat exchanged at constant temperature and pressure is q_p

✓ It is mentioned in chapter 1 that the heat absorbed or released at constant temperature and pressure (q_p) equals the change in the enthalpy of the system (ΔH). 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 ΔH for the following reaction at 1 atm and 25°C:



Solution

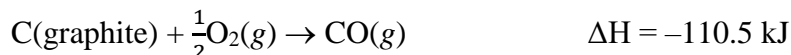
$$\Delta H = \Delta U + R \times T \times \Delta n_g$$

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

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

Practice Exercise

What is ΔU for the formation of 1 mole of CO at 1 atm and 258C?



3.3 Applications of the first law

(RECOGNIZE THE SYMBOLS

BELOW)

Number of moles = n

External pressure = P_{ext}

Initial pressure = P_{initial}

Final pressure = P_{final}

Initial volume = V_{initial}

Final volume = V_{final}

Initial molarity = M_{initial}

Final molarity = M_{final}

Initial temperature = T_{initial}

Final temperature = T_{final}

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

$$\begin{aligned} \text{Heat transferred at constant pressure} &= q_p \\ \text{Change in internal energy} &= \Delta U \\ \text{Change in enthalpy} &= \Delta H \end{aligned}$$

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

$$\Delta T = T_{\text{final}} - T_{\text{initial}} = 0$$

The values of ΔU , ΔH , w , and q , are as follows:

1) ΔU

The internal energy of the perfect gas exclusively depends on its kinetic energy, and 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) ΔH

We knew from chapter 1 that:

$$q_p = C_p \times (T_{\text{final}} - T_{\text{initial}})$$

Therefore, at constant temperature:

$$\Delta H = 0$$

3) q and w

" $\Delta U = q + w$ " and because at constant " $\Delta U = 0$ ", so 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 " $P_{\text{initial}} V_{\text{initial}} = P_{\text{final}} V_{\text{final}}$ " applies and work can be calculated using the following equation:

$$w = nRT \ln \frac{V_{\text{initial}}}{V_{\text{final}}} = nRT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

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

$$\begin{aligned} w &= -P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}}) \\ w &= P_{\text{ext}} (V_{\text{initial}} - V_{\text{final}}) = P_{\text{ext}} \left(\frac{nRT}{P_{\text{initial}}} - \frac{nRT}{P_{\text{final}}} \right) \\ w &= nRT \left(\frac{P_{\text{ext}}}{P_{\text{initial}}} - \frac{P_{\text{ext}}}{P_{\text{final}}} \right) \end{aligned}$$

But if:

$$\begin{aligned} P_{\text{ext}} &= P_{\text{final}} \\ w &= nRT \left(\frac{P_{\text{final}}}{P_{\text{initial}}} - 1 \right) \end{aligned}$$

C) The difference between reversible and irreversible isothermal works:

$$w_{\text{rev}} - w_{\text{irrev}} = - \frac{nRT}{P_{\text{initial}} \times P_{\text{final}}} (P_{\text{initial}} - P_{\text{final}})^2$$

✓ $(P_{\text{initial}} - P_{\text{final}})^2$ is always positive regardless which is higher P_{final} or P_{initial} .

✓ " $\frac{n \times R \times T}{P_{\text{initial}} \times P_{\text{final}}} (P_{\text{initial}} - P_{\text{final}})^2$ " 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_{rev} and w_{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_{rev} and w_{irrev} are positive

This means that the compression work is higher when it is irreversible

Example 3.4

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

Solution

$$\Delta U = \Delta H = 0 \quad \text{AND} \quad w = -q = nRT \ln \frac{V_{\text{initial}}}{V_{\text{final}}}$$

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

$$q = -w = +1729 \text{ J}$$

Practice exercise

Calculate w , q , ΔU and ΔH as a result of the reversible compression of 40 g of O₂(g) at 21 °C from 0.5 atm to 3.5 atm.

Example 3.5

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 °C to a pressure equals external pressure (0.4 atm).

Solution

$$\Delta U = \Delta H = 0$$

$$w = nRT \left(\frac{P_{\text{final}}}{P_{\text{initial}}} - 1 \right)$$

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

$$q = -w = +4357.9 \text{ J}$$

Practice exercise

Calculate w , q , ΔU and ΔH as a result of an isothermal sudden expansion of 2 mol of an ideal gas from 10 atm and 0 °C to 4 atm 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:

$$q = 0$$

$$T_{\text{initial}} \neq T_{\text{final}}$$

$$P_{\text{initial}} \times V_{\text{initial}}^{\gamma} = P_{\text{final}} \times V_{\text{final}}^{\gamma}$$

$$P_{\text{initial}} \times V_{\text{initial}}^{1.67} = P_{\text{final}} \times V_{\text{final}}^{1.67}$$

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 and 4.5 dm³ if its final volume 3.5 dm³.

Solution

$$P_{\text{initial}} V_{\text{initial}}^{1.67} = P_{\text{final}} V_{\text{final}}^{1.67}$$

$$9.5 \text{ atm} \times 4.5^{1.67} \text{ dm}^3 = P_{\text{final}} \times 3.5^{1.67} \text{ dm}^3$$

$$P_{\text{final}} = 14.45 \text{ atm}$$

Practice exercise

Calculate the final pressure as a result of an adiabatic reversible expansion of a fixed quantity of an ideal gas at 9.5 atm and 3.5 dm³ if its final volume became 4.5 dm³.

The value of “ w , ΔH and ΔU ” if the adiabatic processes is reversible:

$$\Delta U = w = C_v \times \Delta T$$

$$\Delta H = C_p \times \Delta T$$

It is clear that the main task in adiabatic processes is knowing the temperature after the change is accomplished (T_{final}). This depends on whether the adiabatic process is reversible or irreversible

FIRST: The value of T_{final} in the adiabatic reversible processes

$$T_{\text{initial}} \times V_{\text{initial}}^{\frac{R}{C_{m,v}}} = T_{\text{final}} \times V_{\text{final}}^{\frac{R}{C_{m,v}}}$$

$$T_{\text{initial}} \times V_{\text{initial}}^{0.67} = T_{\text{final}} \times V_{\text{final}}^{0.67}$$

$$\frac{T_{\text{initial}}}{P_{\text{initial}}^{\frac{R}{C_p}}} = \frac{T_{\text{final}}}{P_{\text{final}}^{\frac{R}{C_p}}}$$

$$\frac{T_{\text{initial}}}{P_{\text{initial}}^{0.4}} = \frac{T_{\text{final}}}{P_{\text{final}}^{0.4}}$$

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right)^{0.67} = T_{\text{initial}} \times \left(\frac{P_{\text{final}}}{P_{\text{initial}}}\right)^{0.4}$$

Example 3.7

Calculate the final temperature of 2.5 mole of an ideal gas after an adiabatic reversible compression from 4.5 dm³ at 298 K to 3.5 dm³. Calculate also q, ΔU, w, and ΔH.

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

Solution

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right)^{0.67}$$

$$T_{\text{final}} = 298 \text{ K} \times \left(\frac{4.5 \text{ dm}^3}{3.5 \text{ dm}^3}\right)^{0.67}$$

$$T_{\text{final}} = 352.65 \text{ K}$$

$$q = 0$$

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

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

$$\Delta U = 1703.85 \text{ J}$$

$$w = \Delta U = 1703.85 \text{ J}$$

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

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

$$\Delta H = 2839.75 \text{ J}$$

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.

SECOND: The value of T_2 in the adiabatic irreversible processes

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{C_{m,v} + R \frac{P_{\text{ext}}}{P_{\text{initial}}}}{C_{m,v} + R \frac{P_{\text{ext}}}{P_{\text{final}}}}\right) = T_{\text{initial}} \times \left(\frac{1.5R + R \frac{P_{\text{ext}}}{P_{\text{initial}}}}{1.5R + R \frac{P_{\text{ext}}}{P_{\text{final}}}}\right)$$

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \frac{P_{\text{ext}}}{P_{\text{initial}}}}{1.5 + \frac{P_{\text{ext}}}{P_{\text{final}}}}\right)$$

But if $P_{\text{ext}} = P_{\text{final}}$:

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \frac{P_{\text{final}}}{P_{\text{initial}}}}{2.5}\right)$$

$$\frac{P_{\text{final}}}{P_{\text{initial}}} = \left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right)^{1.67}$$

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \left(\frac{V_{\text{initial}}}{V_{\text{final}}} \right)^{1.67}}{2.5} \right)$$

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 dm³ at 298 K to 3.5 dm³. Calculate also q, ΔU, w, and ΔH.

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

Solution

$$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \left(\frac{V_{\text{initial}}}{V_{\text{final}}} \right)^{1.67}}{2.5} \right) = 298 \text{ K} \times \left(\frac{1.5 + \left(\frac{4.5 \text{ dm}^3}{3.5 \text{ dm}^3} \right)^{1.67}}{2.5} \right)$$

$$T_{\text{final}} = 404.52 \text{ K}$$

$$q = 0$$

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

$$\Delta U = 12.471 \frac{\text{J}}{\text{mol K}} \times 2.5 \text{ mol} \times (404.52 - 298) \text{ K}$$

$$\Delta U = 3321.03 \text{ J}$$

$$w = \Delta U = 3321.03 \text{ J}$$

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

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

$$\Delta H = 5535.05 \text{ J}$$

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, ΔU, w, and ΔH.

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

TABLE OF SUMMARIZATION

	Isothermal process		Adiabatic process	
	Reversible	Irreversible	Reversible	Irreversible
T_{final}	$T_{\text{final}} = T_{\text{initial}}$		$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right)^{0.67}$ $T_{\text{final}} = T_{\text{initial}} \times \left(\frac{P_{\text{final}}}{P_{\text{initial}}}\right)^{0.4}$	$T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \frac{P_{\text{ext}}}{P_{\text{initial}}}}{1.5 + \frac{P_{\text{ext}}}{P_{\text{final}}}}\right)$ if $P_{\text{ext}} = P_{\text{final}}$ $T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \frac{P_{\text{final}}}{P_{\text{initial}}}}{2.5}\right)$ $T_{\text{final}} = T_{\text{initial}} \times \left(\frac{1.5 + \left(\frac{V_{\text{initial}}}{V_{\text{final}}}\right)^{1.67}}{2.5}\right)$
w	$w = nRT \ln \frac{V_{\text{initial}}}{V_{\text{final}}}$ $w = nRT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$	$w = -P_{\text{ext}} (V_{\text{final}} - V_{\text{initial}})$ $w = nRT \left(\frac{P_{\text{ext}}}{P_{\text{initial}}} - \frac{P_{\text{ext}}}{P_{\text{final}}}\right)$ if $P_{\text{ext}} = P_{\text{final}}$ $w = nRT \left(\frac{P_{\text{final}}}{P_{\text{initial}}} - 1\right)$	$w = C_v \Delta T$	
q	$q = -w$		$q = 0$	
ΔU	zero		$\Delta U = C_v \Delta T$	
ΔH	zero		$\Delta H = C_p \Delta T$	

**TABLE OF COMPARISON BETWEEN VARIABLES IN
EXPANSION AND IN COMPRESSION**

EXPANSION	COMPRESSION
Work done by the system is more when the process is <u>reversible</u> regardless whether it is isothermal or adiabatic	Work done on the system is more when the process is <u>irreversible</u> regardless whether it is isothermal or adiabatic
Work done is more when the process is <u>isothermal</u> regardless whether it is reversible or irreversible	
Increase in volume in an <u>isothermal</u> process is the same for reversible and irreversible processes	Decrease in volume in an <u>isothermal</u> process is the same for reversible and irreversible processes
Change in volume in an <u>isothermal</u> process is <u>more</u> than in an adiabatic process regardless whether it is reversible or irreversible.	
Increase in volume in an adiabatic process is <u>more</u> when the process is <u>irreversible</u> than when is reversible	Decrease in volume in an adiabatic process is <u>more</u> when the process is <u>reversible</u> than when is irreversible
Final volume in an <u>isothermal</u> process is <u>the same</u> in reversible and irreversible processes, and this makes ΔU and ΔH the same too	
Final volume and temperature in an <u>adiabatic</u> process <u>are not the same</u> in reversible and irreversible processes, and this what makes ΔU and ΔH different	
In an adiabatic, decrease in U, which equals the work done, decreases T in <u>reversible</u> process more than in irreversible process	In an adiabatic, increase in U, which equals the work done, increases T in <u>irreversible</u> process more than in reversible process

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°C from 2.28 m^3 to 4.56 m^3 .
2. Calculate the minimum work needed to compress 16 g of $\text{O}_2(\text{g})$ from $1.01325 \times 10^3\text{ Pa}$ to $1.01325 \times 10^5\text{ Pa}$ 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°C) 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°C to 0.4 atm .
5. Calculate q , w , P_2 , 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 , P_2 , 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 dm^3 at 303975 Pa and 298 K , if its final volume becomes 2.86 dm^3 .
7. Calculate q , w , ΔU and ΔH as a result of the sudden expansion of 0.1 kg of $\text{N}_2(\text{g})$ to $1 \times 10^4\text{ Pa}$ without exchanging heat with surroundings, knowing that its initial temperature and pressure were 298 K and $3 \times 10^4\text{ Pa}$, and $C_{v,m} = 12.471\text{ J K}^{-1}\text{ mol}^{-1}$.
8. Calculate q , w , ΔU and ΔH as a result of expansion of 1 mole of an ideal gas at 300 K from $1 \times 10^6\text{ Pa}$ to $1 \times 10^5\text{ Pa}$, knowing that $C_{v,m} = 12.471\text{ J K}^{-1}\text{ mol}^{-1}$, 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 at constant volume or pressure as a result of any change is called "**heat or enthalpy of change**" or "**heat or enthalpy of reaction**"

- At constant temperature and volume, the heat absorbed or released equals the increase or decrease in the internal energy:

$$q_v = \Delta U$$

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

$$q_p = \Delta H$$

- Because most processes are carried out at constant temperature and pressure, changes in enthalpy, ΔH , is more important than changes in internal energy, ΔU .
- The change in the enthalpy is denoted ΔH_{rxn}

4.2 Enthalpy of reaction (ΔH_{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 or the enthalpy of the system denoted by H
- Let the system be (A), changing this system from its initial state, A_{initial} , to its final state, A_{final} , at constant temperature and pressure, will change its enthalpy from H_{initial} to H_{final} . This means that a change in enthalpy by " ΔH_{rxn} " has occurred and:

$$\Delta H_{\text{rxn}} = H_{\text{final}} - H_{\text{initial}}$$

- If the change occurs at 25 °C (298 K) and at the standard pressure, 1 atm (101325 Pa), the change in enthalpy is called **the change in the standard enthalpy** ($\Delta H_{\text{rxn}}^\circ$):

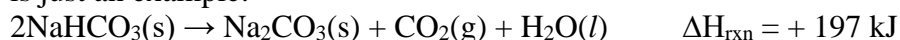
$$\Delta H_{\text{rxn}}^\circ = H_{\text{final}}^\circ - H_{\text{initial}}^\circ$$

- If ΔH_{rxn} is positive, the change or the reaction is described as **endothermic**
- If ΔH_{rxn} is negative, the change or the reaction is described as **exothermic**

4.3 Thermochemical equation and the units of ΔH_{rxn}

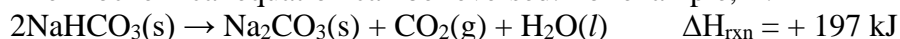
- **First: Thermochemical equation**

- ✓ Thermochemical equation is an equation which shows a balanced chemical equation and the physical state of each substance written as (s), (l), (g), (aq); and the enthalpy of reaction, (ΔH_{rxn}), shown after the equation. The following is just an example:

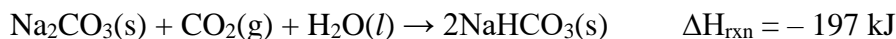


So, any thermochemical equation has the following **musts**:

- a) It **must** be balanced
 - b) State of each substance **must** be specified
 - c) The enthalpy of reaction, (ΔH_{rxn}), **must** be written
- ✓ The unit of ΔH_{rxn} is the unit of energy (usually kJ)
 - ✓ If the reaction is the standard condition, $\Delta H_{\text{rxn}}^\circ$ is the symbol of its enthalpy and is called the standard enthalpy of the reaction
 - ✓ If the reaction isn't at the standard condition, ΔH_{rxn} is the symbol of its enthalpy and is called the enthalpy of the reaction and conditions must be specified
 - ✓ Thermochemical equation can be reversed. For example, if:

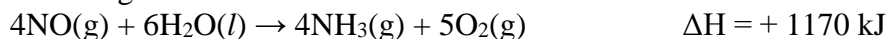


its correct reverse is:

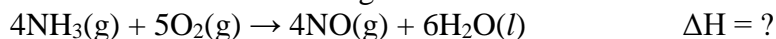


Example 4.1

Knowing that:

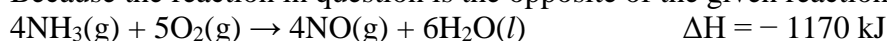


What is ΔH of the following reaction:



Solution

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

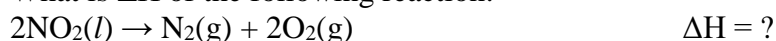


Practice exercise

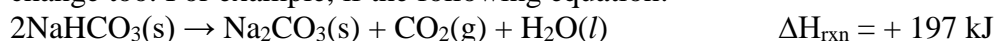
Knowing that:



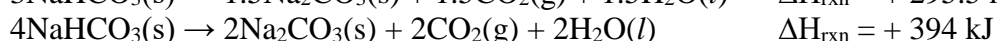
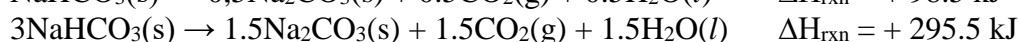
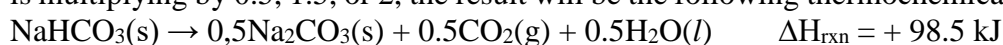
What is ΔH of the following reaction:



- ✓ 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 ΔH will change too. For example, if the following equation:



is multiplying by 0.5, 1.5, or 2, the result will be the following thermochemical:

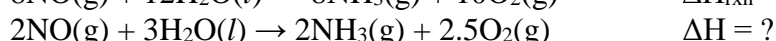
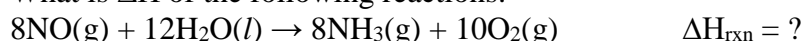


Example 4.2

Knowing that:

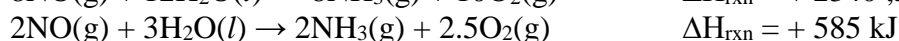
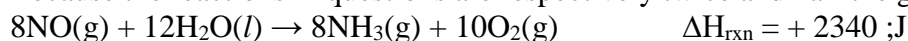


What is ΔH of the following reactions:



Solution

Because the reactions in questions are respectively twice and half the given reaction:

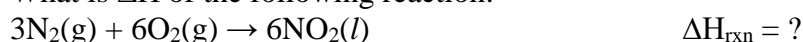


Practice exercise

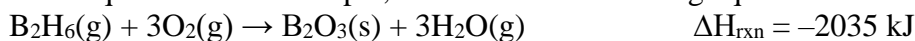
Knowing that:



What is ΔH of the following reaction:



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



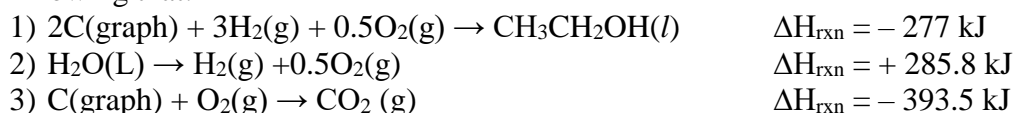
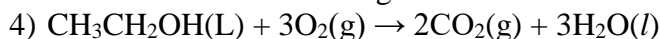
the result is following equation:



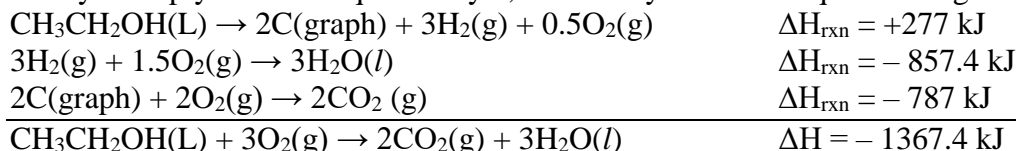
- ✓ This fact is known as "**Hess's Law**" or "**Hess's Law of Heat Summation**". Hess's law is stated in many different ways such as:
- "Enthalpy of a reaction is the same regardless of the way it is carried out"
 - "If a reaction takes place in several steps then its enthalpy is the sum of the enthalpies 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

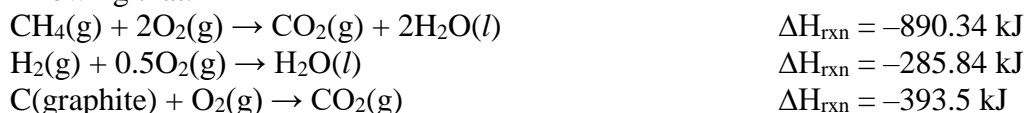
Knowing that:

Calculate ΔH of the following reaction:**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:

**Practice exercise**

Knowing that:

calculate ΔH and ΔU of the following reaction:

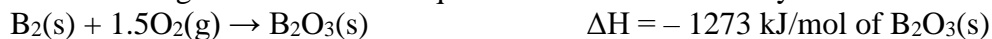
- **Second: The units of ΔH**

- ✓ Let us look to the following thermochemical equation:

What does **-1273 kJ** mean?It means that in this reaction, **1273 kJ** is released:per 2 moles of $\text{B}_2(\text{s})$ or per 1.5 mole of $\text{O}_2(\text{g})$ or per 1 mole of $\text{B}_2\text{O}_3(\text{s})$

- ✓ In thermochemical equations the unit of ΔH is **kJ** not **kJ/mol**

- ✓ The following thermochemical equation is written accurately:



- ✓ The following thermochemical equation is written accurately:



- ✓ The following thermochemical equation is written accurately:



- ✓ The following thermochemical equation is not written accurately:

**4.4 Factors affecting the enthalpy of reaction****1) Chemical nature of substances**

The enthalpy of a substance differs from that of any other substance. This means that heat absorbed (or released) of their reactions differ, for example:

**2) Physical nature of substances**

The enthalpy of a substance in its solid state is lower than in its liquid state and much lower than in its gaseous state. For example:

**3) Amount of substances**

The enthalpy of reaction depends on the amount of the substance. For example:



4) Temperature

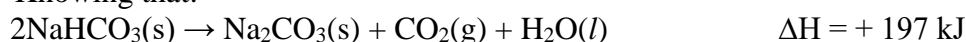
The enthalpy of a substance at a certain temperature differs from that at any other temperature. Therefore, the enthalpy of any reaction differs at different temperature. This effect of temperature will be discussed in more details later

5) Pressure

The enthalpy of a substance at a certain pressure differs from that at any other pressure. Therefore, the enthalpy of a certain reaction differs if it is done at different pressure. This effect of pressure will be discussed in more details later.

Example 4.5

Knowing that:

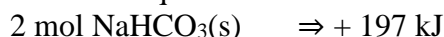


Calculate the

- The heat absorbed, q , as a result of dissociating 0.4 mole of $\text{NaHCO}_3(\text{g})$.
- The heat produced, q , as a result of producing 54 g of $\text{H}_2\text{O}(\text{g})$.

Solution

- From the equation:



$$q = 0.4 \text{ mol} \frac{197 \text{ kJ}}{2 \text{ mol}} = 39.4 \text{ kJ}$$

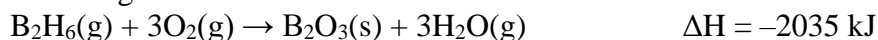
- From the equation:



$$q = 3 \text{ mol} \frac{197 \text{ kJ}}{1 \text{ mol}} = 591 \text{ kJ}$$

Practice exercise

Knowing that:



Calculate the

- The heat released, q , as a result of oxidation of 0.4 mol of $\text{B}_2\text{H}_6(\text{g})$.
- The heat produced, q , as a result of producing 108 g of $\text{H}_2\text{O}(\text{g})$.

4.5 Enthalpies of physical changes and chemical changes

- Physical changes are called **transitions** while chemical changes are called **reactions**. However, both are often called "**reactions**"
- Enthalpies of physical transitions and chemical reactions carry the same names of the physical transitions and of the chemical reactions, for example:
 - ✓ For vaporization, the enthalpy is the enthalpy of vaporization, " $\Delta\text{H}_{\text{vap}}$ "
 - ✓ For sublimation, the enthalpy is the enthalpy of sublimation " $\Delta\text{H}_{\text{subl}}$ "
 - ✓ For combustion, the enthalpy is the enthalpy of combustion " $\Delta\text{H}_{\text{comb}}$ "
 - ✓ For hydrogenation, the enthalpy is the enthalpy of hydrogenation " $\Delta\text{H}_{\text{hydrog}}$ "
- If the change is at the standard conditions (1 atm, and 298 K) its enthalpy is called "standard enthalpy of the change" and denoted " $\Delta\text{H}_{\text{rxn}}^\circ$ ", the "dot" superscript " $^\circ$ " means that the change is at standard conditions

4.5.1 Enthalpies of physical changes

- In any physical change, the substances before and after are the same but their states are different
- The physical changes that will be discussed are:
 - Crystal transition

- 2) Fusion of a solids
 - 3) Vaporization of liquids
 - 4) Sublimation of a solids
 - 5) Electron loss from elements (usually called ionization)
 - 6) Electron gain by elements
 - 7) Dissolving a solute in a solvent
- A **phase** is a specific state of matter that is uniform throughout in composition and state
 - The liquid and vapor states of water are two phases. The term “phase” is more specific than “state” because a substance may exist in more than one solid form, each form is a solid phase. Thus, when the element sulfur is in its solid state it may be found as rhombic sulfur phase or as monoclinic sulfur phase; these two forms are in the solid state but they differ in the manner in which the S₈ molecules stack together
 - Many substances exist in a variety of solid phases; examples are:
 - ✓ Carbon, for instance, exists as graphite, diamond
 - ✓ Calcium carbonate exists as calcite and aragonite
 - ✓ There are at least twelve phases of ice
 - No substance has more than one gaseous phase
 - 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
 - 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** denoted as ΔH_{rxn}
 - If the physical change is at the standard pressure, it is called the **standard enthalpy of transition**, $\Delta H_{\text{trans}}^{\circ}$
 - The following is 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**. The following is an example:



2) Enthalpy of fusion and standard enthalpy of fusion

Fusion, or melting, is the transition of a substance from its solid state to its liquid state. It requires absorption of a certain amount of heat called enthalpy of fusion which 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 it is called the **standard enthalpy of fusion**, $\Delta H_{\text{fus}}^{\circ}$. The following is an example:



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



3) Enthalpy of vaporization and standard enthalpy of vaporization

Vaporization is the transition of a substance from its liquid phase to its gaseous phase. It requires absorption of a certain amount of heat called enthalpy of vaporization, which 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, $\Delta H_{\text{vap}}^{\circ}$** . The following is an example:

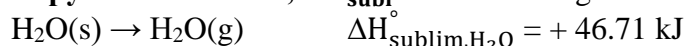


The reverse process of vaporization is called condensation, its enthalpy is negative and is called the enthalpy of condensation.

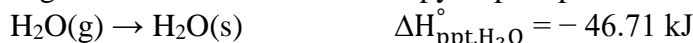


4) Enthalpy of sublimation and standard enthalpy of sublimation

Sublimation is the transition of a substance from its solid phase to its gaseous phase. It requires absorption of a certain amount of heat called enthalpy of sublimation. All enthalpies of sublimation are positive which 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, $\Delta H_{\text{subl}}^{\circ}$** . The following are examples:



The reverse process of sublimation is called precipitation, its enthalpy is negative and is called the enthalpy of precipitation:



- The following table gives $\Delta H_{\text{fus}}^{\circ}$, $\Delta H_{\text{svap}}^{\circ}$ and $\Delta H_{\text{subl}}^{\circ}$ of some substances

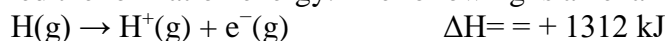
substance	$\Delta H_{\text{fus}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta H_{\text{vap}}^{\circ}/\text{kJ mol}^{-1}$	$\Delta H_{\text{subl}}^{\circ}/\text{kJ mol}^{-1}$
Ammonia, NH_3	5.65	23.4	29.05
Argon, Ar	1.2	6.5	7.7
Benzene, C_6H_6	10.59	30.8	41.39
Ethanol, $\text{CH}_3\text{CH}_2\text{OH}$	4.6	43.5	48.1
Mercury, Hg	2.292	59.30	61.592
Methane, CH_4	0.94	8.2	9.14
Methanol, CH_3OH	3.16	35.3	38.46
Propanone, $\text{CH}_3\text{CO CH}_3$	5.72	29.1	34.82
Water, H_2O	6.01	40.7	46.71

- ✓ **First**, the enthalpy of fusion is much less than the enthalpy of vaporization. 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
- ✓ **Second**, the enthalpy of sublimation equals the sum of the enthalpies of fusion and vaporization. The reason behind this is the fact that enthalpy of any substance is a function of its state. The difference between the enthalpy of the substance in its gaseous state and its enthalpy in its solid state is the same

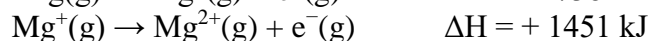
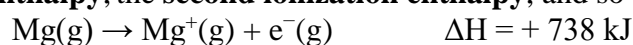
whether it changes from its solid state to its gaseous state directly or its first changes to its liquid state then changes to its gaseous state

5) Enthalpy of electron loss (ionization)

- ✓ Ionization is the endothermic physical process by which electrons are removed from atoms by absorbing energy absorption.
- ✓ It 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, $\Delta H_{\text{ion}}^{\circ}$** . It is also called the ionization energy. The following is an example:



- ✓ We need to consider a succession of ionizations, such as the conversion of Mg to $\text{Mg}^{\text{+}}$ ions, the ionization of $\text{Mg}^{\text{+}}$ ions to $\text{Mg}^{2\text{+}}$ ions, and so on. These successive molar enthalpy changes are called, respectively, the **first ionization enthalpy**, the **second ionization enthalpy**, and so on.



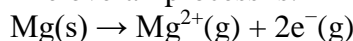
- ✓ The second ionization enthalpy is larger than the first because more energy is needed to remove an electron from a positively charged ion than from the neutral atom

Example 4.6

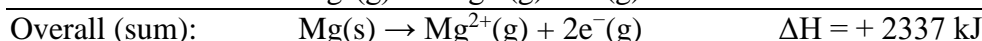
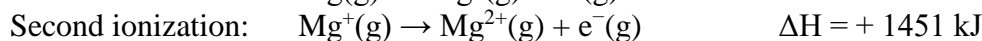
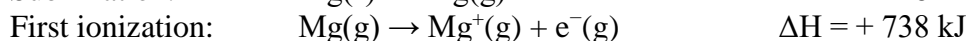
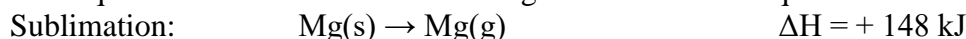
$\Delta H_{\text{sub, Mg, 25}^{\circ}\text{C}}^{\circ} = 148 \text{ kJ mol}^{-1}$, $M_{\text{Mg}}^{\circ} = 24.31 \text{ g/mol}$ and its first and second ionization enthalpies are + 738 kJ and + 1451 kJ respectively. How much energy as heat (at constant T and P) must be supplied to 1.00 g of Mg(s) to produce $\text{Mg}^{2\text{+}}(\text{g})$?

Solution

The overall process is:



This equation is the sum of the following thermochemical equations:



$$n_{\text{Mg}} = \frac{m_{\text{Mg}}}{M_{\text{Mg}}} = \frac{1 \text{ g}}{24.31 \frac{\text{g}}{\text{mol}}} = 0.0411 \text{ mol}$$

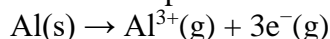
$$q_{\text{p}} = 2337 \frac{\text{kJ}}{\text{mol}} \times 0.0411 \text{ mol} = 96.05 \text{ kJ}$$

Example 4.7

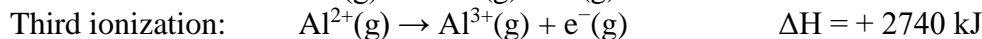
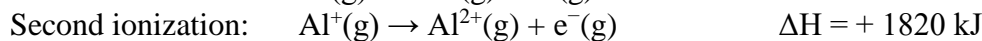
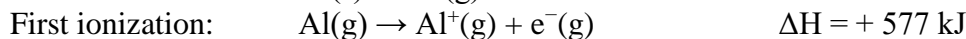
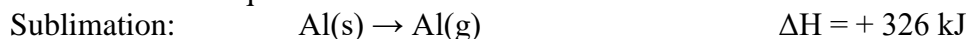
The enthalpy of sublimation of aluminum (molar mass = 26.98 g/mol) is 326 kJ mol^{-1} . Look up ionization enthalpies and calculate the heat that must be supplied at constant pressure to convert 1 g of solid Al(s) to $\text{Al}^{3\text{+}}(\text{g})$ at 25°C.

Solution

The overall process is:



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



Overall (sum):	$\text{Al(s)} \rightarrow \text{Al}^{3+}(\text{g}) + 3\text{e}^{-}(\text{g})$	$\Delta H = + 5463 \text{ kJ}$
$n_{\text{Al}} = \frac{m_{\text{Al}}}{M_{\text{Al}}} = \frac{1 \text{ g}}{26.98 \frac{\text{g}}{\text{mol}}} = 0.0371 \text{ mol}$	$q_{\text{p}} = + 5463 \frac{\text{kJ}}{\text{mol}} \cdot 0.0371 \text{ mol} = 202.48 \text{ kJ}$	

6) Enthalpies of electron gain

- ✓ Electron gain is the gain of electrons by atoms
- ✓ Electron gain is not the reverse of electron loss:
 - By definition, the ionization of hydrogen is written as:

$$\text{H(g)} \rightarrow \text{H}^{+}(\text{g}) + \text{electron}$$
 - The reverse of the ionization of hydrogen must be:

$$\text{H}^{+}(\text{g}) + \text{electron} \rightarrow \text{H(g)}$$
 - By definition, the electron gain of hydrogen is written as:

$$\text{H(g)} + \text{electron} \rightarrow \text{H}^{-}(\text{g})$$
- ✓ 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, $\Delta H_{\text{eg}}^{\circ}$** . The following is an example:

$$\text{O(g)} + \text{e}^{-}(\text{g}) \rightarrow \text{O}^{-}(\text{g}) \quad \Delta H = - 141 \text{ kJ}$$
- ✓ Electron gain by an O^{-} ion is strongly endothermic because it takes energy to push an electron on to an already negatively charged species:

$$\text{O}^{-}(\text{g}) + \text{e}^{-}(\text{g}) \rightarrow \text{O}^{2-}(\text{g}) \quad \Delta H = + 780 \text{ kJ}$$

7) Enthalpies of solution (dissolutions)

- ✓ Dissolving a solid in solute, comprises three actions:
 - 1) *The breaking of attractions within solute particles.* Here ΔH_1 is positive
 - 2) *The breaking of attractions within solvent particles.* Here ΔH_2 is positive
 - 3) *The linking between solute and solvent particles which is called "solvation".* ΔH_3 is negative

(If the solvent is water, **solvation** is given the special term "**hydration**")
- ✓ Enthalpy of solution equals the sum of the enthalpies of the three steps:

$$\Delta H_{\text{solution}} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
- ✓ In most cases, ΔH_3 , which is negative, does not compensate for the sum of ΔH_1 and ΔH_2 , which both are positive:

$$\Delta H_1 + \Delta H_2 \neq \Delta H_3$$

$$\Delta H_{\text{solution}} > 0 \text{ or } \Delta H_{\text{solution}} < 0$$

Enthalpy change for dissolving potassium chloride in water is positive ($\Delta H_{\text{soln,KCl}} = + 17.2 \text{ kJ/mol}$), while the enthalpy change for dissolving potassium hydroxide in water is negative ($\Delta H_{\text{soln,KOH}} = - 57.6 \text{ kJ/mol}$)
- ✓ 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:

$$\Delta H_1 + \Delta H_2 = \Delta H_3$$

$$\Delta H_{\text{solution}} = 0$$
- ✓ 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, $\Delta H_{\text{soln}}^{\circ}$** .

- ✓ 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**, $\Delta H_{\text{infin.dilution}}^{\circ}$.
- ✓ Solution at infinite dilution can be understood by the following illustration:

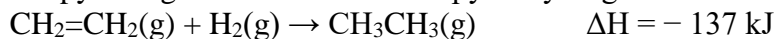
Number moles of H ₂ O(l)	1 mol of HCl(g) is dissolved in		
	5	25	Large
$\Delta H_{\text{solution}}^{\circ}$ (kJ)	- 63.995	- 72.177	- 75.076

- 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

- Chemical reactions are the disappearance of substances (reactants) and the appearance of new substances (products). This is a result of breaking chemical bonds of reactants and forming those of products
- 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 ΔH_{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 the enthalpy change is called “the enthalpy of hydrogenation”:



1) Enthalpy of combustion and standard enthalpy of combustion

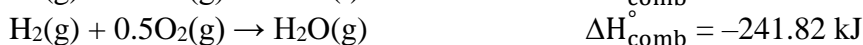
- ✓ **Combustion** is a chemical reaction between a fuel (fuels are organic compounds, especially hydrocarbons, in the gas, liquid or solid phase) and an oxidant accompanied by the production of heat and conversion of chemical species. The release of heat can result in the production of light in the form of either glowing or a flame

Fuel	Enthalpies of combustion (kJ/g)
Hydrogen	- 141.9
Natural Gas	- 54.0
Propane	- 49.9
Butane	- 49.2
Gasoline	- 47.0
Diesel	- 45.0
Ethanol	- 29.7
Coal (Anthracite)	- 27.0
Coal (Lignite)	- 15.0
Wood	- 15.0

- ✓ 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**,

ΔH_{comb} . If the amount combusted is one mole, and the conditions are the standard conditions, it is called **standard enthalpy of combustion**,

$\Delta H_{\text{comb}}^{\circ}$. The following are examples:

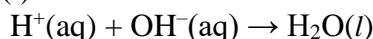


- ✓ The following table shows the standard enthalpy of combustion of some substances:

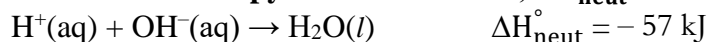
Substance	Combustion reaction	$\Delta H_{\text{comb}}^{\circ}$ (kJ/mol)
methane	$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	- 890
ethane	$\text{C}_2\text{H}_6(\text{g}) + 3.5\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	- 1560
propane	$\text{C}_3\text{H}_8(\text{g}) + 5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	- 2220
butane	$\text{C}_4\text{H}_{10}(\text{g}) + 7.5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$	- 2874
octane	$\text{C}_8\text{H}_{18}(\text{g}) + 12.5\text{O}_2(\text{g}) \rightarrow 8\text{CO}_2(\text{g}) + 9\text{H}_2\text{O}(\text{l})$	- 5460
methanol	$\text{CH}_3\text{OH}(\text{l}) + 1.5\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	- 726
ethanol	$\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	- 1368
propan-1-ol	$\text{C}_3\text{H}_7\text{OH}(\text{l}) + 4.5\text{O}_2(\text{g}) \rightarrow 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O}(\text{l})$	- 2021
butan-1-ol	$\text{C}_4\text{H}_9\text{OH}(\text{l}) + 6\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l})$	- 2671

2) Enthalpy of neutralization and standard enthalpy of neutralization

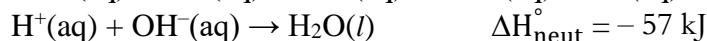
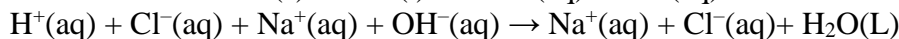
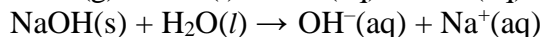
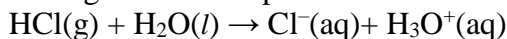
- ✓ **Neutralization** is the reaction between $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$, to produce liquid water $\text{H}_2\text{O}(\text{l})$:



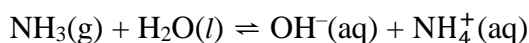
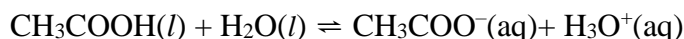
- ✓ The heat released, at constant temperature and pressure, as a result of reaction between $\text{H}^+(\text{aq})$, and $\text{OH}^-(\text{aq})$ to produce liquid water $\text{H}_2\text{O}(\text{l})$ is called the **enthalpy of neutralization** ΔH_{neut} . If the amount of water produced is one mole, and the conditions are the standard conditions, it is called **standard enthalpy of neutralization**, $\Delta H_{\text{neut}}^{\circ}$ and it equals - 57 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
- ✓ We can get $\text{H}^+(\text{aq})$ from an acid and $\text{OH}^-(\text{aq})$ from a base. Therefore, 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 provides their aqueous H^+ and OH^- ions. The following are an examples:



- ✓ This simplified equation justifies defining neutralization reaction as the reaction between $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$.
- ✓ **Weak acids and bases:** Weak acids and bases are partially ionized. The following are an examples:

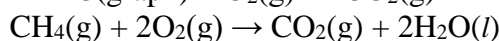
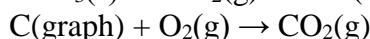
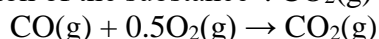


Because these reactions are reversible they do not proceed to completion.

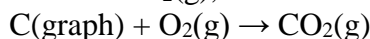
- ✓ When the weak acid and the weak base react their available aqueous ions of H_3O^+ and OH^- combines to produce liquid H_2O and energy. This loss of ions must be replaced by using the energy released to ionize the unionized molecules of the acid and the base. All the reactants are consumed but some 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_2O is produced from the reaction between weak acids and bases and 57 kJ must have been released, the net amount of heat released is less than 57 kJ by the amount consumed to complete ionization.** This is the why, at standard conditions, neutralization involving strong acids and bases releases 57 kJ but less if it involves weak acids and bases

3) Enthalpy of formation and standard enthalpy of formation

- ✓ Any substance can be formed by many ways, any of which can be named “formation reaction of the substance”. $\text{CO}_2(\text{g})$ is an example:



- ✓ Not any reaction is named its **formation reaction**. By convention (or definition) **The formation reaction of a substance is only the reaction which forms only one mole of the substance from the reaction of its elements while they are in their standard states**
- ✓ This definition of the formation reaction has four **musts**:
 - 1) The product **must** only be one substance
 - 2) The amount of the substance formed **must** be one mole
 - 3) The reactants **must** be elements
 - 4) The reacting elements **must** be in their standard states
- ✓ The formation reaction of $\text{CO}_2(\text{g})$, is:



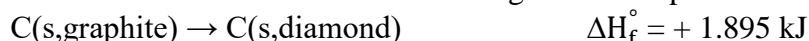
- ✓ The heat absorbed or released, at constant temperature and pressure, as a result of the formation of a substance is its **enthalpy of formation, ΔH_f** . If the amount formed, is one mole, and the pressure is the standard pressure, it is called the **standard enthalpy of formation, ΔH_f°** . The following are examples:



- ✓ According to this strict definition, if the substance is an element in its standard state, it has no formation reaction

The standard enthalpy of formation of any element in its standard state is zero

- ✓ The standard enthalpy of formation of an element in a state other than its reference state is not zero. The following is an example:



Therefore, although $\Delta H_{f,\text{C,graphite}}^\circ = 0$, $\Delta H_{f,\text{C,diamond}}^\circ = +1.895 \text{ kJ mol}^{-1}$

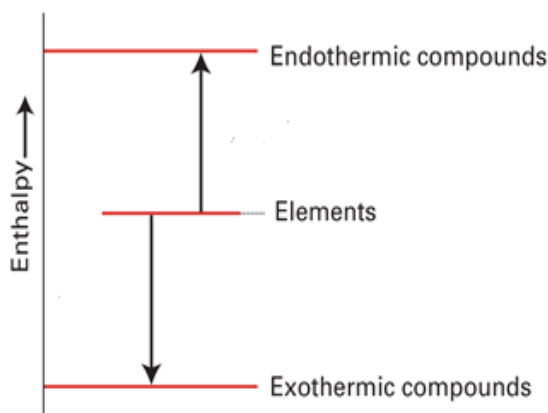
- ✓ The standard enthalpies of formation of substances are always tabulated in chemistry references and textbooks, the enthalpies of formation of substances are always tabulated. An example of such tables is presented here.

compound	ΔH_f° (kJ/mol)	compound	ΔH_f° (kJ/mol)
AgBr(s)	-99.5	C ₂ H ₂ (g)	+226.7
AgCl(s)	-127.0	C ₂ H ₄ (g)	+52.3
AgI(s)	-62.4	C ₂ H ₆ (g)	-84.7
Ag ₂ O(s)	-30.6	C ₃ H ₈ (g)	-103.8
Ag ₂ S(s)	-31.8	n- C ₄ H ₁₀ (g)	-124.7
Al ₂ O ₃ (s)	-1669.8	n- C ₅ H ₁₂ (l)	-173.1
BaCl ₂ (s)	-860.1	C ₂ H ₅ OH(l)	-277.6
BaCO ₃ (s)	-1218.8	CoO(s)	-239.3
BaO(s)	-558.1	Cr ₂ O ₃ (s)	-1128.4
BaSO ₄ (s)	-1465.2	CuO(s)	-155.2
CaCl ₂ (s)	-795.0	Cu ₂ O(s)	-166.7
CaCO ₃	-1207.0	CuS(s)	-48.5
CaO(s)	-635.5	CuSO ₄ (s)	-769.9
Ca(OH) ₂ (s)	-986.6	Fe ₂ O ₃ (s)	-822.2
CaSO ₄ (s)	-1432.7	Fe ₃ O ₄ (s)	-1120.9
CCl ₄ (l)	-139.5	HBr(g)	-36.2
CH ₄ (g)	-74.8	HCl(g)	-92.3
CH ₃ OH(l)	-238.6	HI(g)	+25.9
CO(g)	-110.5	HNO ₃ (l)	-173.2
CO ₂ (g)	-393.5	H ₂ O(g)	-241.8
H ₂ O(l)	-285.8	NH ₄ Cl(s)	-315.4
H ₂ O ₂ (l)	-187.6	NH ₄ NO ₃ (s)	-365.1
H ₂ S(g)	-20.1	NO(g)	+90.4
H ₂ SO ₄ (l)	-811.3	NO ₂ (g)	+33.9
HgO(s)	-90.7	NiO(s)	-244.3
HgS(s)	-58.2	PbBr ₂ (s)	-277.0
KBr(s)	-392.2	PbCl ₂ (s)	-359.2
KCl(s)	-435.9	PbO(s)	-217.9
KClO ₃ (s)	-391.4	PbO ₂ (s)	-276.6
KF(s)	-562.6	Pb ₃ O ₄ (s)	-734.7
MgCl ₂ (s)	-641.8	PCl ₃ (g)	-306.4
MgCO ₃ (s)	-1113	PCl ₅ (g)	-398.9
MgO(s)	-601.8	SiO ₂ (s)	-859.4
Mg(OH) ₂ (s)	-924.7	SnCl ₂ (s)	-349.8
MgSO ₄ (s)	-1278.2	SnCl ₄ (l)	-545.2
MnO(s)	-384.9	SnO(s)	-286.2
MnO ₂ (s)	-519.7	SnO ₂ (s)	-580.7
NaCl(s)	-411.0	SO ₂ (g)	-296.1
NaF(s)	-569.0	SO ₃ (g)	-395.2
NaOH(s)	-426.7	ZnO(s)	-348.0
NH ₃ (g)	-46.2	ZnS(s)	-202.9

- ✓ The standard state of the elements can be looked at as a reference states of the elements and can be looked at as a thermochemical “sea level”, and

enthalpies of formation can be regarded as thermochemical “altitudes” above or below sea level

- ✓ Endothermic formation reactions of a substances have positive enthalpies of formation; exothermic formation reactions of a substances have negative energies of formation



- ✓ Substances that have negative standard enthalpies of formation, such as water, are classified as **exothermic substances**, the opposite, such as nitrogen dioxide, 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
- ✓ The standard enthalpies of formation are very important tool to in calculating the enthalpy of any reaction using the following equation:

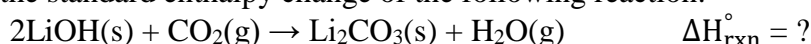
$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f,products}}^{\circ} - \sum \Delta H_{\text{f,reactants}}^{\circ}$$

Example 4.8

From the table below,

	LiOH(s)	CO ₂ (g)	Li ₂ CO ₃ (s)	H ₂ O(g)
$\Delta H_{\text{f}}^{\circ} / \text{kJ mol}^{-1}$	-484.9	-393.5	-1216.0	-241.8

Calculate the standard enthalpy change of the following reaction:



Solution

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_{\text{f}}^{\circ}(\text{products}) - \sum \Delta H_{\text{f}}^{\circ}(\text{reactants})$$

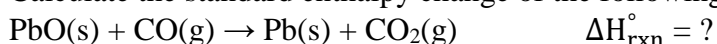
$$\Delta H_{\text{rxn}}^{\circ} = \sum \{(-1216.0) + (-241.8)\} - \sum \{2 \times (-484.9) + (-393.5)\} = -94.5 \text{ kJ}$$

Practice exercise

From the table below,

	PbO(s)	CO(g)	CO ₂ (g)
$\Delta H_{\text{f}}^{\circ} / \text{kJ mol}^{-1}$	-219	-111	-394

Calculate the standard enthalpy change of the following reaction:

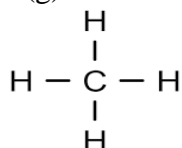


4.6 The bond dissociation energy (bond energy)

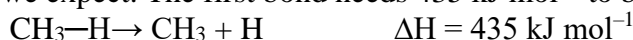
- ✓ When atoms combine together, bonds are formed between them, and this is accompanied by releasing energy
- ✓ When atoms separate from each other, bonds between them are dissociated, and this is accompanied by absorbing energy
- ✓ Formation of a bond is the opposite of its dissociation
- ✓ The word "**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** " ΔH_{bond} ".
- ✓ Let's take methane gas, $\text{CH}_4(\text{g})$:



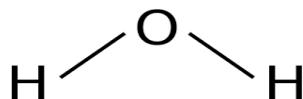
At first glance, we would expect that the amount of energy needed to break any one of them is the same as for any of the other three. However, the case is not as we expect. The first bond needs 435 kJ mol^{-1} to break:



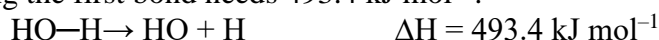
But once is broken the bond strength between the carbon atom and the remaining three hydrogen atoms changes, so the energies required to break them becomes different:



- ✓ Let's take water, $\text{H}_2\text{O} (l)$ as another example:



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



But once this bond is broken the energy required to break the second bond becomes less:

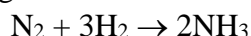


- ✓ Furthermore, the dissociation-bond energy differs for the same bond in different compounds. For example, dissociation-bond energy of the C—H bond in CH_4 differs from that in CH_3CH_3 and from that of CH_2CH_2 or CHCH
- ✓ Sum up the above; it appears that it is much more useful to talk about an "**AVERAGE BOND ENERGY, D_0** ". The average energy for C—H bond in CH_4 is 414 kJ mol^{-1} , for O—H in H_2O is $458.9 \text{ kJ mol}^{-1}$
- ✓ The "**AVERAGE BOND ENERGY**" is also called "**BOND ENERGY**"
- ✓ If the amount of bonds broken is one mole (6.022×10^{23} bonds), and the conditions are the standard conditions, it is called **standard bond energy, B°** , **standard bond enthalpy, $\Delta H_{\text{bond}}^\circ$** or **average standard bond-dissociation energy, D_0**
- ✓ Bond energy is very useful in calculating the enthalpy of any reaction using the following equation:

$$\Delta H_{\text{rxn}}^\circ = \sum B_{\text{reactants}}^\circ - \sum B_{\text{products}}^\circ$$

Example 4.9

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



Use data given in the previous table.

Solution

$$\Delta H_{\text{rxn}}^\circ = \sum B_{\text{reactants}}^\circ - \sum B_{\text{products}}^\circ$$

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

$$\Delta H_{\text{rxn}}^{\circ} = 2249 \text{ kJ} - 2328 \text{ kJ} = -97 \text{ kJ}$$

Practice exercise

Knowing that:

Bond	H—H	C—H	C—C	C=C
Bond energy / kJ mol^{-1}	436	413	347	607

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

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

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
H—H	436	N—N	160
C—H	413	N=O	631
N—H	393	N triple N	941
P—H	297	N—O	201
C—C	347	N—H	388
C—O	358	O—H	464
C—N	305	O—S	265
C—Cl	397	O—Cl	269
C=C	607	O—O	204
C=O	805	C—F	552
O=O	498	C—S	259

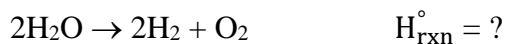
Example 4.10

Knowing that:

Bond	H—H	O=O	O—H
Bond energy / kJ mol^{-1}	436	498	464

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

Solution



$$\Delta H_{\text{rxn}}^{\circ} = \sum B_{\text{reactants}}^{\circ} - \sum B_{\text{products}}^{\circ}$$

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

$$\Delta H_{\text{rxn}}^{\circ} = 1856 \text{ kJ} - 1370 \text{ kJ} = +484 \text{ kJ}$$

Practice exercise

Knowing that:

Bond	H—H	C—H	C—C	C=C
Bond energy / kJ mol^{-1}	?	413	347	607
$\Delta H_{\text{hydrogenation, 1-probene gas}}^{\circ}$	-130 kJ/mol of propene			

Calculate, in kJ mol^{-1} , the bond energy of H_2 .

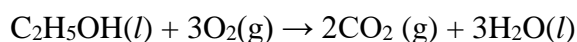
- ✓ As can be seen from the example of water, the O—H bonds in H_2O is the same as in HO but they differ in bond enthalpies. Therefore, there is no choice but to use **mean or averaged bond enthalpies**, ΔH_{B} , which are the averages of bond enthalpies over a related series of compounds
- ✓ For example, the mean O—H bond enthalpy, $\Delta H_{\text{B, H—O}} = 463 \text{ kJ mol}^{-1}$, is the mean of the O—H bond enthalpies in H_2O and several other similar compounds such as methanol, CH_3OH

Example 4.11

Estimate the enthalpy change for the combustion of liquid ethanol to carbon dioxide and liquid water under standard conditions by using the following information.

Bond	C-H	C-C	C-O	O-H	O=O	C=O	H-O
Mean bond enthalpy (kJ/mol)	413	347	358	464	498	805	464

Solution



First:

$$\Delta H_{\text{B,react}} = (5 \text{ mol} \times 412 \text{ kJ}) + (1 \times 347 \text{ kJ mol}) + (1 \text{ mol} \times 358 \text{ kJ}) + (1 \text{ mol} \times 464 \text{ kJ}) + (3 \text{ mol} \times 498 \text{ kJ}) = + 4723 \text{ kJ}$$

Second:

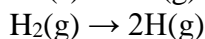
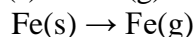
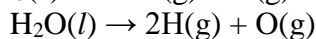
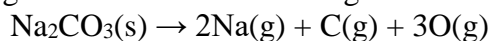
$$\Delta H_{\text{B,prod.}} = (4 \text{ mol} \times 805 \text{ kJ}) + (6 \text{ mol} \times 464 \text{ kJ}). = + 6004 \text{ kJ}$$

$$\Delta H_{\text{rxn}}^{\circ} = \sum B_{\text{reactants}}^{\circ} - \sum B_{\text{products}}^{\circ}$$

$$\Delta H_{\text{reaction}} = + 4723 \text{ kJ} - (+ 6004 \text{ kJ}) = - 1281 \text{ kJ}$$

4.7 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 energy or enthalpy of atomization is the quantity of heat that is absorbed at constant temperature and pressure to achieve atomization. If the atomization is for an element and the quantity produced of the 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**, $\Delta H_{\text{atom}}^{\circ}$ of the element (or the compound)
- ✓ In atomization, all bonds in the substance are broken and none are formed. *Therefore, enthalpies of atomization are always positive.*
- ✓ *If the atomized substance is a compound*, the sum of its bond dissociation energies is its enthalpy of atomization. The following is an example:



- ✓ *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:



- ✓ *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:



- ✓ *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 an example:



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

Example 4.12

Knowing that:

Substance	C(g)	H ₂ (g)	O ₂ (g)
$\Delta H_{\text{atom}}^{\circ} / \text{kJ mol}^{-1}$	716.68	217.97	249.2

and:

Bond	C-H	C-C	C-O	O-H
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Bond energy / kJ mol ⁻¹	413	348	351	463
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Calculate $\Delta H_{\text{rxn}}^\circ$ for the following reaction:

$$2\text{C}(\text{graphite}) + 3\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{CH}_2\text{OH}(\text{l}) \quad \Delta H_{\text{rxn}}^\circ = ?$$

Solution

$$\Delta H_{\text{rxn}}^\circ = \sum B_{\text{reactants}}^\circ - \sum B_{\text{products}}^\circ$$

$$\sum B^\circ(\text{r}) = [2 \times \Delta H_{\text{atom,C}(\text{graphite})}^\circ + 6 \times \Delta H_{\text{atom,H}(\text{g})}^\circ + \Delta H_{\text{atom,O}(\text{g})}^\circ]$$

$$\sum B^\circ(\text{r}) = [2 \times 716.68 + 6 \times 217.97 + 249.2] = 2990.38 \text{ kJ}$$

$$\sum B^\circ(\text{p}) = [5 \times \Delta H_{\text{bonding}(\text{C-H})}^\circ + \Delta H_{\text{bonding}(\text{C-C})}^\circ + \Delta H_{\text{bonding}(\text{C-O})}^\circ + \Delta H_{\text{bonding}(\text{O-H})}^\circ]$$

$$\sum B^\circ(\text{p}) = [5 \times 413 + 348 + 351 + 463] = 3227 \text{ kJ}$$

$$\Delta H_{\text{f,C}_4\text{H}_{10}(\text{L})}^\circ = (2990.38) - (3227) = -236.62 \text{ kJ}$$

Practice exercise

Knowing that:

Substance	C(g)	H(g)	O(g)
$\Delta H_{\text{atom}}^\circ / \text{kJ mol}^{-1}$	716.68	217.97	249.2

and:

Bond	C—H	C—O	O—H
Bond energy / kJ mol ⁻¹	413	351	464

Calculate $\Delta H_{\text{rxn}}^\circ$ for the following esterification of methanoic acid ethanol:

$$\text{HCOOH}(\text{L}) + \text{C}_2\text{H}_5\text{OH}(\text{L}) \rightarrow \text{HCOOC}_2\text{H}_5(\text{L}) \quad \Delta H_{\text{rxn}}^\circ = ?$$

Example 4.13

Estimate the standard enthalpy change for the reaction:

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

Use the following information.

	H—H	O=O	C—H	C—O	O—H	C(s,graph.)	CH3OH(g)
Mean bond enthalpy (kJ/mol)	463	497	412	360	463		
Enthalpy of atomization (kJ/mol)						716.68	
Enthalpy of condensation (kJ/mol)							-38

Solution

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

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

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

Third: $\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{l})$

Sum: $\text{C}(\text{s,graph}) + 2\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{L})$

If we manage to calculate ΔH for the three equations the ΔH of the equation in question can be obtained.

First equation:

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

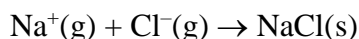
Dissociation of 2 mol $\text{H}_2(\text{g})$: $2\text{H}_2(\text{g}) \rightarrow 4\text{H}(\text{g}) \quad \Delta H = +926 \text{ kJ}$

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

Dissociation of 1/2 mol O ₂ (g)	$\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$	$\Delta H = + 249.17 \text{ kJ}$
Overall, so far:		
$2\text{H}_2(\text{g}) + \text{C}(\text{s,graph}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow 4\text{H}(\text{g}) + \text{C}(\text{g}) + \text{O}(\text{g})$		$\Delta H = + 1891.85 \text{ kJ}$
Second equation:		
Second equation is the reverse of the following equation, which is the equation of atomization of CH ₃ OH(g):		
$\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}) + \text{O}(\text{g})$		
CH ₃ OH has three C—H bonds, one C—O bond and one O—H bond. Therefore, the atomization energy of CH ₃ OH(g), AE _{methanol} , is:		
$\text{AE}_{\text{methanol}} = (3 \text{ mol} \times 412 \text{ kJ}) + (1 \text{ mol} \times 360 \text{ kJ}) + (1 \text{ mol} \times 463 \text{ kJ}) = + 2059 \text{ kJ}$		
$\text{C}(\text{g}) + 4\text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$		$\Delta H = - 2059 \text{ kJ}$
Third equation:		
Third equation is the condensation of gaseous methanol:		
$\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{L})$		$\Delta H = - 38 \text{ kJ}$
$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g}) + \text{O}(\text{g})$		$\Delta H = + 1891.85 \text{ kJ}$
$\text{C}(\text{g}) + 4\text{H}(\text{g}) + \text{O}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{g})$		$\Delta H = - 2059 \text{ kJ}$
$\text{CH}_3\text{OH}(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{L})$		$\Delta H = - 38 \text{ kJ}$
$\text{C}(\text{s}) + 2\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CH}_3\text{OH}(\text{L})$		$\Delta H = - 205.15 \text{ kJ}$
The experimental value is $- 239.00 \text{ kJ}$		

4.8 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 following is an example



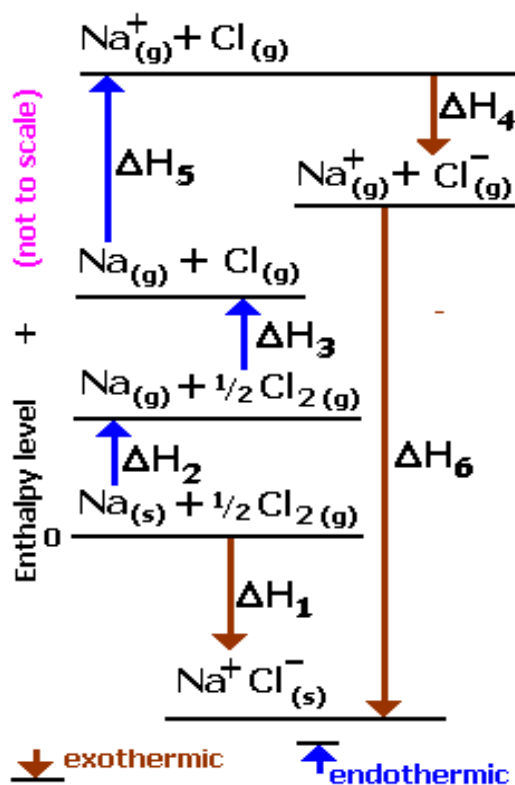
- ✓ The **lattice energy** which is also called the **enthalpy of lattice** is defined as the amount of heat released, at constant temperature and pressure, as a result of forming an ionic substance from its gaseous ions (or the amount of heat absorbed, at constant temperature and pressure, as a result 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, $\Delta H_{\text{lattice}}^\circ$; or standard lattice energy, E_L**
- ✓ It appears that its sign can be either negative or positive depending on whether the ionic substance is formed or dissociated.
- ✓ We will stick to the following definition for Standard Lattice Energy:

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

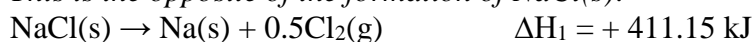


- ✓ Below is one way of presenting how the Born-Haber cycle for NaCl which consists of the following **five** steps:



Step 1: absorption of 411 kJ to decompose 1 mole of NaCl(s) to 1 mole of Na(s) and 0.5 mole of Cl₂(g).

This is the opposite of the formation of NaCl(s):



Step 2: absorption of 107.32 kJ to atomize one mole of Na(s) to one mole of Na(g):



Step 3: absorption of 121 kJ to atomize 0.5 mole of Cl₂(g):



Step 4: absorption of 498.3 kJ to ionize one mole of Na(g):



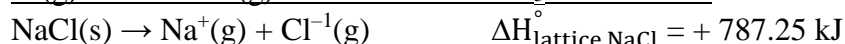
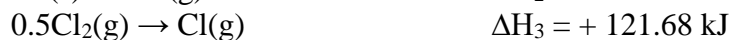
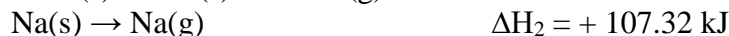
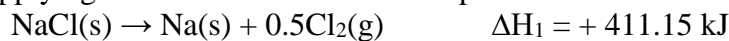
Step 5: release of 351.2 kJ to ionize one mole of Cl(g):



✓ Our aim is to calculate the value of ΔH of the following equation:



✓ By applying Hess's law on these five steps we achieve our aim.



This is the standard lattice energy of NaCl(s) obtained by the Born-Haber cycle, and $\Delta H_{\text{lattice}}^\circ$ of any ionic compound can be determined this way

Example 4.14

Use the information below and Born-Haber method to calculate $\Delta H_{\text{lattice,NaF}}^\circ$.

	$\Delta H_{\text{f,NaF}}^\circ$	$\Delta H_{\text{atom,Na}}^\circ$	$\Delta H_{\text{atom,F}_2}^\circ$	$\Delta H_{\text{ioniz,Na}}^\circ$	$\Delta H_{\text{elec.aff.,F}}^\circ$
kJ mol ⁻¹	- 569.00	+ 107.32	+ 155.00	+ 498.3	- 328.00

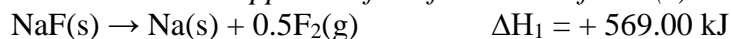
Draw the relevant diagram.

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 F₂(g).

This is the opposite of the formation of NaF(s):



Step 2: absorption of 107.32 kJ to atomize one mole of Na(s) to one mole of Na(g):



Step 3: absorption of 155.00 kJ to atomize 0.5 mole of F₂(g):



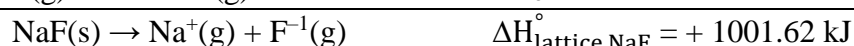
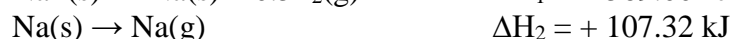
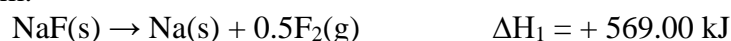
Step 4: absorption of 500 kJ to ionize one mole of Na(g):



Step 5: release of 364 kJ to ionize one mole of F(g):



By applying Hess's law of heat summation on the five steps of born-Haber cycle we achieve our aim.



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

Chose an ionic compound. Obtain from literature the necessary data needed to find its lattice energy. Apply Born-Haber cycle and draw the relevant diagram.

4.9 Effect of pressure and temperature on the enthalpies of reactions

- ΔH of a specified reaction is constant as long as the reaction occurs at the same temperature and pressure. Changing the temperature and/or pressure changes the value of its ΔH
- 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.
- The reaction enthalpy changes with temperature because the enthalpy increases with temperature. Therefore, 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:

$$\int_{T_1}^{T_2} d\Delta H_{\text{rxn}}^\circ = \int_{T_1}^{T_2} dC_p dT$$

$$\Delta H_{\text{rxn},T_2}^\circ - \Delta H_{\text{rxn},T_1}^\circ = \Delta C_p (T_2 - T_1)$$

$$\Delta H_{\text{rxn},T_2}^\circ = \Delta H_{\text{rxn},T_1}^\circ + \Delta C_p (T_2 - T_1)$$

This is true **only** if C_p does not change with temperature, or if its change is negligible. So, we can calculate ΔH at any temperature if we know ΔH at a certain temperature.

- The value of ΔC_p is given as:

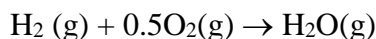
$$\Delta C_p = \sum C_{p,\text{products}} - \sum C_{p,\text{reactants}}$$

Example 4.15

The standard enthalpy of formation of gaseous water at 25°C is $-241.82 \text{ kJ mol}^{-1}$. Estimate its value at 100°C. Use the following information.

	H ₂ O(g)	H ₂ (g)	O ₂ (g)
$C_{p,m}/\text{J K}^{-1} \text{ mol}^{-1}$	33.58	28.48	29.37

Solution



$$\Delta H_{\text{rxn},T_2}^\circ = \Delta H_{\text{rxn},T_1}^\circ + \Delta C_p (T_2 - T_1)$$

$$\Delta C_p = \sum C_{p,\text{products}} - \sum C_{p,\text{reactants}}$$

$$\Delta C_p = C_p(\text{H}_2\text{O},\text{L}) - \{C_p(\text{H}_2,\text{g}) + C_p(\text{O}_2,\text{g})\}$$

$$\Delta C_p = 1 \text{ mol} \times 33.5 \frac{\text{J}}{\text{K mol}} - \left\{ 1 \text{ mol} \times 28.48 \frac{\text{J}}{\text{K mol}} + 0.5 \text{ mol} \times 29.37 \frac{\text{J}}{\text{K mol}} \right\} = -9.95 \frac{\text{J}}{\text{K}}$$

$$(T_2 - T_1) = 373 \text{ K} - 298 \text{ K} = 75 \text{ K}$$

$$\Delta H_{\text{rxn},T_2}^\circ = (1 \text{ mol} \times -241.82 \frac{\text{kJ}}{\text{mol}}) + (-9.95 \frac{\text{J}}{\text{K}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 75 \text{ K}) = -242.57 \text{ kJ}$$

Practice exercise

The standard enthalpy of formation of gaseous ammonia at 298 K is $-46.11 \text{ kJ mol}^{-1}$. Estimate its value at 400 K.

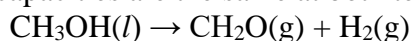
Use the following information.

	NH ₃ (g)	N ₂ (g)	H ₂ (g)
$C_{p,m}/\text{J K}^{-1} \text{ mol}^{-1}$	35.06	29.125	28.824

- The calculation in the previous example shows that the standard reaction enthalpy at the higher temperatures is only slightly different from that 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 4.16

From the data given below at 298 K. calculate ΔH_{rxn} of the following reaction at 398 K. Assume that heat capacities are the same at both temperatures.



	CH ₃ OH(l)	CH ₂ O(g)	H ₂ (g)
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	-234.7	-115.90	
$C_{m,p} / \text{J mol}^{-1} \text{ K}^{-1}$	81.11	35.4	28.836

Solution

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

$$\Delta H_{\text{rxn}}^\circ = \sum \{(-115.90) + (0)\} \text{ kJ} - \sum (-234.7) \text{ kJ} \Delta H_{\text{rxn}}^\circ = +118.8 \text{ kJ}$$

$$\Delta C_p = \sum C_p(\text{products}) - \sum C_p(\text{reactants})$$

$$\Delta C_p = (1 \text{ mol} \times 35.4 \text{ J mol}^{-1} \text{ K}^{-1} + 1 \text{ mol} \times 28.836 \text{ J mol}^{-1} \text{ K}^{-1}) - (1 \text{ mol} \times 81.11 \text{ J mol}^{-1} \text{ K}^{-1}) = -16.874 \text{ J K}^{-1}$$

$$\Delta H_2 = \Delta H_1 + \Delta C_p (T_2 - T_1)$$

$$\Delta H_{398} = \left[\{+118.8 \text{ kJ}\} + \{-16.874 \text{ J K}^{-1} \times (398 - 298) \text{ K} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \right]$$

$$\Delta H_{398} = 117.11 \text{ kJ}$$

Practice exercise

Knowing that $\Delta H_{\text{diss,H}_2\text{O(g)}} = 241.75 \text{ kJ mol}^{-1}$ at 18°C and 1 atm, use the information below to calculate $\Delta H_{\text{diss,H}_2\text{O(g)}}$ at 68°C and 1 atm.

	H ₂ O(g)	H ₂ (g)	O ₂ (g)
C _p / J K ⁻¹ K ⁻¹	33.56	28.83	29.12

4.10 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 (ΔU)

While ΔH is the heat of reaction at constant temperature and pressure, ΔU is the heat of reaction at constant temperature and volume. If ΔU of any change is known ΔH can be calculated from the following equation:

$$\Delta H_{\text{rxn}}^\circ = \Delta U_{\text{rxn}}^\circ + P\Delta V = \Delta U_{\text{rxn}}^\circ + RT\Delta n_g$$

2. Use of the Hess's Law

Hess's law shows that the value of ΔH of a reaction can be calculated from knowing the values of ΔH of some other reactions. introduced during our discussion of the thermochemical equation.

3. Use of the bond dissociation and the atomization energies

$$\Delta H_{\text{rxn}}^\circ = \sum B_{\text{reactants}}^\circ - \sum B_{\text{products}}^\circ$$

4. Use of the values of enthalpies of formations

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_{\text{f,products}}^\circ - \sum \Delta H_{\text{f,reactants}}^\circ$$

5. Use of the value of ΔH at a certain temperature

$$\Delta H_{\text{rxnT}_2}^\circ = \Delta H_{\text{rxnT}_1}^\circ + \Delta C_p (T_2 - T_1)$$

Questions and problems

- Knowing that the formation of 1 mol of $\text{SO}_3(\text{g})$, in a bomb calorimeter, from the reaction between $\text{SO}_2(\text{g})$ and $\text{O}_2(\text{g})$ produces 97030 J of heat at 298 K, calculate ΔH .
- Evaluate $\Delta_n G$ in the following reactions:
 - $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 - $\text{C}(\text{graphite}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$
 - $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$
 - $\text{AgNO}_3(\text{s}) + \text{HCl}(\text{g}) \rightarrow \text{AgCl}(\text{s}) + \text{HNO}_3(\text{l})$
- Calculate ΔU of the following reactions at 25 °C:
 - $\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ $\Delta H = -393.5 \text{ kJ}$
 - $\text{C}(\text{graphite}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})$ $\Delta H = -110.5 \text{ kJ}$
 - $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$ $\Delta H = -89.35 \text{ kJ}$
 - $\text{AgNO}_3(\text{s}) + \text{HCl} \rightarrow \text{AgCl}(\text{s}) + \text{HNO}_3(\text{l})$ $\Delta H = -85.30 \text{ kJ}$
- Knowing that at 25 °C:

$$\text{COCl}_2(\text{g}) + \text{H}_2\text{S}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{COS}(\text{g}) \quad \Delta H = -78.705 \text{ kJ}$$

$$\text{H}_2\text{O}(\text{l}) + \text{CS}_2(\text{s}) \rightarrow \text{H}_2\text{S}(\text{g}) + \text{COS}(\text{g}) \quad \Delta H = -3.420 \text{ kJ}$$
 calculate ΔH of the following reaction:

$$\text{COCl}_2(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \text{H}_2\text{O}(\text{l}) + \text{CS}_2(\text{g})$$
- Knowing that:

$$\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow 2\text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) \quad \Delta H = -890.34 \text{ kJ}$$

$$\text{H}_2(\text{g}) + 0.5\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l}) \quad \Delta H = -285.84 \text{ kJ}$$

$$\text{C}(\text{graphite}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \quad \Delta H = -393.5 \text{ kJ}$$
 calculate ΔU of the following reaction:

$$\text{C}(\text{graphite}) + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g}) \quad \Delta H = ?$$
- Knowing that ΔH_f° , in kJ mol^{-1} , of $\text{CO}_2(\text{g}) = -393.5$, and $\text{H}_2\text{O}(\text{l}) = -285.8$; and:

$$\text{C}_4\text{H}_{10}(\text{g}) + 6.5\text{O}_2(\text{g}) \rightarrow 4\text{CO}_2(\text{g}) + 5\text{H}_2\text{O}(\text{l}) \quad \Delta H_{\text{comb}}^\circ = -2878.5 \text{ kJ}$$
 Calculate ΔH_f° , $\text{C}_4\text{H}_{10}(\text{g})$.
- Knowing that:

Substance	$\text{C}_4\text{H}_{10}(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	124.5	-393.5	-285.8

Calculate, in kJ mol^{-1} , $\Delta H_{\text{comb}, \text{C}_4\text{H}_{10}(\text{g})}^\circ$.

- Knowing that:

Substance	$\text{C}(\text{g})$	$\text{H}(\text{g})$	$\text{O}(\text{g})$
$\Delta H_{\text{atom}}^\circ / \text{kJ mol}^{-1}$	716.68	217.97	249.2

and:

Bond	$\text{C}-\text{H}$	$\text{C}-\text{C}$	$\text{C}-\text{O}$	$\text{O}-\text{H}$
Bond energy / kJ mol^{-1}	413	348	351	463

Calculate, in kJ mol^{-1} , ΔH_f° , $\text{CH}_3\text{CH}_2\text{OH}(\text{l})$.

- Knowing that:


Bond	$\text{H}-\text{H}$	$\text{C}-\text{H}$	$\text{C}-\text{C}$	$\text{C}=\text{C}$
Bond energy / kJ mol^{-1}	426	413	348	610

Calculate, in kJ mol^{-1} , $\Delta H_{\text{hydrogenation, ethylene gas}}^\circ$.


- Knowing that:

Substance	$\text{H}_2\text{O}(\text{g})$	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$
$C_{p,m} / \text{J K}^{-1} \text{ mol}^{-1}$	33.56	28.83	29.12

and $\Delta H_{\text{dissociation, H}_2\text{O}(\text{g})}^\circ$ at 101325 Pa and 18 °C, is 241.75 kJ mol^{-1} , calculate $\Delta H_{\text{dissociation, H}_2\text{O}(\text{g})}^\circ$ at 101325 Pa and 68 °C.



5. THE SECOND LAW OF THERMODYNAMICS



5. THE SECOND LAW

5.3 The Carnot cycle

The Carnot cycle is an example of the reversible cycle. It was named after the French engineer Sadi Carnot (1796-1832). It is the manifestation of a heat engine.

5.3.1 The four processes of Carnot's cycle

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

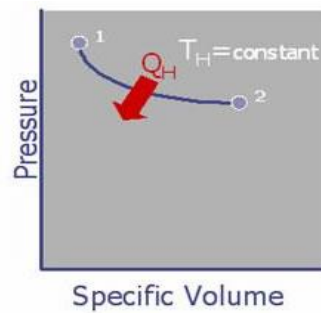
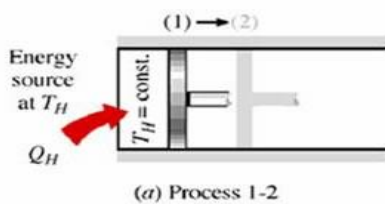
1) First process: reversible isothermal expansion (from state 1 to state 2):

- ✓ This expansion is from volume “ V_1 ” to volume “ V_2 ”
- ✓ Heat is absorbed by the gas at constant high temperature “ T_H ” and an expansion work is done by the gas:

$$Q_1 = nRT_H \ln \frac{V_2}{V_1}$$

AND

$$w_1 = nRT_H \ln \frac{V_1}{V_2}$$



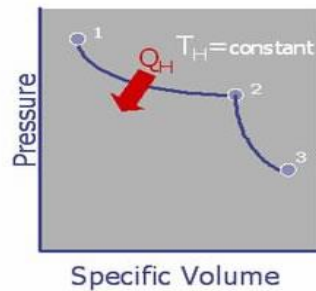
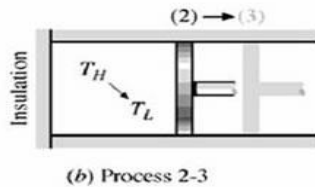
2) Second process: reversible adiabatic expansion from state 2 to state 3

- ✓ This expansion is from volume “ V_2 ” to volume “ V_3 ”
- ✓ No heat is absorbed or released by the gas, but a work is done by the gas and the temperature will decrease from the “ T_H ” to a lower temperature “ T_L ”:

$$Q_2 = 0$$

AND

$$w_2 = C_v (T_L - T_H)$$



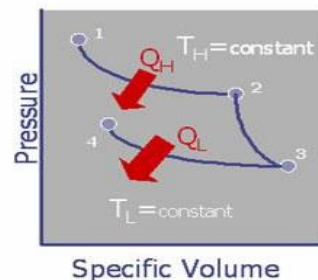
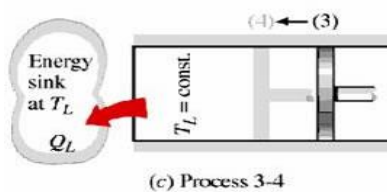
3) Third process: reversible isothermal compression from state 3 to state 4:

- ✓ This compression is from volume “ V_3 ” to volume “ V_4 ”
- ✓ Heat is released by the gas at the low temperature (T_L) and a compression work is done on the gas:

$$Q_L = nRT_L \ln \frac{V_4}{V_3}$$

AND

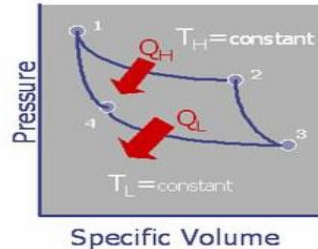
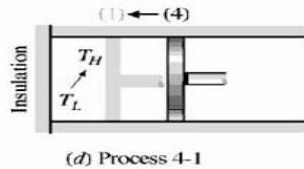
$$w_{3-4} = nRT_L \ln \frac{V_3}{V_4}$$



4) Fourth process: reversible adiabatic compression from state 4 to state 1:

- ✓ This compression is from volume “V₄” to volume “V₁”
- ✓ No heat is absorbed or released by the gas, but a compression work is done on the gas and the temperature will increase from “T_L” to “T_H”:

$$Q_4 = 0 \quad \text{AND} \quad w_4 = C_v (T_H - T_L)$$



5.3.2 The engine efficiency η

- The net work done by the system (w_{net}) is:

$$w_{net} = w_1 + w_2 + w_3 + w_4 = nR(T_L - T_H) \ln \frac{V_1}{V_2}$$

- The heat absorbed by the system is:

$$Q_H = nRT_H \ln \frac{V_2}{V_1}$$

- The engine efficiency denoted " η " is the ratio of work achieved to the heat absorbed:

$$\eta = \frac{w_{net}}{Q_H} = \frac{nR(T_L - T_H) \ln \frac{V_1}{V_2}}{nRT_H \ln \frac{V_2}{V_1}}$$

$$\eta = \left(1 - \frac{T_L}{T_H}\right) \times 100$$

- An 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 1×10^5 Pa is 100 °C and at 5×10^6 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

$$\eta = 1 - \frac{T_L}{T_H} \times 100$$

At 1×10^5 Pa	5×10^6 Pa
$\eta = 1 - \frac{313}{373} \times 100$	$\eta = 1 - \frac{313}{568} \times 100$
$\eta = 16.1\%$	$\eta = 44.9\%$

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 1×10^6 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 of 600 K. Knowing that $C_{m,p} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , w , q , network, and efficiency.

Solution

First: $(\Delta U)_1 = 0$
 $w_1 = nRT \ln \frac{P_2}{P_1} = 1 \times 8.314 \times 600 \times \ln \frac{1 \times 10^5}{1 \times 10^6} = -11486 \text{ J}$
 $q_1 = -w_1 = +11486 \text{ J}$

Second: $q_2 = 0$
 $(\Delta U)_2 = n \times C_{m,v} \Delta T$
 $(\Delta U)_2 = 1 \times (12.471) \times (300 - 600) = -3741 \text{ J}$
 $w_2 = (\Delta U)_2 = -3741 \text{ J}$

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: $q_4 = 0$
 $(\Delta U)_4 = n \times C_{m,v} \Delta T = n \times (C_{m,P} - R) \times \Delta T$
 $(\Delta U)_4 = 1 \times (20.785 - 8.314) \times (600 - 300) = +3741 \text{ J}$
 $w_4 = (\Delta U)_4 = +3741 \text{ J}$

Net: $\Delta U = (\Delta U)_1 + (\Delta U)_2 + (\Delta U)_3 + (\Delta U)_4 = 0$
 $w = w_1 + w_2 + w_3 + w_4 = -5743 \text{ J}$
 $q = q_1 + q_2 + q_3 + q_4 = +5743 \text{ J}$

$\eta = 1 - \frac{T_L}{T_H} \times 100 = 1 - \frac{300}{600} \times 100 = 50\% \quad \text{OR} \quad \eta = \frac{w_{\text{net}}}{Q_H} = \frac{5743}{11486} = 0.50$

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 $C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , w , q , network, and efficiency

5.3.3 The consequences of the Carnot's cycle

The equation ($\eta = 1 - \frac{T_L}{T_H} \times 100$) reveals that:

- 1) Efficiency depends on the initial and final temperature not on the nature of the gas
- 2) Efficiency can be 100% only if $T_L = 0 \text{ K}$ or $T_H = \infty \text{ K}$. Both are impossible. Therefore, it is impossible for the efficiency to be unity (100%)
- 3) It is impossible for heat absorbed to be converted completely to work
- 4) Some of the heat absorbed is always wasted doing no work

5.4 Spontaneity: Spontaneous and nonspontaneous processes

- Many observations suggest that changes can be divided into two classes:
 - 1) A **spontaneous change** is a change that occurs 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 without external interferes
 - 2) A **nonspontaneous change** is a change that can be done only by doing work. It is a change which has no natural tendency to occur by itself
 - 3) The reverse of any spontaneous process cannot occur by itself but it can be achieved 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
 - ✓ water can be decomposed by the passage of an electric current
- 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
- ✓ CO₂ formation from burning C in O₂ is a spontaneous process, but dissociation of CO₂ into C and O₂ 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 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) Natural processes are all spontaneous
 - 2) Occurrence of any process must obey the *first law of thermodynamics*
 - 3) The first law cannot predict the direction a process will take but 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 does not the nonspontaneous process occur?
- The solution to this dilemma is given by the concept of a property of systems named **“entropy”** which was not known to humans before 1857

5.3 The concept of entropy: A new name of newly known property

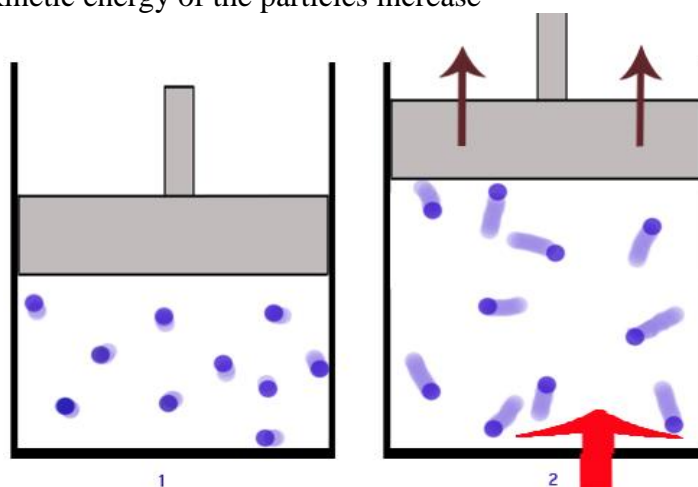
5.3.1 The precursory to the second law

- Many trials were done to invent a heat engine that convert all the heat it absorbed into a useful work but with no success. Work achieved is always less than heat supplied
- Carnot postulated the concept that **“some heat is always lost in the conversion into work”**, and that the efficiency of the heat engines depends only on the temperatures of the heat reservoirs between which the engine is working not on the types of the substance
- In the early 1850s, Rudolf Clausius introduced the argument that in any irreversible process a small amount of heat is lost across the system boundary. He developed 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)

- Heat absorbed in a heat engine is converted partially to work. The question is: *what happened to the rest of the absorbed heat?*

- Why is the work done reversibly higher than that done irreversibly?
- The figure below shows a gas in a cylinder with a piston 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 and we say that heat absorbed by the gas lead the gas to achieve work
- **Other particles** just gain higher speed and higher energy but do not do work
- These particles used the heat they absorbed only to increase their random movement and chaos
- The result reveals that the work done is less than the heat that absorbed
- This is the answer to why all heat is not 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

- Once randomness was realized during the 19th century, scientists paid more attention to it
- Clausius discovered that any system has a property he named “ENTROPY”¹ and chosen the symbol "S" for it
- Entropy is the thermodynamic function of randomness
- The change in the system entropy " ΔS_{syst} " is given by:

$$\Delta S_{\text{syst}} = \frac{q_{\text{rev}}}{T}$$

- It is clear from the above equation that:
 - 1) ΔS_{syst} increases when the system absorbs heat
 - 2) The numerical value of ΔS increases as q increases and T decreases
 - 3) Because the surroundings are very huge, when compared with the system, we can consider its absorbance or release of heat to be reversible:

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T}$$

- 4) Change in the universe entropy is:

$$\Delta S_{\text{univ}} = \Delta S_{\text{syst}} + \Delta S_{\text{surr}}$$

- 5) Because ΔS 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}
- 6) Values of ΔS are small when compared to those of ΔU or ΔH of the same change

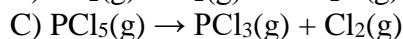
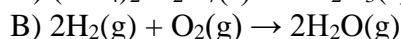
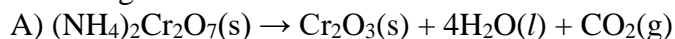
¹ Entropy is a new word originated from two Greece words that mean "energy in change."

- 7) Any change that increases randomness (chaos and disorder) causes an increase in the entropy, and the ΔS will be positive
- 8) If a change, such as decomposition, increases number of substances entropy will increase and ΔS will be positive
- 9) Because particles of matter in its solid state is in a much order than in its liquid state and much more than in its gaseous state, entropy is arranged as follows:

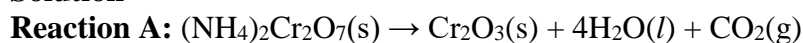
$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$$

Example 5.3

Determine and rationalize if the entropy change will be positive or negative for the following reactions:

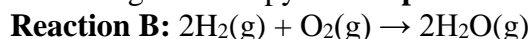


Solution



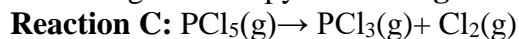
The reactant side contains only one mole of a solid while the product side is not only six moles but one of them is a gas.

The change in entropy will be **positive**.



There are 3 moles on the reactant side and only 2 on the product side.

The change in entropy will be **negative**.

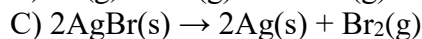
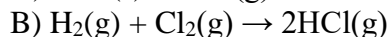
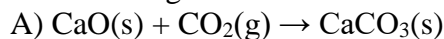


There are more moles on the product side than on the reactant side.

The change in entropy will be **positive**.

Practice exercise

Determine and rationalize if the entropy change will be positive, negative or zero for the following reactions:



5.5 The Second Law statement

Statements that defines the second law are so many. Below are the most used:

- 1) Natural processes are all spontaneous
- 2) Heat cannot be transferred from a cold object to a hot object
- 3) Entropy of the universe always 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 ΔS° , in J/K, for the following changes:

- A) $\text{H}_2\text{O}(l, 373 \text{ K}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(g, 373 \text{ K}, 101325 \text{ Pa})$ $\Delta H = +40.85 \text{ kJ}$
 B) If the standard enthalpy of freezing of water equals -6.008 kJ/mol and the freezing point of water is 0°C , calculate the change in entropy as a result of freezing 44 g of water.

Solution

$$\text{A) } \Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_{\text{boiling}}} = \frac{40.85 \text{ kJ} \times 1000 \frac{\text{J}}{\text{kJ}}}{373 \text{ K}} = 109.5 \text{ J/K}$$

$$\text{B) } \Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}} = \frac{\frac{44 \text{ g}}{18 \frac{\text{g}}{\text{mol}}} \times -6.008 \frac{\text{kJ}}{\text{mol}} \times 1000 \frac{\text{J}}{\text{kJ}}}{273 \text{ K}} = -53.8 \text{ J/K}$$

Practice exercise

Calculate ΔS° , in J/K, for the following changes:

- A) $\text{CH}_3\text{OH}(l, 337.7 \text{ K}, 1 \text{ atm}) \rightarrow \text{CH}_3\text{OH}(g, 337.7 \text{ K}, 1 \text{ atm})$ $\Delta H = +38.3 \text{ kJ}$
 B) If the standard enthalpy of transition of Sn metal from the crystal structure α to the crystal structure β equals $+2.09 \text{ kJ/mol}$ and the transition point is 13°C , calculate the change in entropy as a result of transition 1.5 mol of Sn from α structure to β 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 5.5

The temperature and pressure of an ideal gas are changed from 27°C and 101325 Pa to 127°C and 135100 Pa . Calculate ΔS° . The gas quantity is $4.06 \times 10^{-4} \text{ mol}$.

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

Solution

This is a change in T and P of the same quantity of a gas at constant V:

$$C_p = n \times C_{m,p} = n \times (C_{m,v} + R) = n \times (1.5 \times R + R) = n \times 2.5 \times R$$

$$C_p = 4.06 \times 10^{-4} \text{ mol} \times 2.5 \times 8.314 \frac{\text{J}}{\text{mol K}} = 8.44 \times 10^{-3} \text{ J/K}$$

$$\Delta S_1 = C_p \ln \frac{T_2}{T_1} = 8.44 \times 10^{-3} \text{ J/K} \times \ln \frac{400}{300} = 2.43 \times 10^{-3} \text{ J K}^{-1}$$

$$\Delta S_2 = nR \ln \frac{P_1}{P_2} = 4.06 \times 10^{-4} \text{ mol} \times 8.314 \frac{\text{J}}{\text{mol K}} \times \ln \frac{101325}{135100} = -9.72 \times 10^{-4} \text{ J/K}$$

$$\Sigma \Delta S = \Delta S_1 + \Delta S_2 = (2.43 \times 10^{-3} \text{ J/K}) + (-9.72 \times 10^{-4} \text{ J/K}) = 1.458 \times 10^{-3} \text{ J/K}$$

Practice exercise

Knowing that $C_{v,m} = 12.471 \text{ J/K mol}$, calculate ΔS° for the following change:
 $100 \text{ cm}^3 \text{ Ar}(g, 25^\circ\text{C}, 101325 \text{ Pa}) \rightarrow 125 \text{ cm}^3 \text{ Ar}(g, 99.5^\circ\text{C}, 101325 \text{ Pa})$

Example 5.6

Knowing that $C_{m,v} = 1.5R$, calculate ΔS of the following change:

10 dm^3 ideal gas (27°C , 1 atm) \rightarrow 13.33 dm^3 ideal gas (127°C , 1 atm)

Solution

This is a change in temperature and volume of the same quantity of a gas at constant pressure:

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 10 \text{ dm}^3}{0.0821 \text{ atm} \frac{\text{dm}^3}{\text{mol K}} \times 300 \text{ K}} = \frac{1 \text{ atm} \times 13.33 \text{ dm}^3}{0.0821 \frac{\text{dm}^3}{\text{mol K}} \times 400 \text{ K}} = 0.406 \text{ mol}$$

$$C_v = n \times C_{v,m} = 0.406 \text{ mol} \times 1.5 \times 8.314 \text{ J/K mol} = 5.06 \text{ J/K}$$

$$\Delta S_1 = C_v \times \ln \frac{T_2}{T_1} = 5.06 \text{ J/K} \times \ln \frac{400}{300} = 1.46 \text{ J/K}$$

$$\Delta S_2 = n \times R \times \ln \frac{V_2}{V_1} = 0.406 \text{ mol} \times 8.314 \text{ J/mol K} \ln \frac{13.33}{10} = 0.970 \text{ J/K}$$

$$\Sigma \Delta S = \Delta S_1 + \Delta S_2 = 1.46 \text{ J/K} + 0.970 \text{ J/K} = 2.43 \text{ J/K}$$

Practice exercise

Knowing that $C_{m,v,\text{ideal gas}} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔS for the following change:
 $73.89 \text{ dm}^3 \text{ ideal gas (27 }^\circ\text{C, 1 atm)} \rightarrow 246.3 \text{ dm}^3 \text{ ideal gas (727 }^\circ\text{C, 1 atm)}$

5.6.2 Changes in entropy accompanying irreversible processes

- If the change occurs 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 ΔS is known at a certain temperature (T_1) it can be calculated at any other temperature (T_2) using the following equation:

$$\Delta S_2 = \Delta S_1 + \Delta C_p \ln \frac{T_2}{T_1}$$

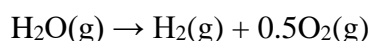
Example 5.7

If $\Delta S_{\text{dissoc,H}_2\text{O}}^\circ = + 44.404 \text{ J/K mol}$ and from the information below at 25°C :

Substance	H ₂ O(g)	H ₂ (g)	O ₂ (g)
$C_{m,p} / \text{J K}^{-1} \text{ mol}^{-1}$	33.56	28.83	29.12

Calculate $\Delta S_{\text{dissoc}}^\circ$ of 1 mole of H₂O(g) at 68°C .

Solution



$$\Delta C_p = \Sigma C_p(\text{p}) - \Sigma C_p(\text{r})$$

$$\Sigma C_p(\text{p}) = (1 \text{ mol} \times 28.83 \text{ J K}^{-1} \text{ mol}^{-1} + 0.5 \text{ mol} \times 29.12 \text{ J K}^{-1} \text{ mol}^{-1}) = 43.39 \text{ J/K}$$

$$\Sigma C_p(\text{r}) = 1 \text{ mol} \times 33.56 \text{ J K}^{-1} \text{ mol}^{-1} = 33.56 \text{ J K}^{-1}$$

$$\Delta C_p = 43.39 \text{ J/K} - 33.56 \text{ J K}^{-1} = 9.83 \text{ J/K}$$

$$\Delta S_2^\circ = \Delta S_1^\circ + \Delta C_p \ln \frac{T_2}{T_1}$$

$$\Delta S_{\text{dissoc,H}_2\text{O(g),341 K}}^\circ = + 44.404 \text{ J/K} + 9.83 \text{ J/K} \times \ln \frac{341 \text{ K}}{298 \text{ K}} = + 45.73 \text{ J/K}$$

Practice exercise

If $\Delta S_{\text{comb,CH}_4,25^\circ\text{C}}^\circ = + 200.0 \text{ J/K mol}$ and from the information at 25°C in the following table:

Substance	CO ₂ (g)	H ₂ O(L)	CH ₄ (g)	O ₂ (g)
$C_{m,p,25^\circ\text{C}} / \text{J K}^{-1} \text{ mol}^{-1}$	73.11	75.291	35.309	29.12

Calculate the standard entropy of combusting 48.0 g of methane ($\Delta S_{\text{comb}77^\circ\text{C}}^\circ$).

Questions and problems

1. Calculate the quantity of heat required to perform a 1000 J of work by an engine that operates between 300K and 400K.
2. Knowing that the boiling point of water at 1×10^5 Pa is 100 °C and at 5×10^6 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.
3. One mole 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 $C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , w , q , net work, and efficiency.
4. 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 of 600 K. Knowing that $C_{m,p} = 20.785 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , w , q , network, and efficiency.
5. Knowing that $\Delta H_{\text{fusion}}^\circ$, H_2O is $6.008 \text{ kJ mol}^{-1}$, calculate the entropy change as a result of melting (fusing or liquefying) 1 mol of ice at 0 °C and 101325 Pa. **OR:** Calculate ΔS° of the following change:
 $\text{H}_2\text{O}(s, 0 \text{ }^\circ\text{C}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(l, 0 \text{ }^\circ\text{C}, 101325 \text{ Pa}) \quad \Delta H = +6.008 \text{ kJ}$
6. Calculate ΔS° of the following change:
 $\text{H}_2\text{O}(l, 373 \text{ K}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(g, 373 \text{ K}, 101325 \text{ Pa}) \quad \Delta H = +40.85 \text{ kJ}$
7. Calculate ΔS° of the following change:
 $\text{Sn}(\alpha, 13 \text{ }^\circ\text{C}, 101325 \text{ Pa}) \rightarrow \text{Sn}(\beta, 13 \text{ }^\circ\text{C}, 101325 \text{ Pa}) \quad \Delta H = +2.09 \text{ kJ}$
8. Knowing that $C_{m,v} = 1.5R$, calculate ΔS° of the following change:
Ideal gas ($10 \text{ cm}^3, 27 \text{ }^\circ\text{C}, 101325 \text{ Pa}$) \rightarrow Ideal gas ($10 \text{ cm}^3, 127 \text{ }^\circ\text{C}, 135100 \text{ Pa}$)
9. Knowing that $C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔS° of the following change:
 $100^3 \text{ Ar}(g, 25 \text{ }^\circ\text{C}, 101325 \text{ Pa}) \rightarrow 125 \text{ cm}^3 \text{ Ar}(g, 99.5 \text{ }^\circ\text{C}, 101325 \text{ Pa})$
10. In an isolated flask with a negligible heat capacity, a 0.556 mol of solid water (ice) at 0 °C is added to 1.11 mol of liquid water at 90 °C. If the enthalpy of fusion of water is 5.98 kJ mol^{-1} , and the molar heat capacity of liquid water is $75.312 \text{ J }^\circ\text{C mol}^{-1}$, calculate the entropy changes of the system and the surroundings.
11. Knowing $C_{m,p,\text{H}_2\text{O}(L)} = 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{m,p,\text{H}_2\text{O}(s)} = 37.2 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{\text{fusion},\text{H}_2\text{O}} = 5980 \text{ J mol}^{-1}$ at 0 °C, calculate the entropy changes of the system, the surroundings, and the universe as a result of the following change:
 $\text{H}_2\text{O}(l, 263 \text{ K}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(s, 263 \text{ K}, 101325 \text{ Pa})$
12. Knowing $C_{m,p,\text{H}_2\text{O}(L)} = 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{m,p,\text{H}_2\text{O}(g)} = 33.58 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{\text{vap},\text{H}_2\text{O},100 \text{ }^\circ\text{C}} = 40660 \text{ J mol}^{-1}$, calculate ΔS_{univ} , ΔS_{sys} , and ΔS_{surr} as a result of:
 $\text{H}_2\text{O}(l, 298 \text{ K}, 1.01 \times 10^5 \text{ Pa}) \rightarrow \text{H}_2\text{O}(g, 398 \text{ K}, 5.00 \times 10^4 \text{ Pa})$
13. Two moles of an ideal gas expanded at 298 K to a volume that is 2.5 times its original volume. Calculate ΔS_{system} , $\Delta S_{\text{surroundings}}$, and $\Delta S_{\text{universe}}$ 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).
14. Knowing that $C_{m,v,\text{N}_2(g)} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate T_2 , V_1 , V_2 , ΔS_{system} , $\Delta S_{\text{surroundings}}$, and $\Delta S_{\text{universe}}$, of the following adiabatic irreversible change:
 $0.1 \text{ kg N}_2(g, 298 \text{ K}, 30 \text{ atm}) \rightarrow 0.1 \text{ kg N}_2(g, T_2, 10 \text{ atm})$
15. Knowing that $C_{p,m,\text{ideal gas}} = 2.5R$, calculate ΔS and V_2 of the following change:
 $10 \text{ dm}^3 \text{ ideal gas } (27 \text{ }^\circ\text{C}, 1 \text{ atm}) \rightarrow V_2 \text{ dm}^3 \text{ ideal gas } (127 \text{ }^\circ\text{C}, 1 \text{ atm})$

16. If 1 mol of an ideal gas expands isothermally at 27 °C to three times its original volume, calculate ΔS_{system} , and $\Delta S_{\text{surroundings}}$ if the process is carried out once isothermally and once freely.
17. Knowing that $C_{v,m} = 12.471 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔS° of the following change:
0.5 dm³ ideal gas(25 °C, 1 atm) → 1 dm³ ideal gas(323 °C, 1 atm)
18. Knowing that $\Delta H_{f,H_2O(L)}^\circ = -286 \text{ kJ mol}^{-1}$, calculate $\Delta S_{\text{surroundings}}^\circ$ as a result of the formation of 1 mol of water at 25 °C and 101325 Pa.



6. THE THIRD LAW OF THERMODYNAMICS



6. THE THIRD LAW OF THERMODYNAMICS (THE ABSOLUTE ENTROPIES)

6.1 The dilemma of C_p at temperatures close to 0 K

- The equation $\Delta S = C_p \ln \frac{T_{\text{final}}}{T_{\text{initial}}}$ shows how to calculate the change in entropy at constant pressure as a result of changing temperature from T_{initial} to T_{final}
- In fact, this equation is derived from the following equation:

$$\Delta S = \int_{T_{\text{initial}}}^{T_{\text{final}}} C_p \frac{T_{\text{final}}}{T_{\text{initial}}}$$

This equation is not correct unless we assume that the value of C_p is constant between these two temperatures

- We know that bringing a substance to a low temperature is not easy and to absolute zero temperature is impossible
- 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 problem because not knowing C_p means loosing ability to determine the value of ΔS
- The solution to this problem was provided in 1912 by Peter Debye
- Let us name the lowest temperature that can be reached for any substance “*Debye temperature*” and give it the symbol “ T_D ”
- Debye equation is written as:

$$\Delta S_{\text{from 0 K to } T_D} = \frac{C_{p,T_D}}{3}$$

At constant pressure, the increase in the entropy of any substance as a result of increasing its temperature from 0 K to T_D equals one third C_{p,T_D}

6.2 The absolute value of S at constant P at any temperature

- Any increase in the value of S of any substance, **at constant P**, resulting from its temperature being above 0 K can be determined as follows:

1) Increase of temperature from 0 K to T_D increases its entropy by $\Delta S_{0 \text{ K to } T_D}$:

$$\Delta S_{0 \text{ K to } T_D} = \frac{C_{p,T_D}}{3}$$

2) Changing the temperature of a substance from T_{initial} to T_{final} , at constant P, changes its entropy by $\Delta S_{T_{\text{initial}} \text{ to } T_{\text{final}}}$ which:

$$\Delta S_{T_{\text{initial}} \text{ to } T_{\text{final}}} = C_p \ln \frac{T_{\text{final}}}{T_{\text{initial}}}$$

3) If the substance undergoes a change in its physical phase, at constant P and T, the change in its entropy can be calculated by:

$$\Delta S_{\text{physical change}} = \frac{\Delta H_{\text{physical change}}}{T_{\text{physical change}}}$$

- In addition to whatever value the entropy has at 0 K, any other increase in the entropy, at constant P, can be determined using the above three equations
- The only remaining task is knowing the value of its entropy at 0K ($S_{0 \text{ K}}$) at the same pressure

6.3 The third law of thermodynamics

- Experimental data proves that entropies for all perfectly ordered crystalline materials must be the same at 0 K
- Because entropy is a measure of disorder, the absence of disorder means that the value of the entropy is zero

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

- The entropy of a perfectly crystallized solid at 0 K is zero:

$$S_{0\text{ K, perfectly ordered}} = 0$$

- The entropy of a non-perfectly crystallized solid at 0 K has a positive value:

$$S_{0\text{ K, disordered}} \neq 0 \neq \text{but } S_{0\text{ K, disordered}} = \text{positive value}$$

The positive value of the entropy of any substance at 0 K is called “**the residual entropy**” and is given the symbol “**S_{res}**”. Therefore, in this case:

- The value of S_{res} can be evaluated once we have a good knowledge of the so called “statistical entropy” which is a part of the “statistical thermodynamics”
- Examples of the values of residual entropy are:

$$S_{\text{res, H}_2\text{O(s)}} = 3.4 \text{ J/K mol and } S_{\text{res, CO(s)}} = 5.8 \text{ J/K mol}$$

6.5 The third law uses

- The statement of the third law denies the existence of total order and the absence 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 chaos

- At standard pressure, the entropy of any substance at 0 K is S₀^o which has a positive value unless the substance is totally ordered with no chaos
- Above 0 K, the entropy of any substance must be more than S₀^o by ΔS
- At standard pressure if the temperature is T the entropy is S_T^o
- The value of S_T^o is more than the value S₀^o by ΔS^o:

$$S_T^o = S_0^o + \Delta S^o$$

$$S_T^o = S_0^o + \int_0^T C_p \frac{dT}{T}$$

- Third law reveals the following aspects:
 - ✓ The value of the residual entropy (S_{res}) can be determined by some very complicated calculations
 - ✓ The heat capacity of any substance at constant pressure, C_p, can be determined at any temperature except below Debye temperature, T_D

6.6 Calculating the absolute entropy at any temperature

The value of the absolute entropy can be calculated at any temperature using the heating (or cooling) curves shown in the figure below. Before reading the following discussion, it is very helpful to look at and inspect the heating curve which consists of the following seven stages

Stage 1: The stage of the residual entropy “S₀”, which is the value of S at 0K

If the substance is 100% ordered with no deformation,

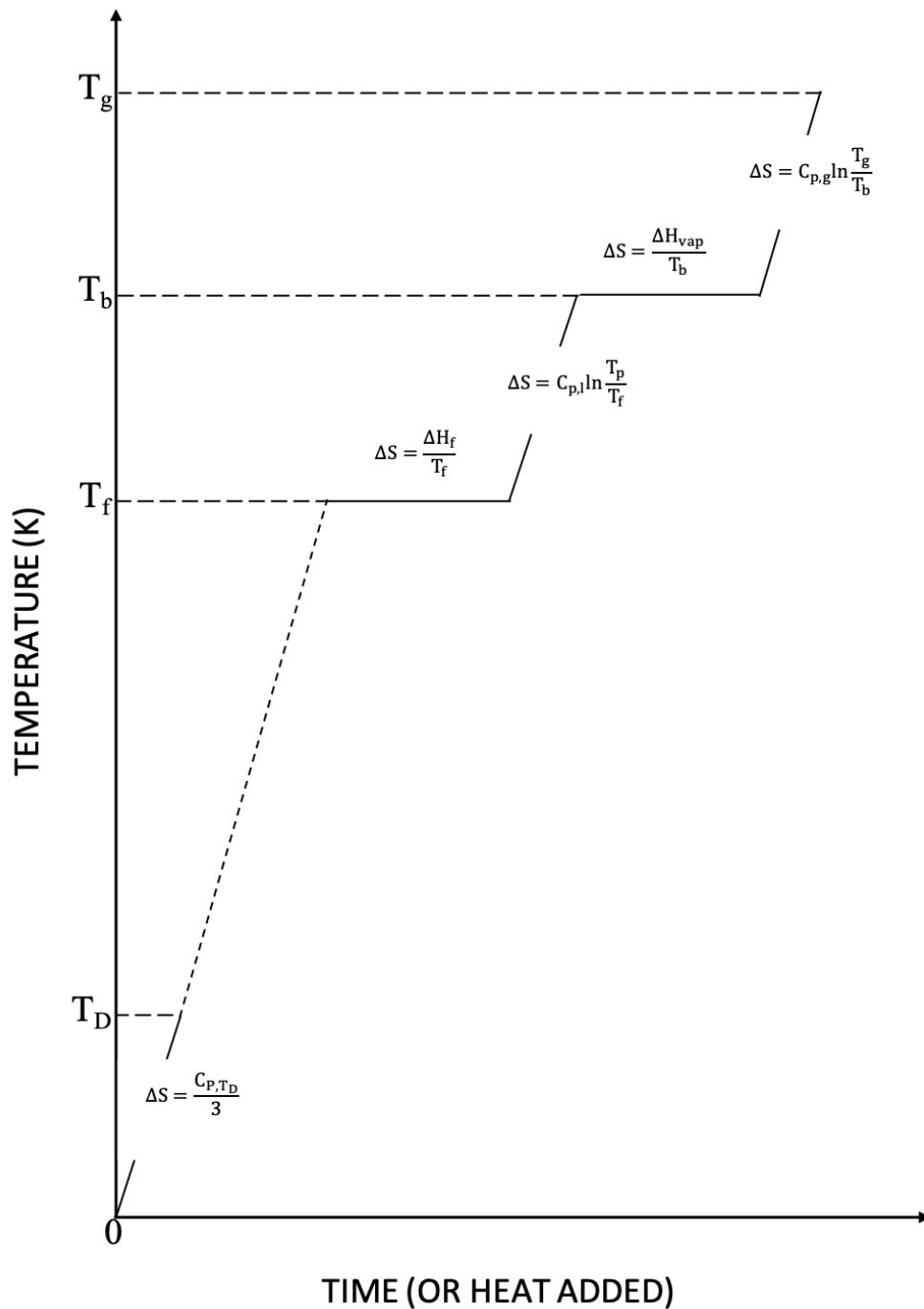
$$S_0 = 0$$

If the substance is not 100% ordered,

$$S_0 = S_{\text{res}}$$

Stage 2: The stage of increasing entropy resulting from increasing temperature from 0 K to T_D, “ΔS_{0→T_D”}

$$\Delta S_{0 \rightarrow T_D} = \frac{C_{p, T_D}}{3}$$



HEATING CURVE OF A SUBSTANCE FROM ABSOLUTE ZERO TEMPERATURE (0K) TO A HIGH TEMPERATURE (T_g), WHICH IS HIGHER THAN BOLING POINT

Stage 3: The stage of increasing entropy resulting from increasing temperature from T_D to the fusion (melting) point " $\Delta S_{T_D \rightarrow T_{fus}}$ "

This depends on the number of crystalline phases the substance has. The above heating curve is for a substance of only one-crystalline phase

✓ If the substance has only one solid phase, as temperature increases from T_D to T_{fus} its entropy increases by " $\Delta S_{T_D \rightarrow T_{fus}}$ ":

$$\Delta S_{T_D \rightarrow T_{fus}} = C_{p,s} \ln \frac{T_{fus}}{T_D}$$

- ✓ If the substance has two solid phases, say α and β , its entropy increases as a result of temperature increase from T_D to $T_{\alpha \rightarrow \beta}$ which is the temperature at which it starts changing from the α phase to the β phase. The value of this increase is " $\Delta S_{T_D \rightarrow T_{\alpha \rightarrow \beta}}$ ":

$$\Delta S_{T_D \rightarrow T_{\alpha \rightarrow \beta}} = C_{p,\alpha} \ln \frac{T_{\alpha \rightarrow \beta}}{T_D}$$

- ✓ The increase in entropy accompanying the change from the α phase to the β phase at the temperature $T_{\alpha \rightarrow \beta}$ 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 resumes increasing from $T_{\alpha \rightarrow \beta}$ to the fusion temperature, T_{fus} . This increase in temperature increases the entropy by " $\Delta S_{T_{\alpha \rightarrow \beta} \rightarrow T_{\text{fus}}}$ ":

$$\Delta S_{T_{\alpha \rightarrow \beta} \rightarrow T_{\text{fus}}} = C_{p,\beta} \ln \frac{T_{\text{fus}}}{T_{\alpha \rightarrow \beta}}$$

(Note: 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 resulting from changing the substance from its solid phase to its liquid phase at its fusion point " ΔS_{fus} "

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}}}$$

Stage 5: The increase in entropy resulting from increasing temperature of the liquid substance from its fusion point to its boiling point " $\Delta S_{T_{\text{fus}} \rightarrow T_b}$ "

$$\Delta S_{T_{\text{fus}} \rightarrow T_b} = C_{p,l} \ln \frac{T_b}{T_{\text{fus}}}$$

Stage 6: The increase in entropy resulting from changing the substance from its liquid state to its gaseous state at its boiling point " ΔS_{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_{gas} ". This increase is " $\Delta S_{T_b \rightarrow T_{\text{gas}}}$ "

$$\Delta S_{T_b \rightarrow T_{\text{gas}}} = C_{p,g} \ln \frac{T_{\text{gas}}}{T_b}$$

Heating curves could start from any initial temperature and end at any final higher temperature. They do not require that initial temperature is 0 K and the final temperature is above boiling point.

Example 6.1

A solid substance is found to be in perfect crystals at 0 K. It is heated from 0 K up to the temperature T_g above its boiling point. The substance, in its solid state, has two crystalline forms **A** and **B**. **A** is the form at low temperatures and **B** is the form at high temperatures.

First: Write the mathematical equations for all changes in the value of the entropy

Second: Write the equation that illustrates the value of its absolute entropy at T_g , (S_{T_g})

Solution

First:

- 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 K to $T_{A \rightarrow B}$: $\Delta S_2 = C_{p,B} \ln \frac{T_{A \rightarrow B}}{T_D}$
- 4) From solid B to solid A at $T_{B \rightarrow A}$: $\Delta S_3 = \frac{\Delta H_{A \rightarrow B}}{T_{A \rightarrow B}}$
- 5) From $T_{A \rightarrow AB}$ to T_{fusion} : $\Delta S_4 = C_{p,A} \ln \frac{T_{\text{fusion}}}{T_{A \rightarrow B}}$
- 6) From solid B to liquid at T_{fusion} : $\Delta S_5 = \frac{\Delta H_{\text{fusion}}}{T_{\text{fusion}}}$
- 7) From T_{fusion} to T_{boiling} : $\Delta S_6 = C_{p,l} \ln \frac{T_{\text{boiling}}}{T_{\text{fusion}}}$
- 8) From liquid to gas at T_{boiling} : $\Delta S_7 = \frac{\Delta H_{\text{vaporization}}}{T_{\text{boiling}}}$
- 9) From T_{boiling} to T_g : $\Delta S_8 = C_{p,g} \ln \frac{T_g}{T_{\text{boiling}}}$

$$\Delta S_{\text{total}} = \Sigma \Delta S = 0 + \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 + \Delta S_5 + \Delta S_6 + \Delta S_7 + \Delta S_8$$

Second:

$$(\Delta S_{\text{total}} = S_{T_g} - S_o). \text{ Therefore, } S_{T_g} = \Delta S_{\text{total}} + S_o = \Delta S_{\text{total}} + 0 = \Delta S_{\text{total}}$$

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_f) and below its boiling point (T_b). The substance, in its solid state, has only one crystalline forms. Write the equations that illustrate how its absolute entropy at T_l (S_{T_l}) can be determined.

6.7 Calculating ΔS of chemical reactions

1. Knowing S° of substances paved the road to obtain the change in the entropy as result of any chemical or physical change
2. Values of S° are usually listed in thermodynamic tables
3. As the standard enthalpy of formation of reactants and products enables us to calculate the standard change in enthalpy of any reaction $\Delta H_{\text{rxn}}^\circ$, S° values of reactants and products enables us to calculate the standard change in entropy for any reaction ΔS° using the following equation:

$$\Delta S^\circ = \Sigma S_{\text{products}}^\circ - \Sigma S_{\text{reactants}}^\circ$$

4. The table below shows Values of S° for some substances

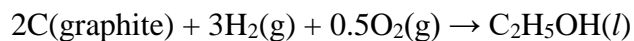
Substance	S° [J/(mol·K)]	Substance	S° [J/(mol·K)]	Substance	S° [J/(mol·K)]
Gases		Liquids		Solids	
He	126.2	H ₂ O	70.0	C (diamond)	2.4
H ₂	130.7	CH ₃ OH	126.8	C (graphite)	5.7
Ne	146.3	Br ₂	152.2	LiF	35.7
Ar	154.8	CH ₃ CH ₂ OH	160.7	SiO ₂ (quartz)	41.5
Kr	164.1	C ₆ H ₆	173.4	Ca	41.6
Xe	169.7	CH ₃ COCl	200.8	Na	51.3
H ₂ O	188.8	C ₆ H ₁₂ (cyclohexane)	204.4	MgF ₂	57.2
N ₂	191.6	C ₈ H ₁₈ (isooctane)	329.3	K	64.7
O ₂	205.2			NaCl	72.1
CO ₂	213.8			KCl	82.6
I ₂	260.7			I ₂	116.1

Example 6.2

From the information in the table below:

Substance	C ₂ H ₅ OH(l)	C(graphite)	H ₂ (g)	O ₂ (g)
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	160.7	5.7	130.684	205.1

Calculate, in the same units, the standard entropy of formation of liquid ethanol (ΔS_f°).

Solution

$$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$$

$$\Sigma S^\circ(\text{products}) = 1 \text{ mol} \times 160.7 \text{ J/K mol} = 160.7 \text{ J/K}$$

$$\Sigma S^\circ(\text{reactants}) = (2 \text{ mol} \times 5.7 \frac{\text{J}}{\text{K mol}} + 3 \text{ mol} \times 130.684 \frac{\text{J}}{\text{K mol}} + 0.5 \text{ mol} \times 205.138 \frac{\text{J}}{\text{K mol}})$$

$$\Sigma S^\circ(\text{reactants}) = 506.021 \frac{\text{J}}{\text{K}}$$

$$\Delta S^\circ = 160.7 \frac{\text{J}}{\text{K}} - 506.021 \frac{\text{J}}{\text{K}} = -345.321 \frac{\text{J}}{\text{K}}$$

Practice exercise

From the information in the table below:

Substance	H ₂ O(g)	H ₂ (g)	O ₂ (g)
S° / J K ⁻¹ mol ⁻¹	188.83	130.684	205.1

Calculate, in the same units, the standard entropy of dissociation of water vapor ($\Delta H S_{\text{dissoc}}^\circ$).

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° , in $\text{J K}^{-1} \text{mol}^{-1}$, of $\text{C}_2\text{H}_5\text{OH(L)} = 160.7$, $\text{C(graphite)} = 5.7$, $\text{H}_2(\text{g}) = 130.684$, $\text{O}_2(\text{g}) = 205.1$, calculate, in the same units, the standard entropy of formation of liquid ethanol ($\Delta H_{S_f}^\circ$).
4. At standard pressure, solid N_2 exist in α crystalline form below 35.61 K, and in β 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 °C:

$$S_0^\circ = 0$$

Its absolute entropy when it is in its α crystalline at 35.51 K (S_α°) is higher than S_0° by 27.17 J K^{-1} .

It changes from α to β at 35.51 K.

$$\Delta H_{\alpha \rightarrow \beta}^\circ = 228.9 \text{ kJ mol}^{-1}$$

$$C_{p,m,\beta} = 40.822 \text{ kJ mol}^{-1}$$

$$T_{\text{fus}} = 63.14 \text{ K}$$

$$\Delta H_{\text{fus}}^\circ = 720.9 \text{ kJ mol}^{-1}$$

$$C_{p,L} = 56.318 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_b = 77.32 \text{ K}$$

$$\Delta H_{\text{vap}}^\circ = 5.535 \text{ kJ mol}^{-1}$$


$$C_{p,g} = 29.055 \text{ J K}^{-1} \text{ mol}^{-1}$$

5. From the following table:


Substance	$\text{H}_2\text{O(g)}$	$\text{H}_2(\text{g})$	$\text{O}_2(\text{g})$
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	188.83	130.684	205.1
$C_{m,p} / \text{J K}^{-1} \text{mol}^{-1}$	33.56	28.83	29.12

Calculate the standard entropy of dissociation of water vapor at 68 °C ($\Delta H_{S_{\text{dissociation}}}^\circ$).

6. Knowing that the absolute entropy (S) of 1 mol of a gas at 298 K is $146 \text{ J K}^{-1} \text{mol}^{-1}$, and $C_{p,m} = 20.9 \text{ J K}^{-1} \text{mol}^{-1}$, calculate its value at 500 K at the same pressure.
7. Knowing that $C_{p,m,\text{ideal gas}} = 23.7 \text{ J K}^{-1} \text{mol}^{-1}$, calculate ΔS and for:
 $3 \text{ mol ideal gas (27 °C, 1 atm)} \rightarrow 3 \text{ mol ideal gas (727 °C, 1 atm)}$



7. THE FREE ENERGY: THE GIBBS AND THE HELMHOLTZ FREE ENERGIES



7. THE FREE ENERGY: THE GIBBS AND THE HELMHOLTZ FREE ENERGIES

7.1 The concept of free energy

- The total energy of the system is its internal energy “U”
- The portion of U that is available to perform thermodynamic work is the free energy
- The energy that cannot be used to perform thermodynamic work is given by the entropy of the system multiplied by its temperature “S × T”
- “S × T” is a thermodynamic state function

7.2 The Gibbs free energy

- One of the problems with entropy calculations is that **we must work out two entropy changes (that in the system and that in the surroundings), and then consider the sign of their sum**
- The **Gibbs energy, G**, (it also referred to as the “Gibbs free energy”) is:

$$G = H - TS$$

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

The restriction is that the changes in “G_{sys}” **must be at constant “P” and “T”**

- Because H, T, and S are state functions, G is a state function

7.3 Total entropy and free energy as spontaneity indicators

- The condition for a process to be spontaneous changes is either:
 $\Delta S_{\text{universe}} > 0$ (under no conditions) **OR** $\Delta G_{\text{sys}} < 0$ (at constant T and P)
- It must be remembered that when a system Gibbs energy decreases the entropy of both the system and its surroundings increases
- **Nonexpansion work**, is any other work arising from the system expansion. It may include electrical or mechanical work
- The value of ΔG for a process gives the maximum nonexpansion work that can be extracted from the process at constant temperature and pressure
- To demonstrate this property, we need to combine the First and Second Laws, and we find at constant temperature and pressure:

$$\Delta G_{\text{sys}} = w'_{\text{max}}$$

- The experimental results show that for the formation of 1 mol H₂O(l) at 25°C and 1 bar, $\Delta H = -286$ kJ and $\Delta G = -237$ kJ:
 - ✓ The two values of ΔH and ΔG mean that up to 237 kJ of nonexpansion work can be extracted from this reaction
 - ✓ If the reaction takes place in a fuel cell, then up to 237 kJ of electrical energy can be generated for each mole of H₂O produced
 - ✓ If no attempt is made to extract any energy as work, then 286 kJ of energy will be produced as heat
 - ✓ If some of the energy released is used to do work, then up to 237 kJ 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? ΔG of the oxidation of 1.0 mol C₆H₁₂O₆(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 ΔG .

$2828 \times 10^3 \text{ J}$ is released by consuming 1 mole of glucose

2.943 J is released by consuming n mole of glucose

$$n = \frac{2.943 \text{ J} \times 1 \text{ mol}}{2828000 \text{ J}} = 1.0407 \times 10^{-6} \text{ mol}$$

$$m = n \times M = 1.0407 \times 10^{-6} \text{ mol} \times 180 \text{ g/mol}$$

$$m = 1.9 \times 10^{-4} \text{ g} = 0.19 \text{ mg}$$

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 thermodynamics, operates at about 25 W ($1 \text{ W} = 1 \text{ J s}^{-1}$). What mass of glucose must be consumed to sustain that power output for an hour?

- If we know the Gibbs energy, then we know the maximum nonexpansion work that we can obtain by doing the reaction

- ❖ The physical significance of G comes from its definition “ $G = H - TS$ ”
- ❖ “ H ” is a measure of the energy that can be obtained from the system as heat
- ❖ “ TS ” is a measure of the energy stored in the random motion of the system particles
- ❖ Work is the energy transferred in an orderly way not from that stored randomly
- ❖ The difference between the total stored energy and the energy stored randomly, i.e. “ $H - TS$ ”, is available for doing work and is called the **Gibbs energy**
- ❖ “ G ” is the energy stored in the orderly motion and of the particles in the system

7.4 The Helmholtz free energy

- The previous discussion on the Gibbs free energy (G) also applies on the Helmholtz free energy (A)
- The difference between the Gibbs free energy (G) and the Helmholtz free energy (A) is that:
 - ✓ “ G ” is the free energy of the system at constant temperature and pressure
“ G ” is the maximum nonexpansion work that can be extracted from the process at constant temperature and pressure
 $\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$ (T and P are constant)
 - ✓ “ A ” is the free energy of the system at constant temperature and volume
“ A ” is the maximum nonexpansion work that can be extracted from the process at constant temperature and volume
 $\Delta A_{\text{sys}} = \Delta U_{\text{sys}} - T\Delta S_{\text{sys}}$ (T and V are constant)

7.5 Comparison between the Gibbs and the Helmholtz free energies

The table below compares between Gibbs and the Helmholtz free energies:

	HELMHOLTZ FREE ENERGY	GIBBS FREE ENERGY
1	$A = U - TS$	$G = H - TS$
2	$\Delta A = \Delta U - T\Delta S$	$\Delta G = \Delta H - T\Delta S$
3	$dA = -SdT - PdV$	$dG = -SdT + VdP$
4	If $dV = 0$ $\left(\frac{\partial A}{\partial T}\right)_V = -S$	If $dP = 0$ $\left(\frac{\partial G}{\partial T}\right)_P = -S$
5	If $dT = 0$ $\left(\frac{\partial A}{\partial V}\right)_T = -P$	If $dT = 0$ $\left(\frac{\partial G}{\partial P}\right)_T = +V$

6	$\Delta A = nRT \ln \frac{V_1}{V_2}$	$\Delta G = nRT \ln \frac{V_1}{V_2}$
	$\Delta A = nRT \ln \frac{P_2}{P_1}$	$\Delta G = nRT \ln \frac{P_2}{P_1}$
	$\Delta A = nRT \ln \frac{C_2}{C_1}$	$\Delta G = nRT \ln \frac{C_2}{C_1}$
7	$\Delta A - \Delta G = - (P_2V_2 - P_1V_1) = - nR\Delta T = - RT\Delta n_g$	

7.6 Spontaneity and free energy

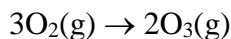
- Whether a process is spontaneous or not is a vital issue to chemists
- Systems seek the lowest possible level of energy and the highest level of entropy
- This tempts us to judge a process that causes a decrease in energy **or** an increase in entropy to be spontaneous
- However, there are many spontaneous cases that involve an increase in energy and a decrease in entropy, for example:
 - ✓ Vaporization of sea water involves increase in energy yet it is a spontaneous process
 - ✓ Plants growing involve a decrease in entropy yet it is spontaneous.
- Free energy is the solution to this dilemma
- From the equation " $\Delta A = \Delta U - T\Delta S$ " or " $\Delta G = \Delta H - T\Delta S$ ", we see how both ΔU or ΔH , and entropy, ΔS , ally in the two equations to restrict spontaneity to these processes that insures only negative values for ΔA or ΔG
- The reason behind this is:

"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 ΔU (or ΔH) and ΔS determines whether the process is spontaneous, nonspontaneous, or at equilibrium:
 - ✓ When ΔU (or ΔH) is positive and ΔS is negative the process will always be nonspontaneous.
 - ✓ When ΔU or (ΔH) is negative and ΔS is positive the process will always be spontaneous.
 - ✓ When both ΔU (or ΔH) and ΔS are positive the process will only be spontaneous at high temperatures.
 - ✓ When both ΔU or (ΔH) and ΔS are negative the process will only be spontaneous at low temperatures.

ΔU or ΔH SIGN	ΔS SIGN	ΔA or ΔG SIGN	TYPE OF PROCESS
+	+	+	NONSPONTANEOUS
		0	EQUILIBRIUM
		-	SPONTANEOUS
+	-	+	NONSPONTANEOUS
-	+	-	SPONTANEOUS
-	-	+	NONSPONTANEOUS
		0	EQUILIBRIUM
		-	SPONTANEOUS

Example 7.2

From the information in the table below, calculate ΔG of the following reaction:



	$\text{O}_3(\text{g})$	$\text{O}_2(\text{g})$
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	142.7	0
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	238.93	205.138

Solution

$$\Delta H_{\text{rxn}}^\circ = \sum \Delta H_{f,\text{products}}^\circ - \sum \Delta H_{f,\text{reactants}}^\circ$$

$$\Delta H_{\text{rxn}}^\circ = (2 \text{ mol} \times 142.7 \text{ kJ mol}^{-1}) - (2 \text{ mol} \times 0) = 285.4 \text{ kJ}$$

$$\Delta S_{\text{rxn}}^\circ = \sum S_{\text{products}}^\circ - \sum S_{\text{reactants}}^\circ$$

$$\Delta S_{\text{rxn}}^\circ = \sum 2 \text{ mol} \times 238.93 \text{ J K}^{-1} \text{ mol}^{-1} - \sum 3 \text{ mol} \times 205.138 \text{ J K}^{-1} \text{ mol}^{-1}$$

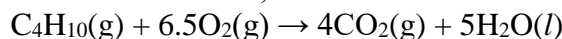
$$\Delta S_{\text{rxn}}^\circ = -137.554 \text{ J K}^{-1}$$

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

$$\Delta G_{\text{rxn}}^\circ = 285.4 \text{ kJ} - 298 \text{ K} \times -137.554 \text{ J K}^{-1} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = +326.39 \text{ kJ}$$

Practice exercise

From the information in the table below, calculate ΔG of the following reaction:



	$\text{C}_4\text{H}_{10}(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	-126.5	0	-393.5	-285.8
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	310.23	205.1	213.74	69.91

7.7 Fugacity, activity, and standard state of matter

On page 17, we discussed "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

7.7.1 Fugacity

- Applying $\left(\frac{\partial G}{\partial P}\right)_T = +V$ to the perfect gas leads to $\left(\Delta G = n \times R \times T \times \ln \frac{P_{\text{final}}}{P_{\text{initial}}}\right)$:

$$\left(\frac{\partial G}{\partial P}\right)_T = +V$$

$$\Delta G = \int_{\text{initial}}^{\text{final}} V dP$$

$$V = \frac{nRT}{P}$$

$$\Delta G = \int_{\text{initial}}^{\text{final}} n \times R \times T \times \frac{dP}{P}$$

$$\Delta G = n \times R \times T \times \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

- Last equation is only correct for the perfect (ideal) gases where $V = \frac{nRT}{P}$ but not for the real (nonideal gases) where $V \neq \frac{nRT}{P}$. Therefore, for nonideal gases:

$$\Delta G \neq n \times R \times T \times \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

- 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 "fugacity" which means "scaping or fleeing tendency"
- Unit of "f" is the same as the unit of "P"
- The relation between "f" and "P" contains a correction factor called **fugacity coefficient** that allows it to replace pressure in the ideal gas law
- Fugacity of a gas is related to its pressure by the following equation

$$f = \gamma_g P$$

- For perfect and for real gases:

$$\Delta G = nRT \ln \frac{f_{\text{final}}}{f_{\text{initial}}}$$

$$\Delta G = nRT \ln \frac{\gamma_{\text{g,final}} \times P_{\text{final}}}{\gamma_{\text{g,initial}} \times P_{\text{initial}}}$$

- ✓ For perfect gases, $\gamma = 100\% = 1$ and $f = P$. Therefore:

$$\Delta G = nRT \ln \frac{f_{\text{final}}}{f_{\text{initial}}} = nRT \ln \frac{P_{\text{final}}}{P_{\text{initial}}}$$

- ✓ For real gases, $\gamma < 1$ and $f = \gamma_g P$, therefore $f < P$. Therefore:

$$\Delta G = nRT \ln \frac{f_{\text{final}}}{f_{\text{initial}}} = nRT \ln \frac{\gamma_{\text{g,final}} \times P_{\text{final}}}{\gamma_{\text{g,initial}} \times P_{\text{initial}}}$$

7.7.2 Activity

- For gases, we know that:

$$\Delta G = G_{\text{final}} - G_{\text{initial}} = nRT \ln \frac{f_{\text{final}}}{f_{\text{initial}}}$$

- If the system's initial state is its standard state, where its free energy is G° and its fugacity is f° , if this system changes to a final state, where its free energy is G and its fugacity is f , then:

$$G - G^\circ = nRT \ln \frac{f}{f^\circ}$$

$$G = G^\circ + RT \ln \left(\frac{f}{f^\circ}\right)^n$$

Where $\frac{f}{f^\circ}$ is called **activity** and symbolized α :

$$\alpha = \frac{f}{f^\circ}$$

$$G = G^\circ + RT \ln (\alpha)^n$$

- If the system is at its standard state, its free energy (G) is (G°):

$$G = G^\circ$$

Therefore:

$$RT \ln (\alpha)^n = 0$$

- The last equation means that $\alpha = 1$ and the substance is in its standard state
- The conclusion:

The standard state of a system is its state at activity equals 1 ($\alpha = 1$)

7.7.3 Standard state of substances

- From the previous discussion, the definition of "standard state" is as follows:

THE STANDARD STATE OF ANY SUBSTANCE IS ITS STATE WHEN ITS ACTIVITY IS EQUALS UNITY

- The value of activity is related to concentration as follows:

$$\alpha = \gamma_{\text{molarity}} \times \text{molarity} = \gamma_{\text{molality}} \times \text{molality} = \gamma_{\text{mol fraction}} \times \text{mol fraction}$$

- When the system is solute in a solvent at infinite dilution, no interactions between system's particles exist, and its activity's coefficient equals to unity. This makes its activity equal to its concentration
- The question now is: could a substance activity be equal to unity? The answer is yes, and this differs from a substance to another 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 this depends on whether the gas is ideal or nonideal.

- ✓ **If the pure gas is ideal:**

$$\alpha = 1 \text{ when } f = 1 \text{ atm}$$

And because:

$$f = \gamma_g P$$

We find that:

$$f = 1 \text{ atm when } p = 1 \text{ atm}$$

And because $\gamma_{\text{ideal gas}} = 1$, the conclusion is as follows:

The ideal gas is in its standard state when $\alpha = 1$ which occurs when $P = 1 \text{ atm}$

✓ **If the pure gas is real (nonideal):**

$$a = 1 \text{ when } f = 1 \text{ atm}$$

And because:

$$f = \gamma_g P$$

we find that:

$$f = 1 \text{ atm when its } P > 1 \text{ atm}$$

And because $\gamma_g < 1$, the conclusion is as follows:

The real gas is in its standard state when $\alpha = 1$ 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; if it is less deviated its pressure becomes closer to its fugacity. At 1 atm pressure the value of the gas fugacity coefficient is so closed to unity. Therefore:

The real gas is in its standard state when $\alpha = 1$ which occurs when $P = 1 \text{ atm}$

2) **WHEN THE SUBSTANCE IS A PURE LIQUID:**

The effect of pressure on liquids' properties is negligible. This means that its particles are 100% active at moderate pressures. Therefore:

Pure liquids are in its standard state when $\alpha = 1$ which occurs when $P = 1 \text{ atm}$

3) **WHEN THE SUBSTANCE IS A PURE SOLID:**

Many solids exist in more than one crystalline form and its particles are more active in its most stable crystalline form. The effect of moderate pressure on solids' properties is small and neglected. Therefore:

Any pure solid in its most stable crystal form becomes in its standard state when $\alpha = 1$ which occurs when $P = 1 \text{ atm}$

4) **WHEN THE SUBSTANCE IS A SOLUTE IN A SOLVENT:**

Because:

$$\alpha = \gamma_{\text{molarity}} \times \text{molarity} = \gamma_{\text{molality}} \times \text{molality} = \gamma_{\text{mol fraction}} \times \text{mol fraction}$$

In order to give the same value of activity, the values of γ_{molarity} , γ_{molality} , and $\gamma_{\text{mol fraction}}$ differ. It is found that activity of a solution particles is almost 100% when concentration equal to unity. Therefore:

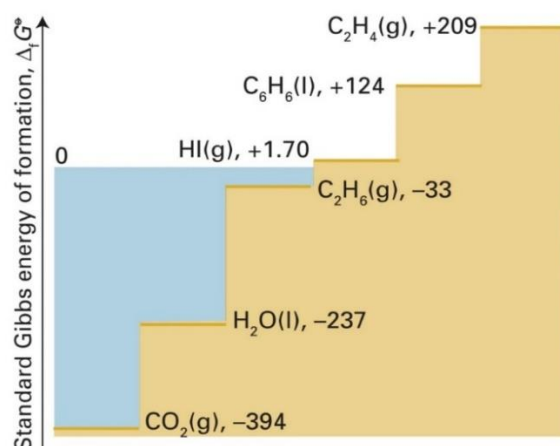
Any solute in is in its standard state when $\alpha = 1$ which occurs when molality = 1 mol kg^{-1}

7.8 Standard free energy of formation

- The reaction which produces a substance from its elements in their standard state is called the **standard formation reaction**. And the standard change in Gibbs energy of any reaction can be calculated as follows:

$$\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_{\text{f}}^{\circ}(\text{products}) - \sum \Delta G_{\text{f}}^{\circ}(\text{reactants})$$

- $\Delta G_{\text{f}}^{\circ}$ of elements when they are in their reference states are zero. On the other hand, $\Delta G_{\text{f}}^{\circ}$ of other substances are either positive or negative
- $\Delta G_{\text{f}}^{\circ}$ values can be looked at as analog of the values of altitudes. The figure below shows this analogy
- If we consider $\Delta G_{\text{f}}^{\circ}$ of elements as the “sea level” of stability, $\Delta G_{\text{f}}^{\circ}$ of compounds will be either above or below this sea level
- If $\Delta G_{\text{f}}^{\circ}$ is positive the substance is above ‘sea level’, it decomposes spontaneously into its elements sinking towards thermodynamic sea level



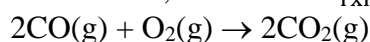
- ✓ If ΔG_f° is positive the substance is above 'sea level', it decomposes spontaneously into its elements sinking towards thermodynamic sea level
- ✓ A compound with $\Delta G_f^\circ > 0$ is **thermodynamically unstable** with respect to its elements and called **endergonic compound**.
- ✓ A compound with $\Delta G_f^\circ < 0$ and is **thermodynamically stable** with respect to its elements and called **exergonic compound**
- There is no point in searching for direct syntheses of a **thermodynamically unstable** compound with respect to its elements because the reaction does not occur in the required direction: its decomposition to its elements is spontaneous
- The following table lists the standard free energies of some substances

compound	ΔG_f° (kJ/mol)	compound	ΔG_f° (kJ/mol)
AgBr(s)	-96.90	MgSO ₄ (s)	-1170.6
AgCl(s)	-109.8	MnO(s)	-362.9
AgI(s)	-66.19	MnO ₂ (s)	-465.2
Ag ₂ O(s)	-30.6	NaCl(s)	-393.17
Ag ₂ S(s)	-11.21	NaF(s)	-546.3
Al ₂ O ₃ (s)	-1582.3	NaOH(s)	-419.2
BaCl ₂ (s)	-806.7	NH ₃ (g)	-26.57
BaCO ₃ (s)	-1134.4	CuO(s)	-129.7
BaO(s)	-520.4	Cu ₂ O(s)	-146.0
BaSO ₄ (s)	-1362.2	CuSO ₄ (s)	-661.8
CaCl ₂ (s)	-748.8	Fe ₂ O ₃ (s)	-742.2
CaCO ₃	-1129.1	Fe ₃ O ₄ (s)	-1015.4
CaO(s)	-603.3	HBr(g)	-53.45
Ca(OH) ₂ (s)	-897.5	HCl(g)	-95.30
CaSO ₄ (s)	-1309.1	HI(g)	+1.70
CCl ₄ (L)	-65.21	HNO ₃ (L)	-80.71
CH ₄ (g)	-50.70	H ₂ O(g)	-228.61
CH ₃ OH(L)	-161.96	NH ₄ Cl(s)	-202.87
CO(g)	-137.17	NH ₄ NO ₃ (s)	-183.87
CO ₂ (g)	-394.39	NO(g)	+86.55
H ₂ O(L)	-237.14	NO ₂ (g)	+51.31
H ₂ O ₂ (L)	-120.42	NiO(s)	-123.56
H ₂ S(g)	-33.4	PbBr ₂ (s)	-330.70

H ₂ SO ₄ (L)	- 689.93	PbCl ₂ (s)	- 314.05
HgO(s)	- 58.49	PbO(s)	- 187.89
HgS(s)	- 50.6	PbO ₂ (s)	- 217.33
KBr(s)	- 380.7	PCl ₃ (g)	- 267.8
KCl(s)	- 408.5	PCl ₅ (g)	- 272.3
KClO ₃ (s)	- 296.31	SiO ₂ (s)	- 856.64
KF(s)	- 537.8	SnO(s)	- 256.8
MgCl ₂ (s)	- 591.8	SnO ₂ (s)	- 519.6
MgCO ₃ (s)	- 1012.1	SO ₂ (g)	- 300.13
MgO(s)	- 596.3	SO ₃ (g)	- 370.4
Mg(OH) ₂ (s)	- 769.47	ZnO(s)	- 318.3

Example 7.3

From the information in the table below, calculate $\Delta G_{\text{rxn}}^{\circ}$ of the following reaction:



	CO ₂ (g)	CO(g)	O ₂ (g)
$\Delta G_f^{\circ}/\text{kJ mol}^{-1}$	- 394	- 137	0

Solution

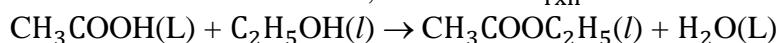
$$\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_{f,\text{products}}^{\circ} - \sum \Delta G_{f,\text{reactants}}^{\circ}$$

$$\Delta G_{\text{rxn}}^{\circ} = (2 \text{ mol} \times -394 \text{ kJ mol}^{-1}) - (2 \text{ mol} \times -137 + 1 \text{ mol} \times 0)$$

$$\Delta G_{\text{rxn}}^{\circ} = -514 \text{ kJ}$$

Practice exercise

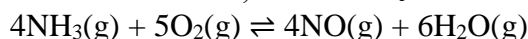
From the information in the table below, calculate $\Delta G_{\text{rxn}}^{\circ}$ of the following reaction:



	CH ₃ COOH(l)	C ₂ H ₅ OH(L)	CH ₃ COOC ₂ H ₅ (L)	H ₂ O(L)
$\Delta G_f^{\circ}/\text{kJ mol}^{-1}$	- 389.9	- 174.78	- 332.7	- 237.13

Example 7.4

From the information in the table below, calculate $\Delta_r G$ of the following reaction:



	NO(g)	H ₂ O(g)	NH ₃ (g)	O ₂ (g)
$\Delta G_f^{\circ}/\text{kJ mol}^{-1}$	+ 186.55	- 228.57	- 16.45	0

Solution

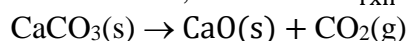
$$\Delta G_{\text{rxn}}^{\circ} = \sum \Delta G_{f,\text{products}}^{\circ} - \sum \Delta G_{f,\text{reactants}}^{\circ}$$

$$\Delta G_{\text{rxn}}^{\circ} = (4 \text{ mol} \times 186.55 \text{ kJ mol}^{-1} + 6 \times -228.57) - (4 \text{ mol} \times -16.45 + 5 \text{ mol} \times 0)$$

$$\Delta G_{\text{rxn}}^{\circ} = -559.42 \text{ kJ}$$

Practice exercise

From the information in the table below, calculate $\Delta G_{\text{rxn}}^{\circ}$ of the following reaction:



	CaCO ₃ (s)	CaO(s)	CO ₂ (g)
$\Delta G_f^{\circ}/\text{kJ mol}^{-1}$	- 1128.8	- 604.3	- 394.36

QUESTIONS AND PROBLEMS

- Calculate ΔG as a result of a reversible compression of 4 mol of an ideal gas at 300 K from 2.02×10^5 Pa to 4.04×10^5 Pa.
- Calculate q , w , ΔU , ΔH , ΔS , ΔA , and ΔG as a result of a reversible expansion of 1 mol of an ideal gas at 300 K from 2 dm^3 to 20 dm^3 .
- Calculate q , w , ΔU , ΔH , ΔS_{system} , ΔS_{surr} , ΔS_{univ} , ΔA , and ΔG as a result of a reversible expansion of 1 mol of an ideal gas against vacuum at 300 K from 1×10^6 Pa to 1×10^5 Pa.
- Calculate q , w , ΔU , ΔH , ΔS , ΔA , and ΔG as a result of vaporization of 1 mol of toluene at its boiling point, 384 K. $\Delta H_{\text{vap}}^{\circ}(\text{toluene}) = 33.42 \text{ kJ mol}^{-1}$.
- Calculate ΔA and ΔG of the following change:

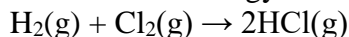
$$\text{H}_2\text{O}(l, 1 \text{ atm}, 100 \text{ }^{\circ}\text{C}) \rightarrow \text{H}_2\text{O}(g, 1 \text{ atm}, 100 \text{ }^{\circ}\text{C})$$
- Knowing that $C_{m,p,\text{H}_2\text{O}(l)} = 75.42 \text{ J K}^{-1} \text{ mol}^{-1}$, $C_{m,p,\text{H}_2\text{O}(s)} = 37.2 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta H_{\text{fusion},\text{H}_2\text{O},273 \text{ K}} = 5980 \text{ J mol}^{-1}$, calculate ΔG of the following change:

$$\text{H}_2\text{O}(l, 263 \text{ K}, 101325 \text{ Pa}) \rightarrow \text{H}_2\text{O}(s, 263 \text{ K}, 101325 \text{ Pa})$$
- 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 ΔG of the following change:

$$\text{H}_2\text{O}(l, 300 \text{ K}, 1.01 \times 10^5 \text{ Pa}) \rightarrow \text{H}_2\text{O}(g, 300 \text{ K}, 1.01 \times 10^4 \text{ Pa})$$
- From the table below:

Substance	$\text{H}_2(g)$	$\text{Cl}_2(g)$	$\text{HCl}(g)$
BE / kJ mol^{-1}	435	240	430
S / $\text{J K}^{-1} \text{ mol}^{-1}$	130.59	222.96	186.68

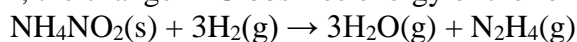
calculate, in kJ, the change in Gibbs free energy of the following reaction:



- From the table below:

Substance	$\text{NH}_4\text{NO}_2(s)$	$\text{H}_2(g)$	$\text{H}_2\text{O}(g)$	$\text{N}_2\text{H}_4(g)$
ΔH_f° / kJ mol^{-1}	-365	0	-242	50
S° / $\text{J K}^{-1} \text{ mol}^{-1}$	150	130	189	120

calculate, in kJ K^{-1} , the change in Gibbs free energy of the following reaction:



- Knowing that $\Delta U = -2880 \text{ kJ}$ and $\Delta S = 182.4 \text{ J K}^{-1}$ for the following reaction:

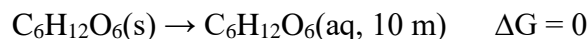
$$\text{C}_6\text{H}_{12}\text{O}_6(s) + 6\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 6\text{H}_2\text{O}(g)$$
 calculate ΔA , ΔG , the maximum work can be done, and the useful work. Calculate the difference between ΔA and ΔG , and what does it represent.
- Knowing that: $\Delta U = 2.88 \text{ kJ}$ and $\Delta S = 182.4 \text{ J K}^{-1}$ for the following reaction:

$$\text{malate} \rightarrow \text{fumarate} \quad \Delta G = 3 \text{ kJ}$$

$$\text{fumarate} \rightarrow \text{aspirate} \quad \Delta G = -15.5 \text{ kJ}$$
 calculate ΔG of the following change:

$$\text{malate} \rightarrow \text{aspirate} \quad \Delta G = ?$$

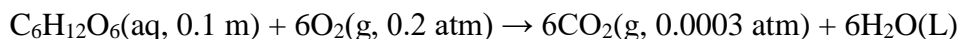
- Knowing that:



and from the following table:

Substance	$\text{C}_6\text{H}_{12}\text{O}_6(s)$	$\text{CO}_2(g)$	$\text{H}_2\text{O}(l)$
ΔG_f° / kJ mol^{-1}	-913	-395	-237

calculate, in kJ mol^{-1} , the change in Gibbs free energy as a result of glucose oxidation in our bodies:




13. Calculate the difference between ΔA and ΔG of the following change at 300 K:


$$\text{H}_2(\text{g}, 1.01 \times 10^5) + 0.5\text{O}_2(\text{g}, 1.01 \times 10^5) \rightarrow \text{H}_2\text{O}(\text{L}, 1.01 \times 10^5)$$
14. 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 vaporization of water is $40.85 \text{ kJ mol}^{-1}$, calculate ΔH , ΔS , and ΔG of the following change:

$$\text{H}_2\text{O}(\text{L}, 300 \text{ K}, 1.01 \times 10^5 \text{ Pa}) \rightarrow \text{H}_2\text{O}(\text{g}, 300 \text{ K}, 1.01 \times 10^4 \text{ Pa})$$
15. Calculate ΔG as a result of doubling the pressure of 4 mol of an ideal gas at 300 K.
16. Calculate q , w , ΔU , ΔH , ΔS , ΔA , and ΔG as a result of changing the volume of 1 mol of an ideal gas to 10 times its original volume.
17. Using the values of ΔS° and ΔH° calculate ΔH° of the following reaction:

$$\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$$
18. 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 $-136 \text{ J K}^{-1} \text{ mol}^{-1}$.
- Calculate the change in Gibbs energy.
 - Is the reaction spontaneous?
 - Calculate the total change in entropy of the system and the surroundings.
19. The change in Gibbs energy that accompanies the oxidation of $\text{C}_6\text{H}_{12}\text{O}_6(\text{s})$ to carbon dioxide and water vapor at 25°C is $-2828 \text{ kJ mol}^{-1}$. How much glucose does a person of mass 65 kg need to consume to climb through 10 m?
20. 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.
- Given that the change in Gibbs energy for the hydrolysis of ATP corresponds to $\Delta G = -31 \text{ kJ mol}^{-1}$ under the conditions prevailing in a typical cell, can the hydrolysis drive the formation of glutamine?
 - How many moles of ATP must be hydrolyzed to form 1 mol of glutamine?
21. The hydrolysis of acetyl phosphate has $\Delta G = -42 \text{ kJ mol}^{-1}$ 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?
22. Suppose that the radius of a typical cell is 10 μm and that inside it 106 ATP molecules are hydrolyzed each second. What is the power density of the cell in watts per cubic meter ($1 \text{ W} = 1 \text{ J s}^{-1}$). A computer battery delivers about 15 W and has a volume of 100 cm^3 . Which has the greater power density, the cell or the battery?



8. THERMODYNAMIC EQUILIBRIUM: CHEMICAL EQUILIBRIA



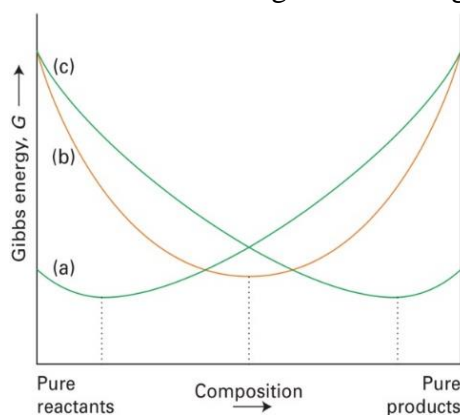
8. THERMODYNAMIC EQUILIBRIUM: CHEMICAL EQUILIBRIUM

8.1 The concept of thermodynamic equilibrium

- “Equilibrium” means “state of balance”. Chemical thermodynamics predicts:
 - 1) Whether reactants have a spontaneous tendency to change into products
 - 2) The composition of the mixture at equilibrium
 - 3) How composition at equilibrium is affected by changing the conditions
- Knowing whether equilibrium favors reactants or products is an indication of the feasibility of a process
- At equilibrium, the system experiences no changes when it is isolated

8.2 Thermodynamic background

- *At any condition* the only thermodynamic criterion for any spontaneous change is “ $\Delta S_{\text{univ}} > 0$ ”
- *At constant T and P*, the change is spontaneous when “ $\Delta G_{\text{sys}} < 0$ ”
- The advantage of the entropy (S) over the Gibbs free energy (G) is that it works with no need to keep any property constant
- The advantage of the Gibbs free energy (G) over the entropy (S) is that it focuses only on the system
- *At constant temperature and pressure, a reaction mixture tends to adjust its composition until its Gibbs free energy is a minimum*
- The mixture at equilibrium may contain no reactants or no products. Also, it may contain a considerable amount of both. The question “**to what extent would a reaction proceed?**” can be clarified using the following figure



- ✓ **The line (a)** shows that the mixture at equilibrium contains a little amount of the products. This means that **little** amount of reactants converts into products before G reached its minimum value. Here, the reaction “*does not go*” and it is **irreversible** because G reaches its minimum when the reaction is shifted completely to the **reactants**
- ✓ **The line (c)** shows that the mixture at equilibrium contains a large amount of the products. This means that **large** amount reactants converts into products before G reached its minimum value. Here, the reaction “*goes*” and it is **irreversible** because G reaches its minimum when the reaction is shifted completely to the **products**
- ✓ **The line (b)** shows that the mixture at equilibrium contains substantial amounts of reactants and products as G has reached its minimum value. The reaction “*goes both ways*” and it is **reversible** because G reaches its minimum when the amounts of reactants and products become **constant**

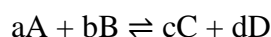
8.3 The four criteria of thermodynamic equilibrium

- 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 the system is in equilibrium if:
 - $\Delta U = 0$ at constant T and S: $(\Delta U)_{T,S} = 0$
 - $\Delta S = 0$ at constant T and U: $(\Delta S)_{T,U} = 0$
 - $\Delta A = 0$ at constant T and U: $(\Delta A)_{T,U} = 0$
 - $\Delta G = 0$ at constant T and P: $(\Delta G)_{T,P} = 0$
- Due to the easiness of keeping T and P constant, $(\Delta G)_{T,P}$ is the favored one
- We should notice that:
 Since $G = H - TS$, it takes into account H, T and S. Because $H = U + PV$, G also takes into account U, P and V. Therefore, it takes into account T, P, V, U and S

8.4 The reaction Gibbs energy: Direction of change

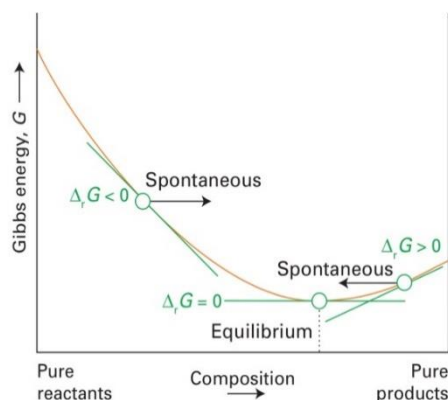
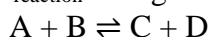
- For the general symbolic reaction:



The Gibbs energy is:

$$\Delta G_{\text{reaction}} = (cG_{m,C} + dG_{m,D}) - (aG_{m,A} + bG_{m,B})$$

- The molar Gibbs energy 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 $G_{m,A}$ and $G_{m,B}$ are high, $\Delta_r G < 0$ and the slope of G is negative, the reaction is spontaneous from left to right
- ✓ When the mixture is rich in the products C and D and because $G_{m,C}$ and $G_{m,D}$ are high, $\Delta_r G > 0$ and the slope of G is positive and the reaction is spontaneous, from right to left
- ✓ Where $\Delta G = 0$, the reaction has no tendency to form either products or reactants, and the spontaneities of the reaction in both directions are equal

8.5 Free energy and equilibrium: The vant' Hoff isotherm

- For simplicity, let the reaction be “ $aA \rightleftharpoons bB$ ”:

$$\Delta G = bG_B - aG_A = nRT \ln \frac{[B]^b}{[A]^a}$$

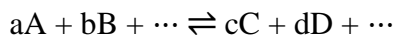
$$G_A = G_A^\circ + RT \ln [A]^a$$

$$G_B = G_B^\circ + RT \ln [B]^b$$

$$\Delta G = G_B - G_A = \{G_B^\circ + RT \ln [B]^b\} - \{G_A^\circ + RT \ln [A]^a\}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[B]^b}{[A]^a}$$

- Generally, if the reaction is:



$$\Delta G = \Delta G^\circ + RT \ln \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

$$\Delta G = \Delta G^\circ + R \times T \times \ln \frac{\Pi[\text{PRODUCTS}]^{n_p}}{\Pi[\text{REACTANTS}]^{n_r}}$$

$$\frac{\Pi[\text{PRODUCTS}]^{n_p}}{\Pi[\text{REACTANTS}]^{n_r}} = Q$$

where Q is called "the reaction quotient". Therefore:

$$\Delta G = \Delta G^\circ + R \times T \times \ln Q$$

This last equation is one of the most important equations in thermodynamics and is called **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*:

$$\Delta G^\circ = -R \times T \times \ln K_e$$

From last two equations:

$$\Delta G = R \times T \times \ln \frac{Q}{K_e}$$

vant' Hoff isotherm is any one of last three equations.

Example 8.1

From the following table calculate ΔG° and K of the reaction:



Substance	C(graphite)	H ₂ (g)	CH ₄ (g)
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	0	0	-74.83
$S^\circ / \text{J K}^{-1} \text{ mol}^{-1}$	5.68	130.59	186.19

Solution

The reaction is the standard formation of CH₄(g). therefore, its $\Delta H^\circ = -74 \text{ kJ}$

$$\Delta S^\circ = \Sigma S^\circ(\text{p}) - \Sigma S^\circ(\text{r})$$

$$\Sigma S^\circ(\text{p}) = 1 \text{ mol} \times 186.19 \frac{\text{J}}{\text{mol K}} = 186.19 \frac{\text{J}}{\text{K}}$$

$$\Sigma S^\circ(\text{r}) = 1 \text{ mol} \times 5.68 \frac{\text{J}}{\text{mol K}} + 2 \text{ mol} \times 130.59 \frac{\text{J}}{\text{mol K}} = 266.86 \frac{\text{J}}{\text{mol K}}$$

$$\Delta S^\circ = 186.19 \frac{\text{J}}{\text{mol K}} - 266.86 \frac{\text{J}}{\text{mol K}} = -80.67 \frac{\text{J}}{\text{mol K}} = -0.08067 \frac{\text{kJ}}{\text{mol K}}$$

$$\Delta G^\circ = (\Delta H^\circ) - (T\Delta S^\circ) = (-74 \frac{\text{kJ}}{\text{mol}}) - (298 \text{ K} \times -0.08067 \frac{\text{kJ}}{\text{mol K}}) = -49.96 \frac{\text{kJ}}{\text{mol}}$$

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{-49.96 \frac{\text{kJ}}{\text{mol}} \times 1000 \frac{\text{J}}{\text{kJ}}}{8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K}} = 20.5$$

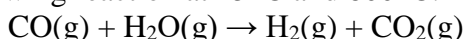
$$K = 8 \times 10^8$$

Practice exercise

From the following table at 25 °C:

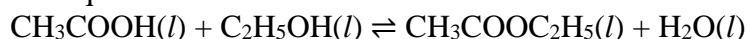
Substance	H ₂ (g)	CO(g)	H ₂ O(g)	CO ₂ (g)
$\Delta G_f^\circ / \text{kJ mol}^{-1}$	0	-137.27	-228.59	-394.38

calculate K_p of the following reaction at 25 °C and 800 °C:



Example 8.2

Write the reaction quotient for the esterification reaction:

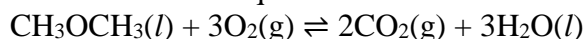


Solution

$$Q = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5] \times [\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}] \times [\text{C}_2\text{H}_5\text{OH}]}$$

Practice exercise

Write the reaction quotient for the combustion of dimethyl ether: reaction:



Example 8.3

Calculate the equilibrium constant for the following reaction at 25 °C:



Solution

$$\Delta G^\circ = -RT \ln K$$

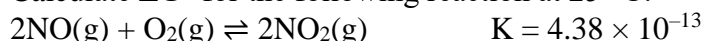
$$3.4 \frac{\text{kJ}}{\text{mol}} = -8.314 \frac{\text{J}}{\text{K mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 298 \text{ K} \times \ln K$$

$$\ln K = -1.37$$

$$K = 0.25$$

Practice exercise

Calculate ΔG° for the following reaction at 25 °C:



Example 8.4

Calculate ΔG° , in kJ, for the following reaction at 25 °C:



Solution

$$\Delta G^\circ = -RT \ln K = -8.314 \frac{\text{J}}{\text{K mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 298 \text{ K} \times \ln 1.58 \times 10^{-9} = 50.2 \text{ kJ}$$

Practice exercise

Calculate the equilibrium constant for the following reaction at 25 °C:



- We conclude from the equation “ $\Delta G^\circ = -RT \ln K_e$ ”:
 - 1) If $K \gg 1$ ($K > 10^3$ and $\Delta G_{\text{reaction}} < -17 \text{ kJ}$ at 25°C):
The reaction has a strong tendency to form products and the reaction is thermodynamically feasible ($\Delta G_{\text{reaction}} < 0$). Reactions of this type are called **exergonic**
 - 2) If $K \ll 1$ ($K < 10^{-3}$ and $\Delta G > +17 \text{ kJ}$ at 25°C)
The reaction has a weak tendency to form products and the reaction is not thermodynamically feasible ($\Delta G_{\text{reaction}} > 0$). Reactions of this type are called **endergonic**
 - 3) If K is comparable to 1 (between 10^{-3} and 10^3)
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 $\Delta S_{\text{reaction}} > 0$: $\Delta G_{\text{reaction}} > 0$ and $K > 1$ at high temperatures
- 2) If $\Delta H_{\text{reaction}} > 0$ and $\Delta S_{\text{reaction}} < 0$: $\Delta G_{\text{reaction}} > 0$ and $K < 1$ at all temperatures
- 3) If $\Delta H_{\text{reaction}} < 0$ and $\Delta S_{\text{reaction}} > 0$: $\Delta G_{\text{reaction}} > 0$ and $K > 1$ at all temperatures
- 4) If $\Delta H_{\text{reaction}} < 0$ and $\Delta S_{\text{reaction}} < 0$: $\Delta G_{\text{reaction}} < 0$ and $K > 1$ at low 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_a , where:

$$K_a = \frac{\prod \text{products activities}^{n_p}}{\prod \text{reactants activities}^{n_r}}$$

2) If expressed in terms of molarities it will be denoted as K_c , where:

$$K_c = \frac{\prod \text{products molarities}^{n_p}}{\prod \text{reactants molarities}^{n_r}}$$

3) If expressed in terms of pressures it will be denoted as K_p , where:

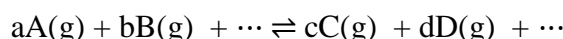
$$K_p = \frac{\prod \text{products pressures}^{n_p}}{\prod \text{reactants pressures}^{n_r}}$$

4) if expressed in terms of mole fractions it will be denoted as K_x , where:

$$K_x = \frac{\prod \text{products mole fractions}^{n_p}}{\prod \text{reactants mole fractions}^{n_r}}$$

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 either their concentrations or their pressures. For example:



$$K_c = \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

$$K_p = \frac{P_C^c P_D^d \dots}{P_A^a P_B^b \dots}$$

- Because the ideal gas law relates pressure to concentration as follows:

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

Where M is the molarity. The relation between K_c and K_p is:

$$K_p = K_c (RT)^{\Delta n_g}$$

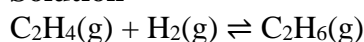
Δn_g is the difference between number of moles of gases produced and reacted:

$$\Delta n_g = \sum n_g(\text{products}) - \sum n_g(\text{reactants})$$

Example 8.5

Knowing that ΔG_f° , in kJ mol^{-1} of ethane is -32.89 and of ethylene is 68.12 , calculate ΔG° and K_p of the hydrogenation of 1 mol of ethylene.

Solution



$$\Delta G^\circ = \sum \Delta G_f^\circ(p) - \sum \Delta G_f^\circ(r)$$

$$\Delta G^\circ = [(-32.89 \frac{\text{kJ}}{\text{mol}})] - [(-68.12 \frac{\text{kJ}}{\text{mol}}) + 0] = -101.1 \frac{\text{kJ}}{\text{mol}} = -101100 \frac{\text{J}}{\text{mol}}$$

$$\ln K_p = -\frac{\Delta G^\circ}{RT} = -\frac{-101100 \frac{\text{J}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol K}} \times 298 \text{ K}} = 40.77$$

$$K_p = 5 \times 10^{17}$$

Practice exercise

Calculate ΔG° of the following change:



8.8 Factors affecting equilibrium

- If the value of the equilibrium constant is high, the quantity of products is much more than the quantity of reactants. We express this case by saying that the “equilibrium position is shifted to the right”
- If the value of the equilibrium constant is low, the quantity of products is much less than the quantity of reactants. We express this case by saying that the “equilibrium position is shifted to the left”
- The response of equilibrium to changes in conditions obeys a famous principle known as Le Chatelier’s principle:

“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 way of expressing vant’ Hoff equation is:

$$\frac{d \ln K}{d \frac{1}{T}} = - \frac{\Delta H^\circ}{R}$$

K for endothermic reactions will increase as temperature “T” increases, and vice versa as clarified here:



The forward reaction favors absorbing heat: so, as T increases the amounts of products will increase and the value of the equilibrium constant increases and the equilibrium position is shifted to the right.

If the reaction is exothermic as below:



The forward reaction favors releasing heat: so, as T increases the amounts of products will decrease and the value of the equilibrium constant decreases and the equilibrium position is shifted to the left.

If the value of the equilibrium constant is “K₁” at temperature T₁, then if the temperature becomes T₂ the value of the equilibrium constant becomes K₂ and can be calculated using the following equation:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \times \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$$

Example 8.6

Calculate ΔH° of a reaction if raising its temperature from 25 °C to 35 °C doubles the value of its equilibrium constant.

Solution

$$\ln \frac{K_2}{K_1} = \ln \frac{2 \times K_1}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$$

$$\ln 2 = \frac{\Delta H^\circ}{8.314 \frac{\text{J}}{\text{mol K}}} \left(\frac{308 \text{ K} - 298 \text{ K}}{308 \text{ K} \times 298 \text{ K}} \right)$$

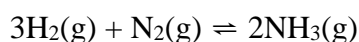
$$\Delta H^\circ = 52882.28 \text{ J} = 52.88 \text{ kJ}$$

Practice exercise

Calculate ΔG° and ΔS° of a reaction at 1200 K if its equilibrium constant at 1225 K is 3.28×10^{-3} and its ΔH° is 216.7 kJ.

8.8.2 Effect of changing concentration

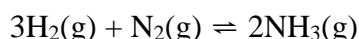
Let’s take the following reaction at equilibrium:



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 (the reaction position *shifts* toward that direction). **This change is a change in only the equilibrium position because the equilibrium constant remains the same as temperature does not change.**

8.8.3 Effect of changing pressure

Let’s take the same reaction at equilibrium:

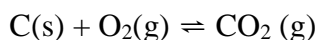
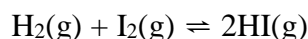


Changing the pressure means that the volume either:

- ✓ decreases and the total pressure increases
- ✓ increases and the total pressure decreases

According to LeChatelier's principle increasing the pressure forces the reaction to go faster in the direction that decreases the number of moles of gases (in our example it will shift to the right). **This change is a change in only the equilibrium position because the equilibrium constant remains the same as temperature does not change.**

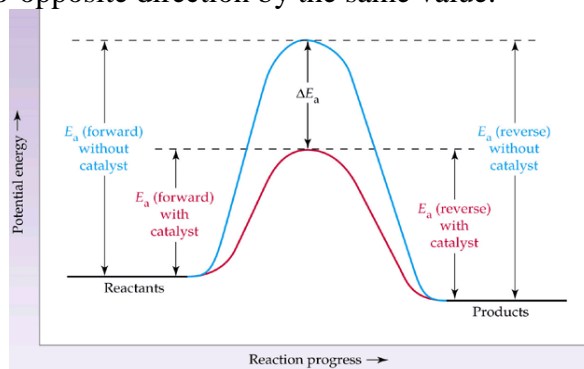
Sometimes number moles of gases on both sides of the equation are equal:



In such cases changing the volume (the pressure) will not shift the equilibrium toward any direction. **No change in the equilibrium position or constant.**

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 equations for the reaction in both directions are:

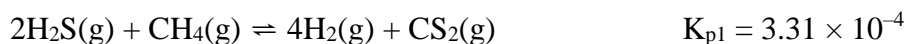
$$\ln k_{\text{forward}} = \ln A_{\text{forward}} - \frac{E_{\alpha, \text{forward}}}{RT}$$

$$\ln k_{\text{reverse}} = \ln A_{\text{reverse}} - \frac{E_{\alpha, \text{reverse}}}{RT}$$

Because A, R, and T are constant. And because E_a decreased in both directions by the same value, the increase in "lnk", and consequently the increase in the reaction rates 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

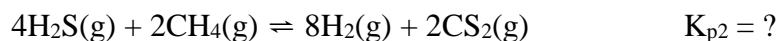
- Any chemical reaction equation such as:



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:

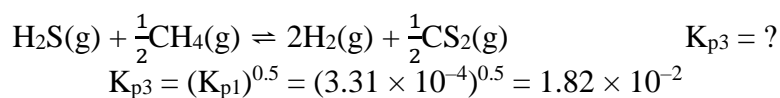
- ✓ If the equation is for multiplied by 2:



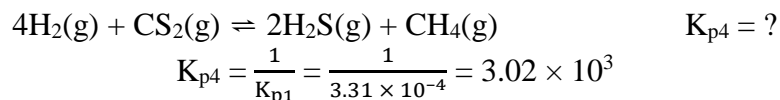
the equilibrium constant can be calculated as follows:

$$K_{p2} = (K_{p1})^2 = (3.31 \times 10^{-4})^2 = 1.1 \times 10^{-7}$$

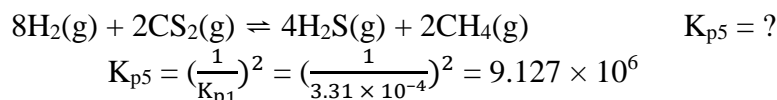
- ✓ If the equation is for multiplied by $\frac{1}{2}$:



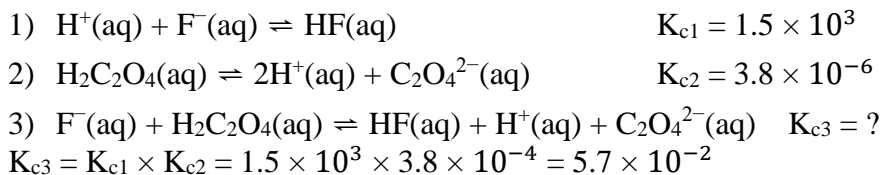
B) If we reverse the equation, we can calculate the equilibrium constant of the resulting equation by inverting the equilibrium constant of the first. The following is an example:



C) If we multiply the equation by any number and reverse it, we can calculate its equilibrium constant by raising the equilibrium constant of the original equation to a power that equals the same number, then inverting the resulting value. The following is an example:



D) If we make a summation for two or more equations, the equilibrium constant of the resultant equation is the product of multiplication of the equilibrium constant of the summed equations:



QUESTIONS AND PROBLEMS

1. From the following table:

Substance	C(graphite)	H ₂ (g)	CH ₄ (g)
$\Delta G_f^\circ / \text{kJ mol}^{-1}$	0	0	- 74.83
$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$	5.68	130.59	186.19

calculate ΔG° and K of the reaction:



2. Calculate ΔG° of the following change:

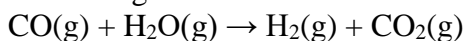


3. Knowing that ΔG_f° , in kJ mol^{-1} of ethane is - 32.89 and of ethylene is 68.12, calculate ΔG° and K_p of the hydrogenation of 1 mol of ethylene.

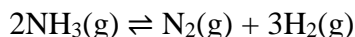
4. From the following table at 25 °C:

Substance	H ₂ (g)	CO(g)	H ₂ O(g)	CO ₂ (g)
$\Delta G_f^\circ / \text{kJ mol}^{-1}$	0	- 137.27	- 228.59	- 394.38
$\Delta H_f^\circ / \text{kJ mol}^{-1}$	0	- 110.52	- 241.83	- 392.51

calculate K_p of the following reaction at 25 °C and 800 °C:



5. Calculate ΔH° of a reaction if raising its temperature from 25 °C to 35 °C doubles the value of its equilibrium constant.
6. Calculate ΔG° and ΔS° of a reaction at 1200 K if its equilibrium constant is 3.28×10^{-3} at 1225 K and its ΔH° is 216.7 kJ.
7. Knowing that ΔG_f° of NH₃(g) is -16.6 / kJ mol^{-1} , calculate the equilibrium constant of the following reaction:




8. Knowing that:




A) Calculate ΔG° .

B) Calculate ΔG when $P_A = 20 \text{ atm}$ and $P_B = 1 \text{ atm}$.

C) Calculate the value of P_B at which A can not change to B.



9.THERMODYNAMIC EQUILIBRIUM: PHYSICAL EQUILIBRIA OF PURE SUBSTANCES



9. THERMODYNAMIC EQUILIBRIUM: PHYSICAL EQUILIBRIUM OF PURE SUBSTANCES

9.1 The physical change

- Boiling, freezing, and the conversion of graphite to diamond are examples of **phase transitions** and physical change
- Any physical system could be in one or more than one state (phase), gas, liquid, and solid. If the properties of a system are fixed and do not experience any forces, we say that the system is in a *physical equilibrium*
- Physical equilibrium can exist between several phases of one component, between several components in one phase, or between several components in several phases
- We will limit our discussion here only to physical equilibrium between several phases of one component

9.2 The condition of stability

- The Gibbs energy of one mole of the substance, (the molar Gibbs energy) is:

$$G_m = \frac{G}{n}$$

- The molar Gibbs energy, G_m , is an intensive property and depends on the phase. (at the same temperature and pressure $G_{m,H_2O(l)} \neq G_{m,H_2O(g)}$)
- 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:

$$\Delta G = (n \times G_{m(2)}) - (n \times G_{m(1)}) = n \times (G_{m(2)} - G_{m(1)})$$

- Because a spontaneous change at constant **T** and **P** is accompanied by a negative value of ΔG , the 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 T and P 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 freeze (at 1 atm, ice has a lower molar Gibbs energy than liquid water when the temperature is below 0°C and water converts spontaneously into ice)

Example 9.1

At 298 K, $\Delta G_{298 K, \alpha\text{-Sn to } \beta\text{-Sn}} = + 0.13 \text{ kJ mol}^{-1}$. Which is the reference state of tin at this temperature $\alpha\text{-Sn}$ or $\beta\text{-Sn}$?

Solution

The **reference state** of an element is its most stable form under the prevailing conditions.



Because ΔG has a positive value, this change is nonspontaneous. Therefore $\alpha\text{-Sn}$ is the reference state of tin at this temperature.

9.3 The variation of Gibbs energy with pressure and temperature

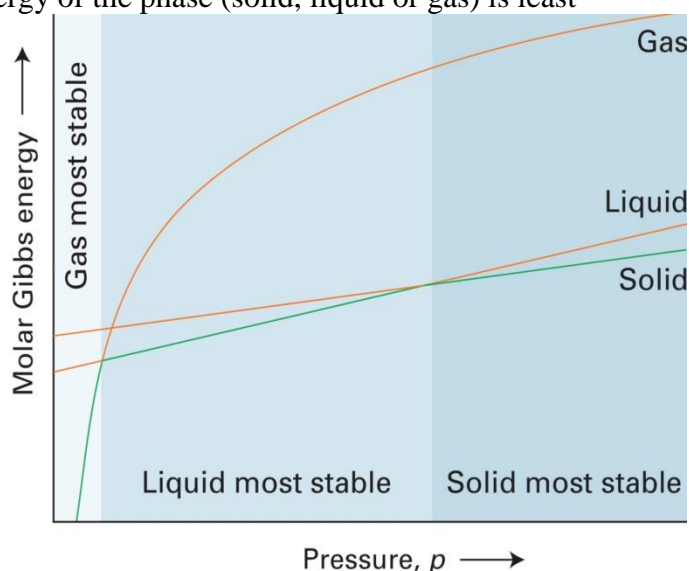
9.3.1 The variation of Gibbs energy with pressure

- At constant temperature, the change in the pressure of one mole of a substance by ΔP leads to a change in the molar Gibbs energy by ΔG_m :

$$\Delta G_m = V_m \Delta P$$

" V_m " is the molar volume of the substance. Its value is always positive. This expression is valid when V_m is constant in the pressure range of interest

- ✓ Because V_m is positive, the molar Gibbs energy increases ($\Delta G_m > 0$) when the pressure increases ($\Delta p > 0$)
- ✓ For a given change in pressure, the resulting change in molar Gibbs energy is greatest for substances with large molar volumes
- ✓ Because V_m of a gas is much larger than that of a liquid or a solid, the dependence of G_m on P is much greater for a gas than for a liquid or a solid
- For most substances (*water is not one of them*), V_m of the liquid phase is greater than that of the solid phase
- The following figure shows The figure shows three lines for the three states. It shows how G_m for a substance changes with P and which state (gas, liquid, solid) is more stable at a certain case
 - ✓ 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 the phase (solid, liquid or gas) is least



- 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 (the substance is more stable when it is a solid)
 - 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 (the substance is more stable when it is a liquid)
 - 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 (the substance is more stable when it is a gas)
- ✓ 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:

$$(G_{m,P_{\text{final}}} - G_{m,P_{\text{initial}}}) = V_m (P_{\text{final}} - P_{\text{initial}})$$

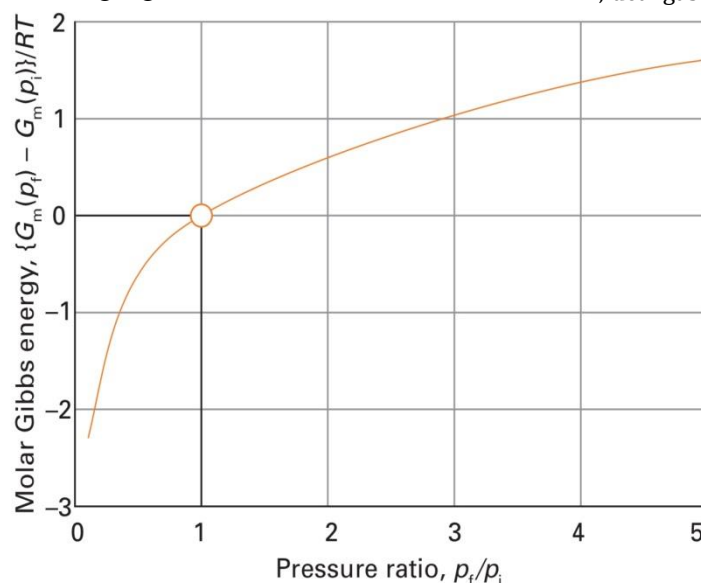
$$G_{m,P_{\text{final}}} = G_{m,P_{\text{initial}}} + V_m (P_{\text{final}} - P_{\text{initial}})$$

Increasing the pressure from P_{initial} to P_{final} causes an increase in the molar Gibbs energy by a value equals to $V_m \times (P_{\text{final}} - P_{\text{initial}})$

- ✓ If the substance is solid or liquid, and because $V_{m,\text{liquid}}$ and $V_{m,\text{solid}}$ are so small, the dependence of G_m on pressure is very weak and negligible
- ✓ If the substance is a gas, and because $V_{m,\text{gas}}$ is so large, the dependence of G_m on pressure is very strong
- ✓ 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 $G_{m,\text{ideal gas}}$ and the pressure



- ✓ 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

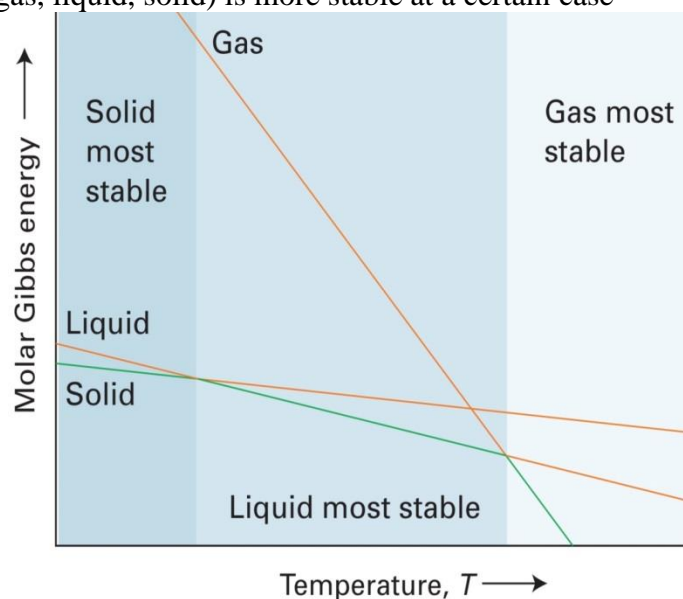
- At constant P the change in the T of one mole of a substance by ΔT leads to a change in the molar Gibbs energy by ΔG_m :

$$\Delta G_m = - S_m \Delta T$$

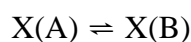
S_m is the molar entropy of the substance and it always has a positive value

- This equation is valid when S_m is constant in the temperature range of interest
- Because S_m is positive increasing T makes ΔG_m negative (increasing temperature decreases G_m)
- For a given ΔT the change in molar Gibbs energy (ΔG_m) is proportional to the molar entropy (S_m)
- The value of $S_{m,\text{gas}}$ is tremendously greater than that 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 between them is not large
- 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 for the liquid is more than for the solid
- The following figure shows how G_m of 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:
 - 1) **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 (the substance is more stable when it is a solid)
 - 2) **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 (the substance is more stable when it is a liquid)
 - 3) **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 (the substance is more stable when it is a gas)
- 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. **At the transition temperature there is no tendency for either phase to change into the other and the two phases are in equilibrium**
- Above the solid–liquid transition temperature, the liquid is thermodynamically more stable; below it, the solid phase is more stable.
- To simplify the above discussion, suppose the substance we have is **X**, which is existing in equilibrium between phases (A) and (B) at the same T and P :



Because A and B are in equilibrium, 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 equation can be written in different identical forms.
 - ✓ A form which helps to calculate the change in pressure per 1 temperature degree:

$$\frac{\Delta P}{\Delta T} = \frac{\Delta H}{T\Delta V}$$

- ✓ A form which helps to calculate the change in temperature per 1 pressure unit:

$$\frac{\Delta T}{\Delta P} = \frac{T\Delta V}{\Delta H}$$

- ✓ A form which helps to calculate the change in volume per 1 temperature degree:

$$\frac{\Delta V}{\Delta T} = \frac{\Delta H}{T\Delta P}$$

- ✓ A form which helps to calculate the change in temperature per 1 volume unit:

$$\frac{\Delta T}{\Delta V} = \frac{T\Delta P}{\Delta H}$$

Example 9.2

Knowing that at 100 °C and 1 atm the molar volume of $H_2O(l)$ is $0.019 \text{ dm}^3 \text{ mol}^{-1}$, the molar volume of $H_2O(g)$ is $30.199 \text{ dm}^3 \text{ mol}^{-1}$, and the molar enthalpy of vaporization of water is $40.82 \text{ kJ mol}^{-1}$, calculate the change in water boiling point accompanying the change in pressure by 1 mmHg.

Solution

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

$$\frac{dT}{dP} = \frac{373 \text{ K} \times (30.199 - 0.019) \frac{\text{dm}^3}{\text{mol}} \times 10^{-3} \frac{\text{m}^3}{\text{dm}^3}}{40.82 \frac{\text{kJ}}{\text{mol}} \times 10^3 \frac{\text{J}}{\text{kJ}}} = 2.76 \times 10^{-4} \text{ K Pa}^{-1} = 0.037 \text{ K mmHg}^{-1}$$

Changing the pressure by 1 mmHg changes boiling point by 0.037 K.

Practice exercise

Knowing for benzene (C_6H_6) that its normal solidification (freezing) point is 5 °C, molar volume when liquid is $87.282 \text{ cm}^3 \text{ mol}^{-1}$, molar volume when solid is $82.68 \text{ cm}^3 \text{ mol}^{-1}$, and standard molar enthalpy of solidification is $-9.984 \text{ kJ mol}^{-1}$, calculate the change in pressure needed to change its freezing point by 1 °C.

Example 9.3

Knowing for H_2O that its freezing point is 273 K, molar volume when liquid is $18.0036 \text{ cm}^3 \text{ mol}^{-1}$, molar volume when solid is $19.6335 \text{ cm}^3 \text{ mol}^{-1}$, and its standard molar enthalpy of freezing is $-6.03 \text{ kJ mol}^{-1}$, calculate the change in its freezing point accompanying the change in pressure by 1 atm.

Solution

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} = \frac{273 \text{ K} \times (18.0036 - 19.6335) \frac{\text{cm}^3}{\text{mol}} \times 10^{-6} \frac{\text{m}^3}{\text{cm}^3}}{-6.03 \frac{\text{kJ}}{\text{mol}} \times 10^3 \frac{\text{J}}{\text{kJ}}} = +0.0738 \times 10^{-8} \frac{\text{K m}^3}{\text{J}}$$

$$\frac{dT}{dP} = +7.48 \times 10^{-3} \text{ K atm}^{-1}$$

Changing the pressure by 1 atm changes freezing point by 0.00748 K.

Practice exercise

If the molar volume of monoclinic sulfur is more than that in rhombic solid sulfur by $3.226 \text{ cm}^3/\text{mol}$, the transition point from monoclinic form to rhombic at 1 atm is $95.4 \text{ }^\circ\text{C}$, and the 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 Clausius-Clapeyron equation (Special cases of the Clapeyron equation)

Clausius modified Clapeyron equation to the following equation:

$$\Delta P = P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln \frac{T_2}{T_1}$$

- Vaporization process:**

- ✓ When a liquid is vaporized the volume becomes much larger to the extent that the liquid volume can be neglected (**Molar volumes of liquid and gaseous water at 1 atm and $0 \text{ }^\circ\text{C}$ are 0.018 L and 22.4 L respectively. The difference between these two values is 22.383 L**):

$$22.383 \text{ L} \approx 22.4 \text{ L}$$

$$\Delta V = V_g - V_l \approx V_g$$

- ✓ In the case of vaporization:

$$\Delta P = \frac{\Delta H_{\text{vap}}}{\Delta V} \times \frac{\Delta T}{T}$$

Because " $V = \frac{nRT}{P}$ ", Clausius ended at the following equation known as **Clausius-Clapeyron equation**:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \times \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$$

Example 9.4

From the following table for decane:

$P_{\text{vap}} / \text{torr}$	10	40
$t / \text{ }^\circ\text{C}$	55.7	150.6

Calculate: A) ΔH_{vap}

B) ΔS_{vap} at $100 \text{ }^\circ\text{C}$

Solution

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{T_2 - T_1}{T_1 \times T_2} \right)$$

$$\ln \frac{10 \text{ torr}}{40 \text{ torr}} = \frac{\Delta H_{\text{vap}}}{8.314 \frac{\text{J}}{\text{K mol}}} \left(\frac{328.7 \text{ K} - 423.6 \text{ K}}{423.6 \text{ K} \times 328.7 \text{ K}} \right)$$

$$\Delta H_{\text{vap}} = 16919 \text{ J/mol} = 16.92 \text{ kJ/mol}$$

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T} = \frac{16919 \frac{\text{J}}{\text{mol}}}{373 \text{ K}} = 45.33 \text{ J/K mol}$$

Practice exercise

Knowing that $\Delta H_{\text{vap,ethanol}} = 38.7 \text{ kJ mol}^{-1}$, and $t_{\text{boiling,ethanol}}^\circ = 78.4 \text{ }^\circ\text{C}$, calculate the pressure at which ethanol boils at $25 \text{ }^\circ\text{C}$.

Example 9.5

Knowing that $\Delta H_{\text{vap,ethanol}} = 38.7 \text{ kJ mol}^{-1}$, and $t_{\text{boiling,ethanol}}^\circ = 78.4 \text{ }^\circ\text{C}$, calculate the pressure at which ethanol boils at $25 \text{ }^\circ\text{C}$.

Solution

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{T_2 - T_1}{T_1 \times T_2} \right) \quad \Rightarrow \quad \Rightarrow \quad \ln \frac{P_2}{1} = \frac{38700}{8.314} \left(\frac{298 - 351.4}{351.4 \times 298} \right)$$

$$P_2 = 0.09313 \text{ atm} = 70.78 \text{ mmHg} = 9436 \text{ Pa}$$

Practice exercise

From the following information of an organic compound:

$$T_{\text{freezing}} = 80\text{ }^{\circ}\text{C}$$

$$P_{\text{vap, liquid, }85.95\text{ }^{\circ}\text{C}} = 10\text{ mmHg}$$

$$P_{\text{vap, liquid, }119.45\text{ }^{\circ}\text{C}} = 40\text{ mmHg}$$

$$P_{\text{vap, solid, }52.6\text{ }^{\circ}\text{C}} = 1\text{ mmHg}$$

triple point is $80\text{ }^{\circ}\text{C}$ and 1 atm

Calculate:

A) ΔH_{vap}

B) T_{boiling}

C) ΔS_{vap} at T_{boiling}

D) P_{vap} at T_{freezing}

E) $\Delta H_{\text{sublimation}}$

F) $\Delta H_{\text{freezing}}$

G) Temperature at which P_{vap} of the solid

compound is $1 \times 10^{-5}\text{ mmHg}$.

- **Fusion (melting) process**

When a substance fuses (melts) from its solid state to its liquid state:

$$\Delta V = V_l - V_s$$

$$\Delta P = \frac{\Delta H_{\text{fus}}}{V_l - V_s} \frac{\Delta T}{T}$$

For most substances, ΔV is positive, and for some little substances is negative.

Accordingly, increasing pressure mostly increases temperature.

- **Sublimation process**

When a substance sublimates from its solid 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 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.
2. 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.
1. Knowing for H₂O that its 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 solidification is 6.03 kJ mol⁻¹, calculate the change in its solidification point accompanying the change in pressure by 1 atm.
2. 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 cm³ 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.
3. From the following table:

P _{vap} / torr	10	40
t / °C	55.7	150.6

- calculate ΔH_{vap} and ΔS_{vap} of decane at 100 °C and at its normal boiling point.
4. Knowing that $\Delta H_{\text{vap,ethanol}}^{\circ} = 38.7 \text{ kJ mol}^{-1}$, and $T_{\text{boiling,ethanol}}^{\circ} = 78.4 \text{ °C}$, calculate the pressure at which ethanol boils at 25 °C.
 5. From the following information of an organic compound:
 $t_{\text{solidification}} = 80 \text{ °C}$
 $P_{\text{liquid vap, 85.8 °C}} = 10 \text{ mmHg}$
 $P_{\text{liquid vap, 119.3 °C}} = 40 \text{ mmHg}$
 $P_{\text{solid vap, 52.6 °C}} = 1 \text{ mmHg}$
 triple point = 80 °C and 1 atm
 Calculate:
 A) ΔH_{vap} B) T_{boiling} C) ΔS_{vap} at T_{boiling} D) P_{vap} at T_{freezing}
 E) $\Delta H_{\text{sublimation}}$ F) $\Delta H_{\text{freezing}}$ G) Temperature at which P_{vap} of the solid compound is $1 \times 10^{-5} \text{ mmHg}$.
 6. Knowing that $\Delta H_{\text{vap,water}} = 42.3 \text{ kJ mol}^{-1}$, calculate the pressure at which water boils at 25 °C.