

UNIVERSITY OF ANBAR

COLLEGE OF ENGINEERING

CHEMICAL & PETROCHEMICAL ENGINEERING



PHYSICAL CHEMISTRY

Prepared

By

Khaled J. Hamid

PHYSICAL CHEMISTRY

Course Objectives/Goals

The goals of this course are to enable students to:

1. explore the scope of physical chemistry and its importance to chemical engineering education.
2. develop a fundamental understanding of the basic principles of physical chemistry.
3. develop problem-solving ability based on relevant laws and mathematical equations.

Course Learning Outcomes

By the end of successful completion of this course, the student will be:

1. able to demonstrate an understanding of gas behavior (ideal and real gases) using different equations of state and kinetic molecular model.
2. able to demonstrate an understanding of thermodynamics laws and their applications.
3. able to demonstrate knowledge about kinetics laws, define the rate of reaction and the rate constant.
4. skilled in problem solving and analytical reasoning as applied to scientific problems.
5. able to develop their knowledge in terms of Catalysis, includes heterogeneous and homogeneous catalysis, and Nanotechnology.

Pre-requisites: CHE1112 General Chemistry

Students' Assessment:

Students are assessed as follows:

Assessment Tool(s)	Date	Weight (%)
Semester activities. These include quizzes, classroom interactions, Presentations.	During the 15 Weeks	10%
Progress Exam 1	Week-6	20%
Progress Exam 2	Week-14	20%
Final Exam	Week-16	50%
Total		100%

- **Exams**

There are two progressive exams in this course, each one will be given a weight of 20 % out of 50. The final exam will deserve 50% of the course and will be scheduled according to the University rules.

- **Missed Exams**

There will be no makeup exams or quizzes. In general, where an absence occurs without a prior consent, the absence will be unexcused and the student will receive zero.

- **Exam Re-grading:**

I will be pleased to re-grade exams' papers or problems that you believe to have been unfairly graded. Please note that the paper of a re-grade may be higher score, a lower score, or no change of score.

- **Quizzes**

We will usually have a quiz during the first or last 15-20 minutes of the lecture. The exception will be the week when there is also a Midterm exam. Quizzes are worth a lot, 5 – 10% out of 50% of the course. Each quiz will be approximately 3-5 questions in total length. Students will not be notified about these quizzes *in advance*.

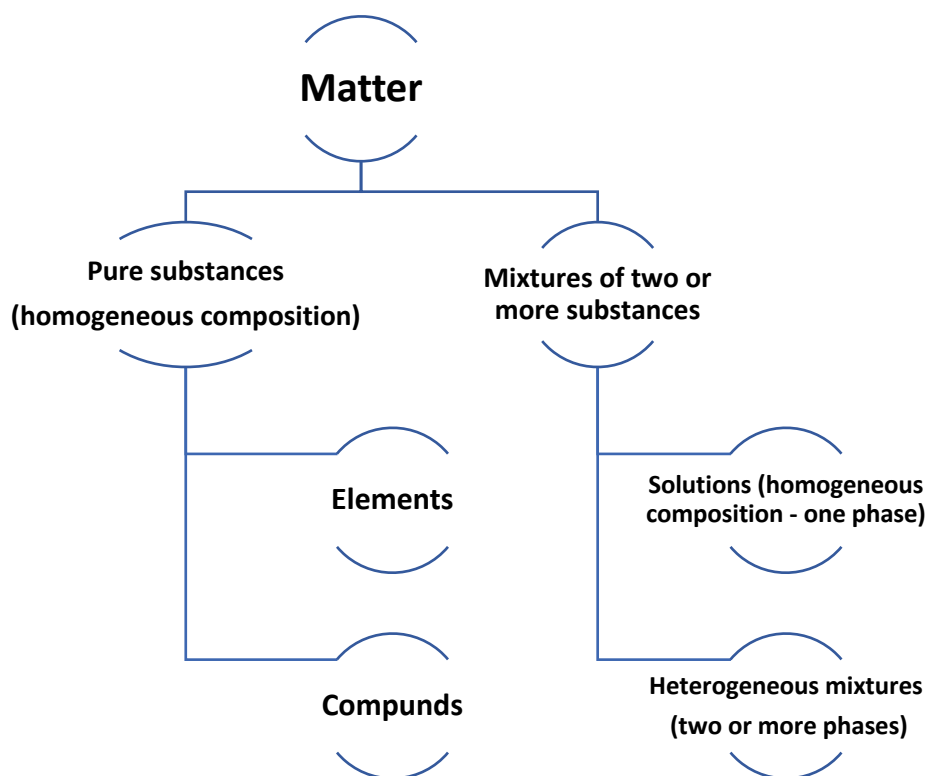
What is Physical Chemistry?

Physical chemistry is the branch of chemistry that study the matter behaves and how chemical reactions occur. The principles of physical chemistry provide a framework for all branches of chemistry, such as:

- **Organic chemists** use kinetics studies to figure out the mechanisms of reactions, use quantum-chemistry calculations to study the structures and stabilities of reaction intermediates, and use nuclear-magnetic-resonance (NMR) to help determining the structure of compounds.
- **Inorganic chemists** use quantum chemistry and spectroscopy to study bonding.
- **Analytical chemists** use spectroscopy to analyze samples.
- **Biochemists** use kinetics to study rates of enzyme- catalyzed reactions; use thermodynamics to study biological energy transformations, osmosis, and membrane equilibrium.
- **Environmental chemists** use thermodynamics to find the equilibrium composition of lakes and streams, use chemical kinetics to study the reactions of pollutants in the atmosphere, and use physical kinetics to study the rate of dispersion of pollutants in the environment.
- **Chemical engineers** use thermodynamics to predict the equilibrium composition of reaction mixtures, use kinetics to calculate how fast products will be formed, and use principles of thermodynamic phase equilibria to design separation procedures such as fractional distillation.

Bulk matter

A **matter** is anything that has mass and occupies space. It consists of a number of atoms, molecules or ions.



The different types of physical states are called **states of matter**, so there are three states of matter:

- A **solid** is a rigid form of matter. It has a definite shape and occupies a fixed volume (at a particular temperature and pressure).
- A **liquid** is a fluid form of matter. It occupies a fixed volume (at a particular temperature and pressure) but has no fixed shape. Additionally, it takes up the shape of the container.
- A **gas** is also a fluid form of matter. It spreads out to fill the space containing it and takes up the shape of the container.

liquids and solids are examples of a **condensed state** of matter. A liquid and a gas are examples of a **fluid** form of matter: they flow in response to forces (such a gravity) that are applied.

Solids and liquids do not expand very much when we heat them, while gases expand a lot. Gases can be compressed by increasing the pressure, whereas liquids and solids cannot easily be compressed except at high pressures.

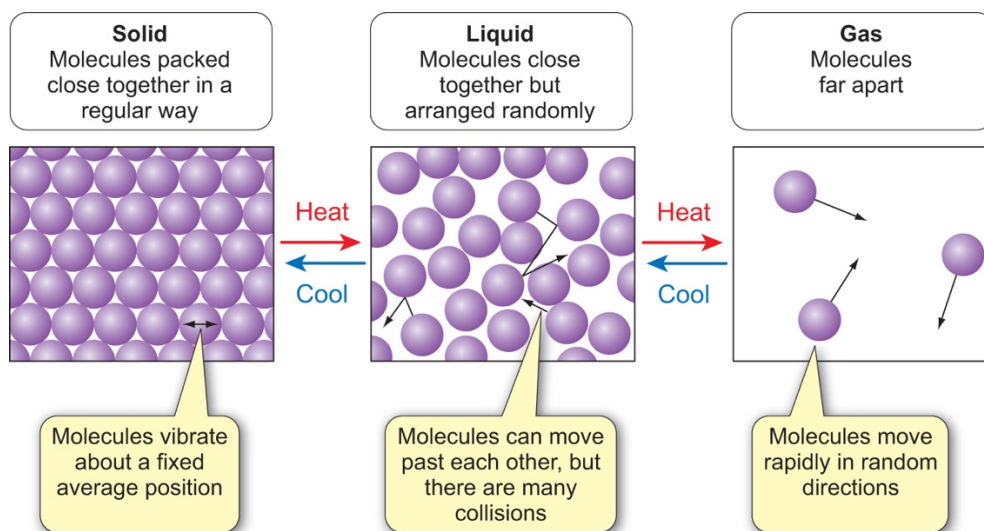


Figure 1: This chart shows the Kinetic-molecular model for the structure of matter

A solid is rigid because the molecules cannot easily move past one another due to strong interactions between them. The molecules do vibrate, though, about fixed average positions. The vibrations become more vigorous as the temperature is raised, until the molecules have enough energy to move from their fixed positions and the solid melts to form a liquid.

The molecules in a liquid are still very close together but they are able to move around in a restricted way. On further heating, the molecules gain more energy and move around faster. Eventually, they have enough energy to overcome completely the attractions of the other molecules in the liquid and escape from the surface to form a gas.

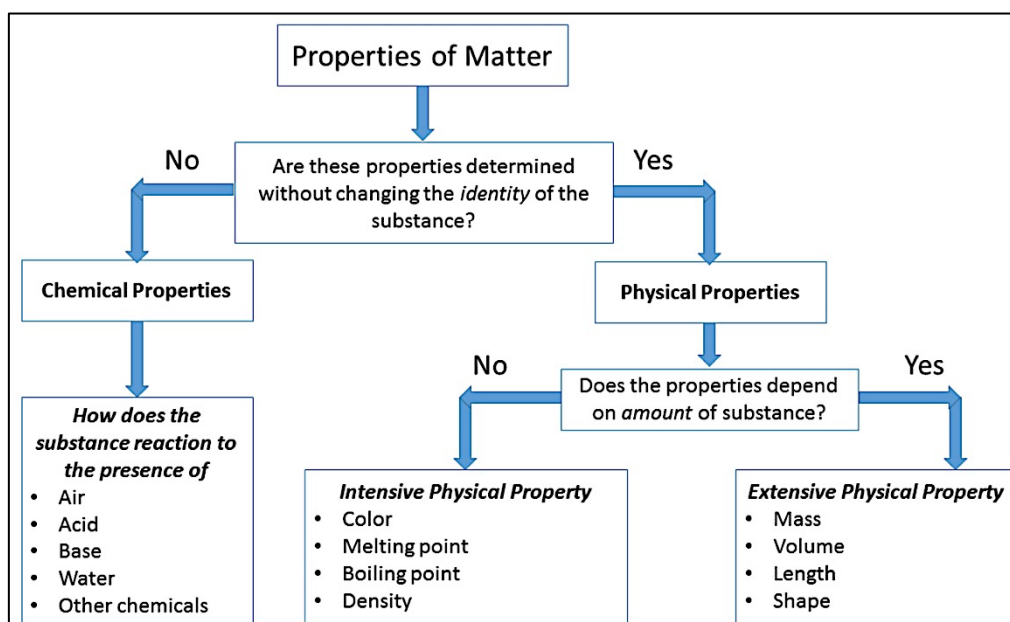
(**Note:** when a molecular solid changes from **solid to liquid and then to gas**, it is only the intermolecular attractions between the molecules that are broken, not the covalent bonds within the molecules)

Fluids
 The molecules in a fluid have enough energy to overcome the forces between molecules and move past one another so that the substance flows. A liquid flows under the influence of gravity (or other force) from one container to another. A gas spreads out to fill the space containing it.

Gases and Vapors
 The term '**vapor**' is often used for the gaseous state of a substance that is normally a solid or a liquid at RT. For example, chemists talk about water vapor or sodium vapor lamps, but oxygen and carbon dioxide are gases.

Properties of matter

- **Physical properties** are those properties that can be measured and observed without changing the composition of the substance.
- **Chemical properties** are those properties that can describe the ability of a substance to form new substances, either by reaction with other substances or by decomposition.



Flow chart indicates the Properties of a matter

Phase Change (or Transition)

Phase change or **Phase transition** is a transition process from one phase to another. The three states of matter are different phases.

The transitions between the three states of matter usually take place quickly. So, at 1 atm pressure, the temperature at which:

- a solid changes into a liquid is called its **normal melting point (m.p or T_m)**;
- a liquid changes into a gas is called its **normal boiling point (b.p or T_b)**.

1. Melting and Freezing

Melting is an endothermic process. Energy is taken in from the surroundings to overcome intermolecular attractions so that the molecules can move past one another.

The enthalpy change of 1 mol of the substance is called the **enthalpy change of fusion**, $\Delta_{fus}H^\circ$, and values are always have a positive sign.

The enthalpy change for the reverse process, **freezing**, is called the **enthalpy change of freezing**, $\Delta_{freezing}H^\circ$, which is an exothermic process and values always have a negative charge.

$$\Delta_{fus}H^\circ = -\Delta_{freezing}H^\circ$$

2. Vaporization and Condensation

Vaporization is an endothermic process taking in energy from the surroundings. Whereas, **condensation** is the reverse process and should be an exothermic process.

The enthalpy change of 1 mol of the substance is called the **enthalpy change of vaporization**, $\Delta_{vap}H^\circ$, and values are always have a positive sign. While, the enthalpy change for the reverse process, **condensation**, is called the **enthalpy change of**

condensation, $\Delta_{\text{cond}}H^\ominus$, which is an exothermic process and values always have a negative charge.

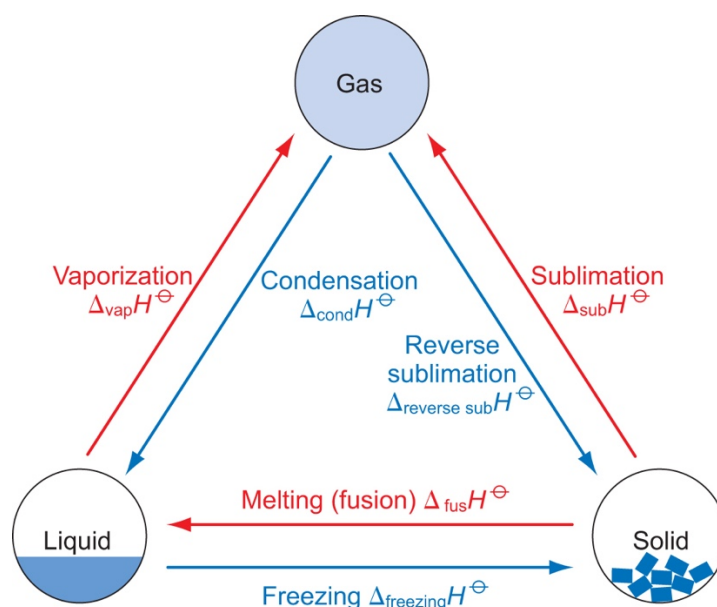
$$\Delta_{\text{vap}}H^\ominus = -\Delta_{\text{cond}}H^\ominus$$

3. Sublimation and reverse sublimation

Sublimation process is the conversion of a solid directly to vapor. This process is an endothermic process, whereas the **reverse sublimation** is an exothermic process.

$$\Delta_{\text{sub}}H^\ominus = -\Delta_{\text{reverse sub}}H^\ominus$$

The figure below shows the transitions between the three states of matter and the enthalpy changes of state involved.



This Figure illustrates the Transitions between the three states of Matter

Unit Conversion

One of the benefits of using the metric system is the ease with which we can convert from one unit to another. We do this by using the relationships between units—math equations called equivalent units.

To convert from one unit to another we must use a **conversion factor**. A conversion factor is a ratio of equivalent quantities. These conversion factors are formed from equivalent units. For example, since $1\text{ m} = 100\text{ cm}$, we could write two ratios: $\frac{1\text{ m}}{100\text{ cm}}$ or $\frac{100\text{ cm}}{1\text{ m}}$. In both cases the ratio is 1 since the units are equal.

$$\text{Unit 1} \times \text{Conversion factor} = \text{Unit 2}$$

Variables of matter (Variables of State)

The physical state of a sample of a substance, its physical condition, is defined by its physical properties. The variables that needed to specify the state of a system are the **amount of substance** it contains, n , the **volume** it occupies, V , the **pressure**, P , and the **temperature**, T :

- The amount of substance, n ,** is a measure of the number of specified entities (atoms, molecules or group of ions)

Unit:

mol: 1 mole of a substance = 6.022×10^{23} mol⁻¹ of N_A (Avogadro's constant)

Mathematically:

$$n (\text{mol}) = \frac{\text{mass}(\text{g})}{\text{Molar mass} (\text{g} \cdot \text{mol}^{-1})}$$

- Volume** is a measure of the quantity of space that the sample occupies.

Unit:

m³ (cubic meter)

However, chemists work with much smaller volumes (cm³) cubic centimeter, dm³ cubic decimeter and liter

$$1\text{ L} = 1000\text{ ml} = 1000\text{ cm}^3 = 1\text{ dm}^3$$

$$1\text{ m}^3 = 1000\text{ L}$$

3. Density, ρ ,

is the ratio of the mass of a substance to the volume occupied by that mass; it is the mass per unit of volume and is given by the equation below. It's a physical property of almost everything around us.

$$\rho = \frac{m}{v}$$

SI unit of density Kg/m^3 , g/cm^3 or g/ml

4. Pressure, P ,

Pressure is defined as force divided by the area to which the force is applied. The greater the force acting on a given area, the greater the pressure. The origin of the force exerted by a gas is the incessant battering of the molecules on the walls of its container. The collisions are so numerous that they exert an effectively steady force, which is experienced as a steady pressure.

Units:

The SI unit of pressure, the pascal (Pa), is defined as 1 newton per metre-squared:

$$1 \text{ Pa} = 1 \text{ N/m}^2$$

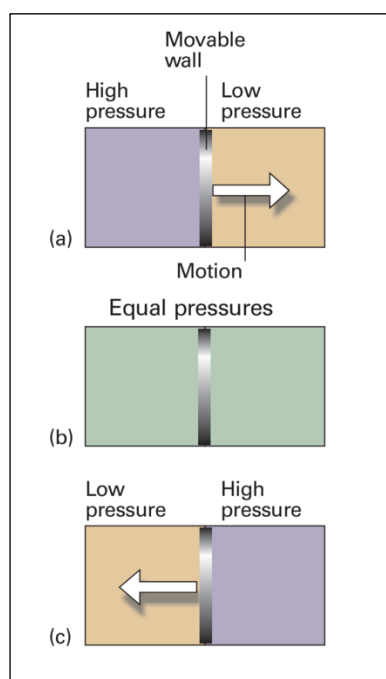
$$1 \text{ Pa} = 1 \text{ kg}\cdot\text{m/s}^2$$

Several other units are still widely used; of these units, the most commonly used are atmosphere ($1 \text{ atm} = 1.013 25 \times 10^5 \text{ Pa}$ exactly) and bar ($1 \text{ bar} = 10^5 \text{ Pa}$). A pressure of 1 bar is the standard pressure for reporting data.

$$\text{Pressure, } P = \frac{\text{Force, } F}{\text{Area, } A}$$

If two gases are in separate containers that share a common movable wall (Fig. below), the gas that has the higher pressure will tend to compress (reduce the volume of) the gas that has lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed.

There will come a stage when the two pressures are equal and the wall has no further tendency to move. This condition of equality of pressure on either side of a movable wall (a 'piston') is a state of mechanical equilibrium between the two gases. The pressure of a gas is therefore an indication of whether a container that contains the gas will be in mechanical equilibrium with another gas with which it shares a movable wall.



The measurement of pressure

The pressure exerted by the atmosphere is measured with a barometer. The original version of a barometer (which was invented by Torricelli, a student of Galileo) was an inverted tube of mercury sealed at the upper end. When the column of mercury is in mechanical equilibrium with the atmosphere, the pressure at its base is equal to that exerted by the atmosphere. It follows that the height of the mercury column is proportional to the external pressure.

1 atm	760	torr
	760	mm Hg
	76	cm Hg
	101,325	Pa
	101.325	kPa
	29.9	in. Hg
	14.7	lb/in ²

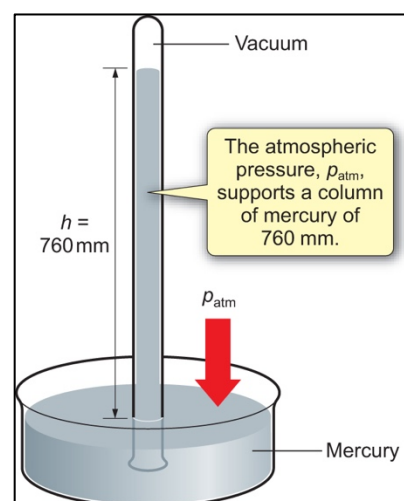
The column of mercury in the tube is held up by the atmospheric pressure; the higher the pressure, the longer of the column of mercury that is supported. Therefore, the pressure is equal to:

$$P = h \times \rho \times g$$

h: height

ρ: density

g: acceleration of gravity = 9.81 m/s²



Question:

Why we use mercury rather than water?

Around RT, the density of mercury is 13.6 g.cm⁻³ and that of water is 1.00 g.cm⁻³. Calculate the height of a column of each liquid that would be supported by a pressure of 1 atm, and suggest ***why*** mercury is used in barometers rather than water.

5. Temperature, T

Temperature is a measure of the intensity of thermal energy, or how hot a system is, regardless of its size. Or, it is the measure of the internal energy of a system.

The term heat refers to the flow of energy due to a temperature difference. Heat always flows from a region of higher temperature to one of lower temperature. The common laboratory instrument for measuring temperature is a thermometer. The temperature of a system can be expressed by several different scales. Three commonly used temperature scales are:

- a. **Celsius scale, °C:** is the temperature scale that used in most of the world. It's based on the **boiling** and **freezing** points of water:

Freezing point = 0°C

Boiling point = 100°C

$$^{\circ}\text{C} = \frac{(^{\circ}\text{F} - 32)}{1.8}$$

$$^{\circ}\text{C} = K - 273$$

- b. **Kelvin scale, K:** it is the **SI base** unit of temperature. It is a thermodynamics or absolute temperature scale.

Absolute zero (zero Kelvin) is the lowest temperature that can be obtained theoretically. (the coldest temperature possible)

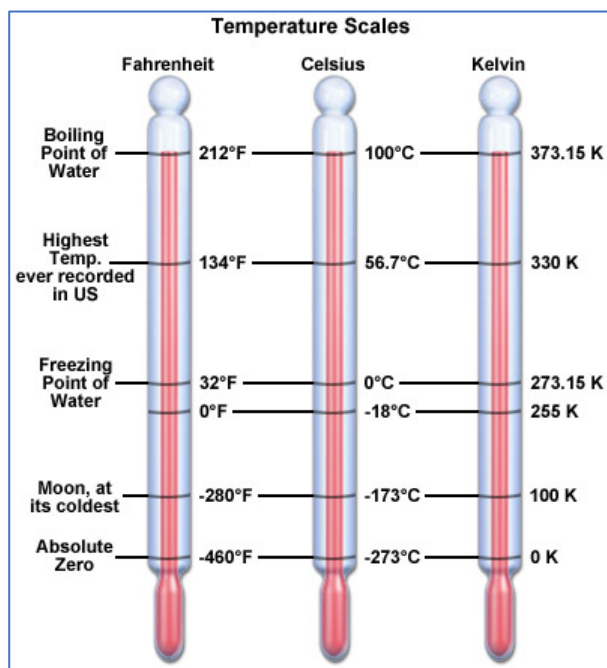
$$K = ^{\circ}\text{C} + 273$$

- c. **Fahrenheit, °F :** it is also based on water, defines the normal freezing and boiling points. It commonly uses in the USA.

Freezing point of water = 32°F

Boiling point of water = 212°F

$$^{\circ}\text{F} = 1.8^{\circ}\text{C} + 32$$



This figure shows the three scales of Temperature includes freezing and boiling points of water.

GASES

Properties, Behavior and Equations of state

Gases are the least dense and the most mobile among the three states of matter. A **gas** molecule moves at very high velocities and has high kinetic energy.

General Characteristics of Gases

1. Expansibility

Gases have limitless expansibility. They expand to fill the entire vessel they are placed in.

2. Compressibility

Gases are easily compressed by application of pressure to a movable piston fitted in the container.

3. Diffusibility

Gases can diffuse rapidly through each other to form a homogeneous mixture.

4. Pressure

Gases exert pressure on the walls of the container in all directions.

5. Effect of Heat

The Perfect Gas

Firstly: The Perfect Gas law

The equation of state of a gas at low pressure was established by combining a series of empirical laws. The volume of a given sample of a gas depends on the temperature and pressure applied to it. Any change in temperature or pressure will affect the volume of the gas. As results of experimental studies from 17th to 19th century, scientists derived the relationships among the pressure, temperature and volume of a given mass of gas. These relationships, which describe the general behavior of gases, are called the **gas laws**.

Parameters of a gas:

A gas sample can be described in terms of four parameters (measurable properties):

- (1) the volume, V of the gas
- (2) its pressure, P
- (3) its temperature, T
- (4) the number of moles, n , of gas in the container

Boyle's law:

Through a series of experiments, Robert Boyle (1627–1691) determined the relationship between the pressure (P) and volume (V) of a particular quantity of a gas. This relationship of P and V is known as Boyle's law:

At constant temperature (T), the volume (V) of a fixed mass of a gas is inversely proportional to the pressure (P), which may be expressed as:

$$V \propto \frac{1}{P} \quad P_1V_1 = P_2V_2 \quad (\text{for different conditions})$$

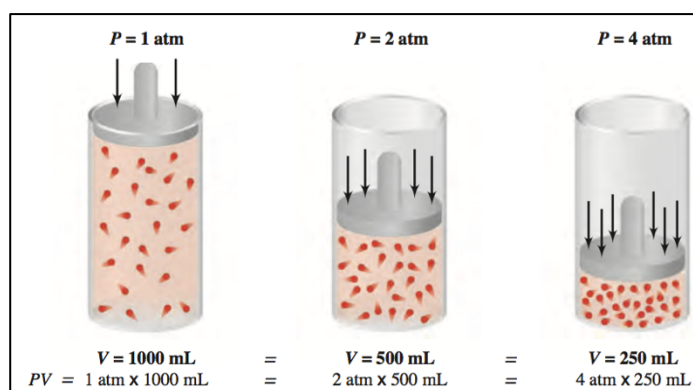


Figure 1

Charles' law:

In 1787 the French Physicist J. A. C. Charles observed the effect of temperature on the volume of a gas. As we see in the figure below, the net result is an increase in volume due to an increase in temperature.

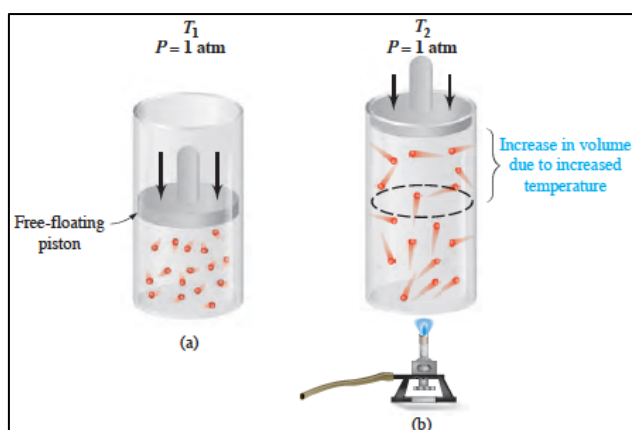


Figure 2

At constant pressure, the volume of a fixed mass of any gas is directly proportional to the absolute temperature, which may be expressed as

$$V \propto T \quad , \quad \frac{V_1}{T_1} = \frac{V_2}{T_2} \quad (\text{for different conditions})$$

Avogadro's law:

The volume of a gas depends on the temperature, the pressure, and the number of gas molecules. Different gases at the same temperature have the same average kinetic energy. Hence, if two different gases are at the same temperature, occupy equal volumes, and exhibit equal pressures, each gas must contain the same number of molecules. This statement is true because systems with identical **PVT** properties can be produced only by equal numbers of molecules having the same average kinetic energy.

Equal volumes of different gases at the same temperature and pressure contain the same number of molecules.

$$V \propto n \quad , \quad \frac{V_1}{n_1} = \frac{V_2}{n_2} \quad (\text{for different conditions})$$

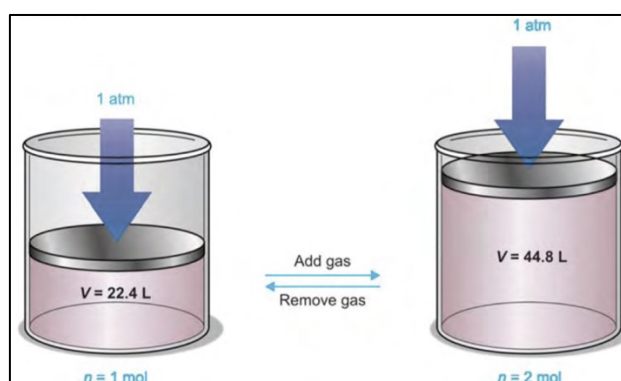


Figure 3

Combined Gas laws:

Boyle's Law and Charles' Law can be combined into a single relationship called the **Combined Gas Law**

Boyle's law $V \propto \frac{1}{P}$ (T, n constant)

Charles' law $V \propto T$ (P, n constant)

Therefore, $V \propto \frac{T}{P}$ (n constant)

For a fixed mass of gas, the volume is directly proportional to kelvin temperature and inversely proportional to the pressure.

$$\frac{PV}{T} = k \quad (n \text{ constant})$$

If the pressure, volume and temperature of a gas be changed from P_1, V_1 and T_1 to P_2, T_2 and V_2 , then

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Gay-Lussac's law

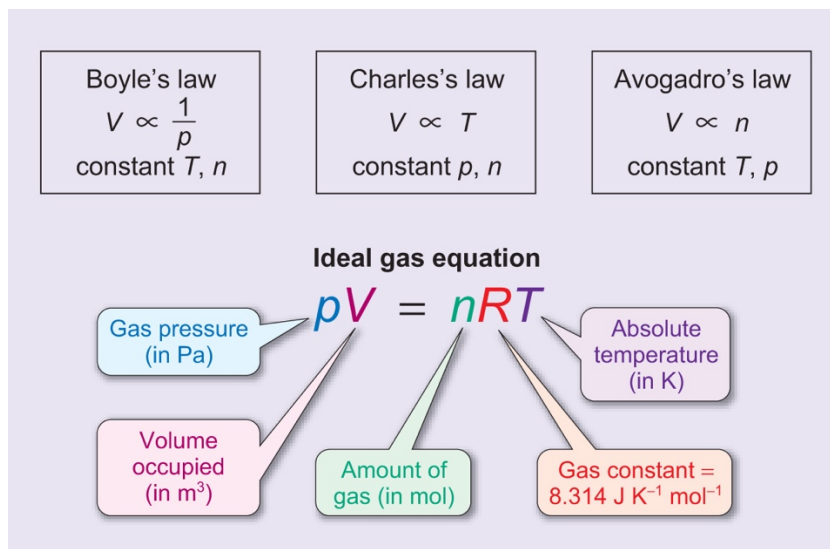
In 1802 Joseph *Gay-Lussac* as a result of his experiments established a general relation between the pressure and temperature of a gas. This is known as **Gay-Lussac's Law or Pressure-Temperature Law**. It states that:

At constant volume, the pressure of a fixed mass of gas is directly proportional to the Kelvin temperature or absolute temperature.

$$P \propto T \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

Ideal Gas law:

Now we can summarize the whole above relationships that used in gas calculations by combining them in a single equation:



Where V is the volume, P is the pressure, T is the temperature, n is the number of molecules of moles, and R as known is the ideal gas constant. The units of R depend on the units of P , V and T . In addition, we can calculate R by taking **1 mole** of a gas at **STP** conditions:

$$R = \frac{PV}{nT} = \frac{(1 \text{ atm})(22.4 \text{ L})}{(1 \text{ mol})(273 \text{ K})} = 0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

Values of gas constant, R

- $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
- $0.0821 \text{ L} \cdot \text{atm} / \text{mol} \cdot \text{K}$
- $8.314 \text{ Pa m}^3 \text{ K}^{-1} \text{ mol}^{-1}$
- $62.3 \text{ mmHg L K}^{-1} \text{ mol}^{-1}$

Secondly: Mixtures of GasesDalton's Law of Partial Pressures:

There is plenty of space between the molecules in a gas. This means that, when gases mix together, the molecules can easily intermingle (mix).

The figure below shows three containers of equal volume. The first one contains a gas exerting a pressure P_A , the second one contains a different gas exerting a pressure P_B . While in the third container, the two gases occupy the same volume together.

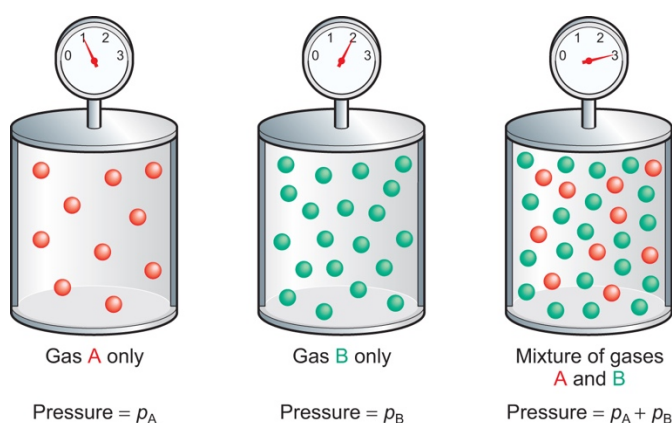


Figure 4

Therefore, the total pressure is simply the sum of the two individual pressures. This is expressed in **Dalton's law**:

The total pressure of a mixture of gases is the sum of the partial pressures exerted by each individual gas.

The **partial pressure**: is the pressure that can be exerted if the gas was alone in the container.

In general, for a mixture of gases, A, B, C,

$$P_{\text{total}} = P_A + P_B + P_C + \dots = \sum_i P_i$$

To describe the proportion of each component in a mixture, the mole fraction, X , of the component is used. This is given by:

Mole fraction of gas A:
$$X_A = \frac{\text{number of moles of A}}{\text{total number of moles}} = \frac{n_A}{n_{\text{total}}}$$

Note:

- ❖ The sum of the mole fractions for all the components in a mixture is equal to (1).
- ❖ The mole fraction has no units because it is a ratio.

For an ideal gas, at constant V and T , $P_A \propto n_A$
 So, for a component A in a mixture of gases

$$\frac{P_A}{P_{total}} = \frac{n_A}{n_{total}} = X_A, \quad \text{So,} \quad \frac{P_A}{P_{total}} = X_A$$

then the partial pressure:

$$P_A = X_A P_{total}$$

The Real Gases

For many gases (such as N_2 , O_2 , and He) at around atmospheric pressure, the ideal gas equation describes their behaviour very well. However, these gases are termed nonideal or real gases. The behavior of other gases (such as CO_2 and butane) deviates slightly from the ideal model behavior even at atmospheric pressure. So how might ideal gas equation be tested?

An ideal gas obeys Boyle's law under all conditions. If the volume of a fixed amount of a gas is measured as a function of pressure at constant temperature, a plot of P versus $1/V$ will give a straight line if the gas obeys Boyle's law. As shown in Figure 5, there is a very good agreement between Boyle's law and experimental data at low pressures but deviations from ideal behavior occur when the pressure increases.

An alternative approach is to plot P versus V . Plots of pressure versus volume at fixed temperatures are called ***p-V isotherms***. Examples for three temperatures are shown in the figure below, where the solid lines are predicted from the ideal gas equation and the points are experimental measurements. There is a good fit of the experimental results to ideal behavior, particularly at higher temperatures and lower pressures. However, at low temperatures or high pressures, there are marked deviations from ideal behavior.

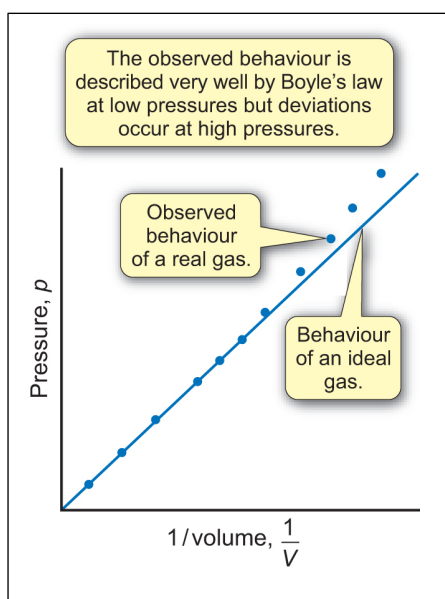


Figure 5

Comparison of the behavior of a real gas with that of an ideal gas (the straight line)

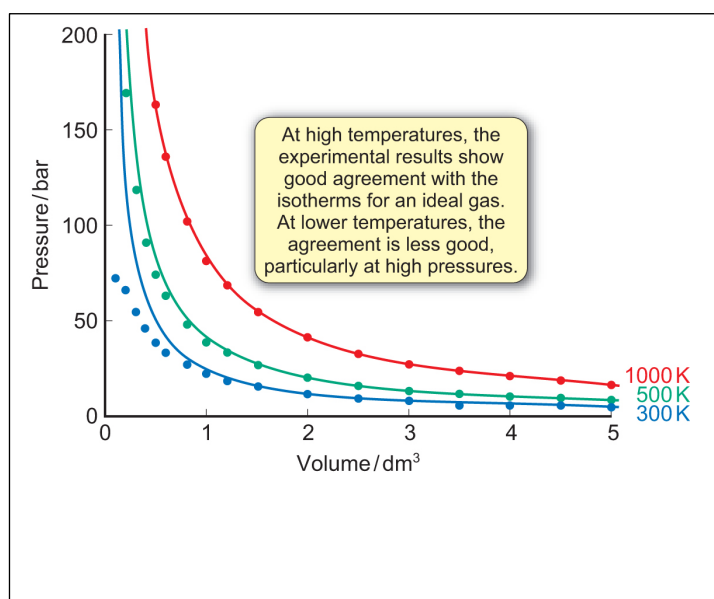


Figure 6

P-V isotherms for gases. The points show experimental measurements; the solid lines show the behavior of an ideal gas

The plots in Figure 5 and 6 Suggest that pressure of a sample of a gas can be increased indefinitely with little change in gas behavior. However, this does not happen in reality because, if the pressure is increased enough, especially at low temperatures, the gas will start liquefy, as shown in Figure 7.

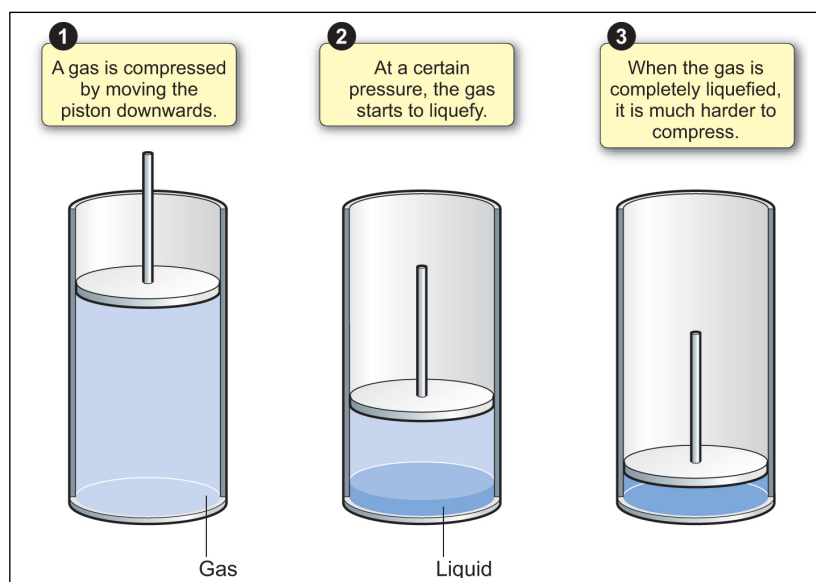
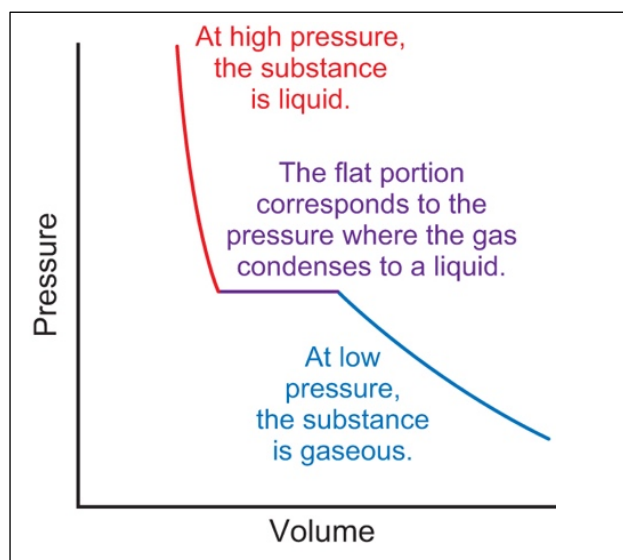


Figure 7

In Figure , at low pressures, the isotherm looks like that for an ideal gas. However, as the pressure increases, a value is reached where the gas starts to liquefy and noticeable decrease in volume occurs with no change in gas pressure (the flat step in the graph). When all the gas has turned to liquid, the curve is much steeper since it takes very large pressure changes to significantly change the volume of a liquid -it is much less compressible.

Figure 8: A $p - V$ isotherm showing condensation of a real gas.

Some experimental data for the isotherms of carbon dioxide CO_2 , Figure ..., demonstrate the behavior of a real gas at different temperatures. At 50°C , the isotherms look like that for an ideal gas. At this T , the compound exists as a gas at any pressure. While at low temperature of 20°C , the isotherm shows that liquefaction occurs when the pressure reached about 60 atm.

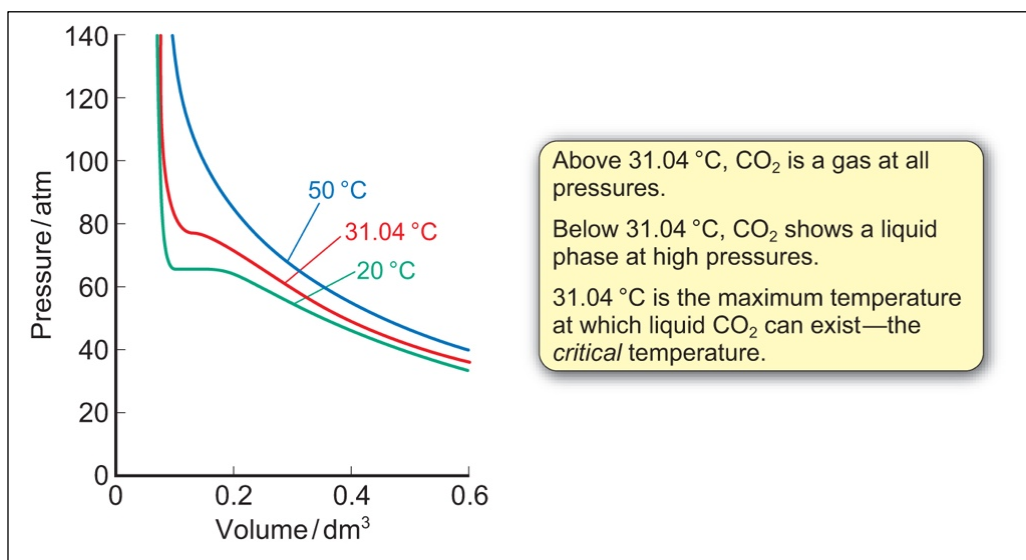


Figure 9: Experimental $p - V$ isotherms for 1 mol of carbon dioxide, CO_2 .

At 31.4 °C, the behavior is different and the isotherm shows a point of inflection. 31.4°C is the highest temperature at which the liquid CO_2 can exist and known as the critical temperature T_c . Above T_c , the gas cannot be liquified simply by increasing the pressure. Liquid CO_2 can only exist below T_c .

To summarize, real gases show deviations from the perfect gas law because molecules interact with one another. A point to keep in mind is that **repulsive forces** between molecules assist expansion and **attractive forces** assist compression.

Two assumptions that are defining an ideal gas:

1. The size of the molecules is negligible.
2. There are no intermolecular interactions.

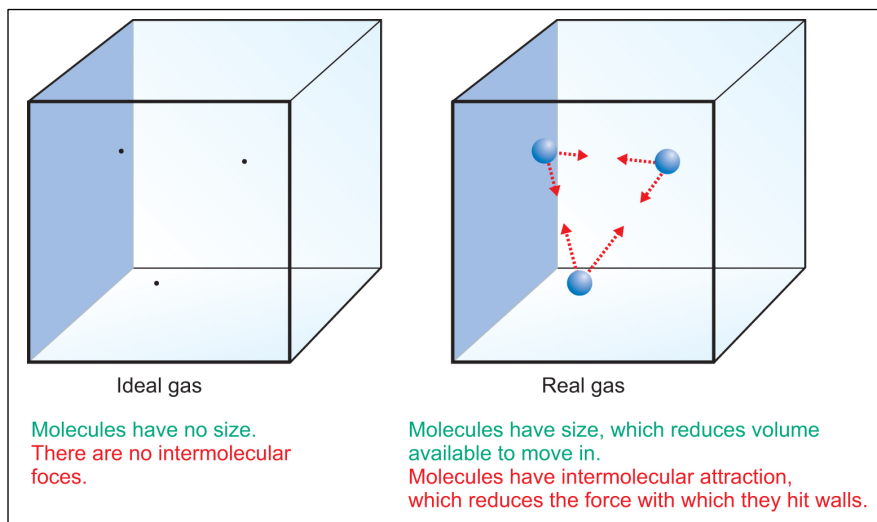


Figure 10

(a) The compression factor

The compression factor, Z , of a gas is the ratio of its measured molar volume, $V_{m(r)} = V/n$, to the molar volume of a perfect gas, $V_{m(i)}$, at the same pressure and temperature:

$$Z = \frac{V_m}{V_m^\circ}$$

Because the molar volume of a perfect gas for **1 mol** is equal to: $V_m^\circ = RT/P$, an equivalent expression is

$$Z = \frac{PV_m}{RT}$$

Because for a perfect gas $Z = 1$ under all conditions, deviation of Z from 1 is a measure of departure from perfect behaviour. Some experimental values of Z are plotted in Fig. 1.14. At very low pressures, all the gases shown have $Z \approx 1$ and behave nearly perfectly. At high pressures, all the gases have $Z > 1$, signifying that they have a larger molar volume than a perfect gas. Repulsive forces are now dominant. At intermediate pressures, most gases have $Z < 1$, indicating that the attractive forces are reducing the molar volume relative to that of a perfect gas.

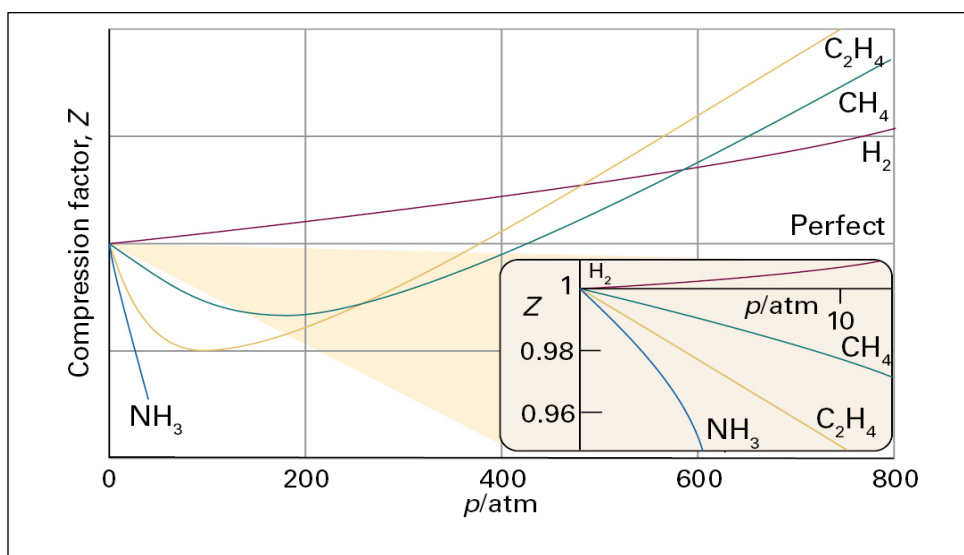


Figure 11: The variation of the compression factor Z , with pressure for several gases at 0°C

(b) The van der Waals equation for gases:

The first successful attempt to account for the behavior of real gases was introduced by the Dutch physicist Johannes van der Waals in 1873. He started from the ideal gas equation and introduced some additional terms to account for the behavior of real gases.

1. The first correction accounts for the attractions between the molecules. These mean that, in a real gas, the pressure is somewhat less than in the ideal case. Thus, van der Waals suggested that a correction factor should be added to the actual value of (**P**) to make up for the slightly reduced pressure, and so obtain the ideal value:

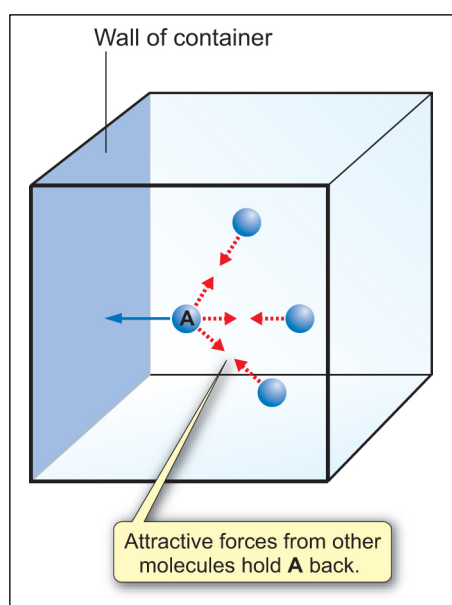


Figure 12

2. The second correction concerns the finite size of the molecules. Because the molecules have a small volume of their own, the volume in which molecules can move is less than the total volume of the container. So, van der Waals subtracted a correction factor from the actual value of V to allow for this reduction. This takes the form $(V - nb)$, where the value of (**b**) is a constant related to the volume of the molecules.

$$\left(p + a \left(\frac{n}{V} \right)^2 \right) (V - nb) = nRT$$

The diagram includes the following annotations:

- Ideal pressure:** Indicated by a green bracket above the term $p + a \left(\frac{n}{V} \right)^2$.
- Ideal volume:** Indicated by a red bracket above the term $(V - nb)$.
- Measured pressure:** A callout box pointing to the variable p .
- Correction factor to account for intermolecular attractions:** A callout box pointing to the term $a \left(\frac{n}{V} \right)^2$.
- Measured volume:** A callout box pointing to the variable V .
- Correction factor to account for the finite size of the molecules:** A callout box pointing to the term $-nb$.

The constants a and b are called the *van der Waals* coefficients. Therefore, a represents the strength of attractions interactions between the molecules. They are characteristic of each gas but independent of the temperature.

Effusion and Diffusion

In 1833, Thomas Graham studied the effusion of a range of gases and found that:

At a given temperature and gas pressure, the rate of effusion (the number of molecules passing through the hole per second) is inversely proportional to the square root of the molar mass.

$$\text{Rate of effusion} \propto \frac{1}{\sqrt{M}}$$

The effusion process in which gas molecules pass through a small hole such as a pore in a membrane, as shown in the figure below. Therefore, effusion can be defined as the process when gas molecules escape through a tiny hole into an evacuated space.

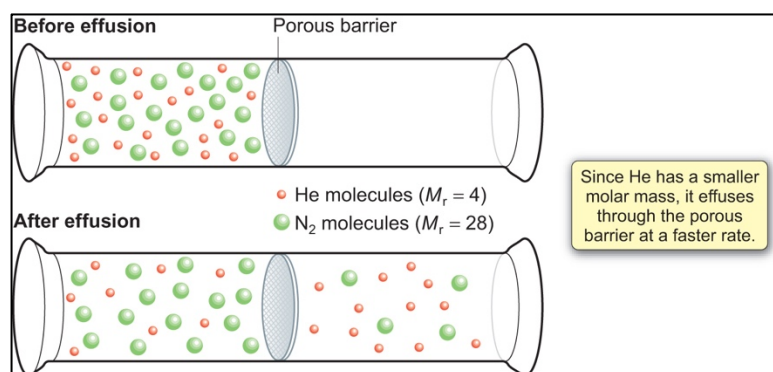


Figure 13

For a mixture of two gases, A and B , with molar masses, M_A and M_B , the *Graham's law* of effusion can be written as:

$$\frac{\text{Rate of effusion of } A}{\text{Rate of effusion of } B} = \sqrt{\frac{M_B}{M_A}}$$

Gases with different molar masses will effuse at different rates. A gas with a low molar mass (such as helium) effuses faster than a gas with higher molar mass (such as Nitrogen). This explains why a balloon filled with helium collapses faster than if filled with air.

The process of **Diffusion** also depends on the movement of molecules. The figure below illustrates how **diffusion** differs from **effusion**. Diffusion occurs when two (or more) gases come into contact and mix. There are large spaces between molecules, so they can easily mix.

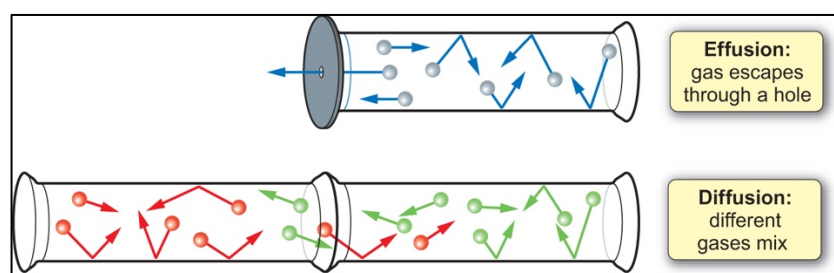


Figure 14

Diffusion is the random motion or movement of gas molecules from a region of high concentration to a region of lower concentration.

Exercises

- 1) What volume will 2.5L of a gas occupy if the pressure is changed from 760 mmHg to 630 mmHg?
- 2) A given mass of hydrogen occupies 40.0L at 700 torr. What volume will occupy at 5 atm pressure?
- 3) A 36.4 L volume of methane gas is heated from 25 °C to 88 °C at constant pressure. What is the final volume of the gas?
- 4) Under constant-pressure conditions, a sample of hydrogen gas initially at 190.4 °F and volume of $(9.6 \times 10^{-3} \text{ m}^3)$ is cooled until its final volume, which is 3.4 L. What is its final temperature?
- 5) Calculate the density of CO₂ in g/L at 0.99 atm and 55°C.
- 6) A gas-filled balloon having a volume of 2.5L at 1.2 atm and 25 °C is allowed to rise to the atmosphere (about 30 Km above the surface of the Earth), where the temperature and pressure are -23°C and $3 \times 10^{-3} \text{ atm}$, respectively. Calculate the final volume of the balloon.
- 7) Calculate the volume of a gas (in mL) of 88.4 g of CO₂ at STP conditions.
- 8) 3.036g of a gas occupy a volume of 426 cm³ at 273 K and 1 atm pressure. Calculate the molar mass of the gas.
- 9) At 27°C and 1 atm pressure, the density of a gaseous hydrocarbon is 1.22 g.dm⁻³. What is the hydrocarbon?
- 10) A sample of hydrogen gas was found to have a pressure of 110 kPa when the temperature was 20.0 °C. What can its pressure be exerted to be when the temperature is 7.0 °C?
- 11) At 100 °C and 16.0 kPa, the mass density of phosphorus vapor is 0.6388 Kg.m⁻³. What is the molecular formula of phosphorus under these conditions? (M of P is 30.97)
- 12) Calculate the pressure exerted by 22g of ethane behaving as a perfect gas when confined to 1000 cm³ at 25°C.

- 13)** A storage tank contains 2 moles of Ar, 3 moles of O₂ and 5 moles of N₂ at a total pressure of 1000 torr. Calculate the partial pressure of each gas.
- 14)** A storage tank contains Nitrogen, Oxygen and Carbon dioxide. The partial pressure of Nitrogen and Oxygen gas are 600 torr and 150 torr, respectively. The total pressure is 825 torr. What is the partial pressure and mole fraction of Carbon Dioxide?
- 15)** Calculate the pressure exerted by 1.0 mol H₂S behaving as a van der Waals gas when it is confined under the following conditions:
- (i) at 273.15 K in 22.414 dm³,
 - (ii) at 500 K in 150 cm³.
- 16)** A gas at 350 K and 12 atm has a molar volume 12 per cent larger than that calculated from the perfect gas law. Calculate:
- (i) The compression factor under these conditions.
 - (ii) The molar volume of the gas.
- Which are dominating in the sample, the attractive or the repulsive forces?
- 17)** How much faster is the rate of effusion of helium than carbon dioxide, when both gases are at the same temperature?

THERMODYNAMICS

Thermodynamics is the branch of science that deals with the transformations of energy as heat or work. Thermodynamics is concerned with the study of **macroscopic** systems, those consisting of large, measurable amounts of matter. It does not deal with the properties of individual molecules.

Thermodynamics terms and basic concepts

An important part of the study of thermodynamics is a few terms and definitions that must be understood clearly:

➤ **System, Boundary, Surroundings**

- **A system** is any part of the Universe that is of interest (chosen for studying).
- **Surrounding** is the rest of the universe.
- **A boundary** is the actual or notional surface that separates the system from its surrounding.

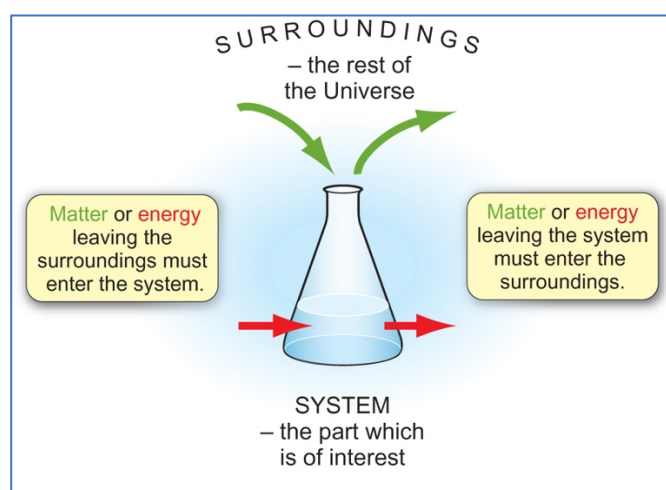


Figure 1: The system and surroundings. A change for the system causes a change with the same magnitude (size) but with opposite sign in the surroundings.

➤ Types of Thermodynamic systems

There are three types of thermodynamic systems depending on the nature of the boundary:

1. **An open system:** is a system in which both matter and energy can be exchanged with the surroundings.

Hot water contained in a beaker placed on laboratory table is an open system. The water vapour (matter) and also heat (energy) is transferred to the surroundings through the imaginary boundary.

2. **A closed system:** is a system that can exchange only energy with the surroundings.

A specific quantity of hot water contained in a sealed tube, is an example of a closed system. While no water vapor can escape from this system, it can transfer heat through the walls of the tube to the surroundings.

3. **An isolated system:** is a system that can be no exchange energy and matter with the surroundings.

Let us consider a system 100 ml of water in contact with its vapor in a closed vessel which is insulated. Since the vessel is sealed, no water vapor (matter) can escape from it. Also, because the vessel is insulated, no heat (energy) can be exchanged with the surroundings.

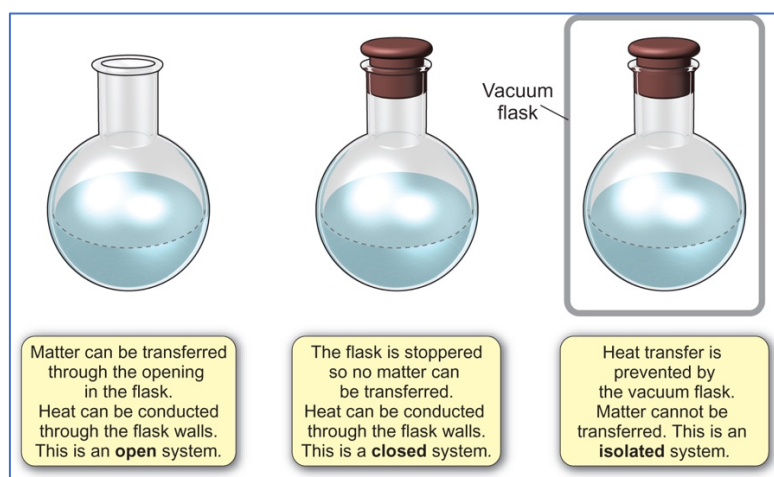


Figure 2: Types of Thermodynamic systems

➤ **Properties of a system: Intensive and Extensive properties**

The macroscopic or bulk properties of a system (volume, pressure, mass, etc.) can be divided into two classes:

(a) Intensive properties

(b) Extensive properties

Intensive Properties

A property which does not depend on the quantity of matter present in the system, is known as an intensive Property.

Some examples of intensive properties are *pressure, temperature, density, and concentration*.

If the overall temperature of a glass of water (our system) is 20°C, then any drop of water in that glass has a temperature of 20°C. Similarly, if the concentration of salt, NaCl, in the glass of water is 0.1 mole/litre, then any drop of water from the glass also has a salt concentration of 0.1 mole/litre.

Extensive Properties

A property that does depend on the quantity of matter present in the system, is called an Extensive Property.

Some examples of extensive properties are *volume, number of moles, enthalpy, entropy, and Gibbs' free energy*. Some of these properties are unfamiliar to you but these will be defined and illustrated later.

Intensive properties	Extensive properties
Temperature	Mass
Pressure	Length
Density	Volume
Specific heat capacity	Amount of substance
Molar heat capacity	Enthalpy
Concentration	Entropy
All molar properties	Gibbs free energy

➤ State of a system

The fundamental properties which determine the state of a system are pressure (P), temperature (T), volume (V), mass and composition. Since a change in the magnitude of such properties alters the state of the system, these are referred to as **State functions**.

A state function is a property that its values depend only on the current state of the system.

The most important thing to remember about a state function is that the change in value of the function depends only on the final and initial conditions. It is independent on the path between them. For example, internal energy, entropy, enthalpy, Gibbs free energy, mass, pressure, volume, temperature, ... etc. Therefore, for any state function, X

$$\Delta X = X_{final\ state} - X_{initial\ state}$$

➤ Thermodynamic Processes

When a thermodynamic system changes from one state to another, the operation is called a Process. These processes involve the change of conditions (temperature, pressure and volume). The various types of thermodynamic processes are:

(1) Isothermal Processes

Those processes in which the temperature remains fixed, are termed isothermal processes. This is often achieved by placing the system in a thermostat (a constant temperature bath).

(2) Adiabatic Processes

Those processes in which no heat can flow into or out of the system, are called adiabatic processes. Adiabatic conditions can be approached by carrying the process in an insulated container such as 'thermos' bottle. High vacuum and highly polished surfaces help to achieve thermal insulation.

(3) Isobaric Processes

Those processes which take place at constant pressure are called isobaric processes. For example, heating of water to its boiling point and its vaporization take place at the same atmospheric pressure.

(4) Isochoric Processes

Those processes in which the volume remains constant are known as isochoric processes. The heating of a substance in a non-expanding chamber is an example of isochoric process.

(5) Cyclic Process

When a system in a given state goes through a number of different processes and finally returns to its initial state, the overall process is called a cycle or cyclic process.

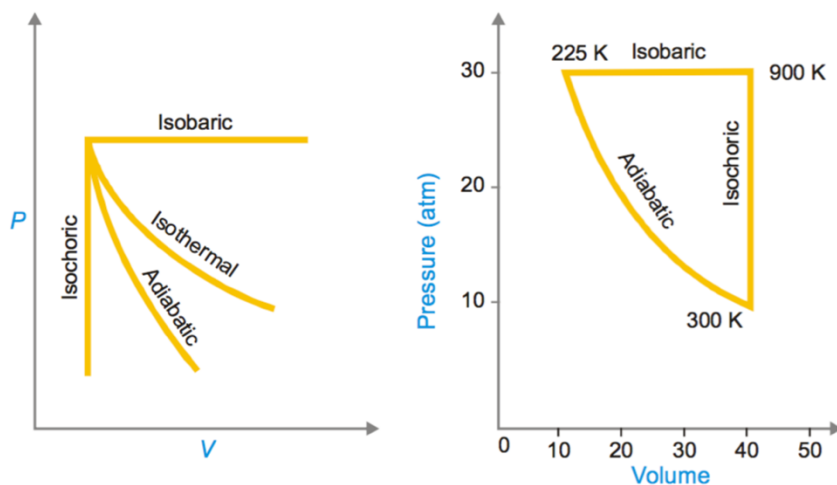


Figure 3: Types of Thermodynamic Processes

Work, Heat & Energy

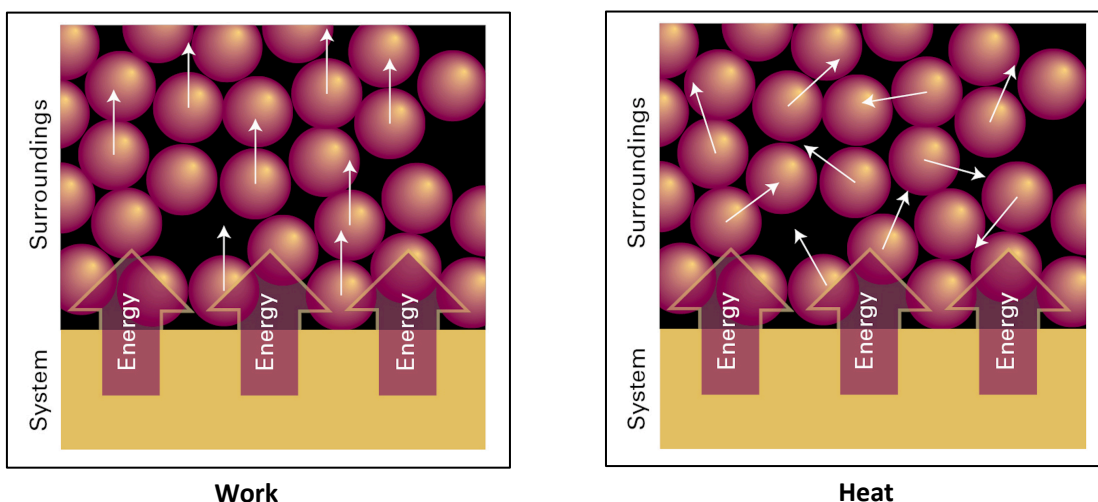
➤ Work

Mechanical work:

The fundamental physical property in thermodynamics is work: **work** is motion against an opposing force. Doing work is equivalent to raising a weight somewhere in the surroundings. An example of doing work is the expansion of a gas that pushes out a piston and raises a weight. A chemical reaction that drives an electric current through a resistance also does work, because the same current could be driven through a motor and used to raise a weight.

$$dw = F dz \quad (\text{definition of work})$$

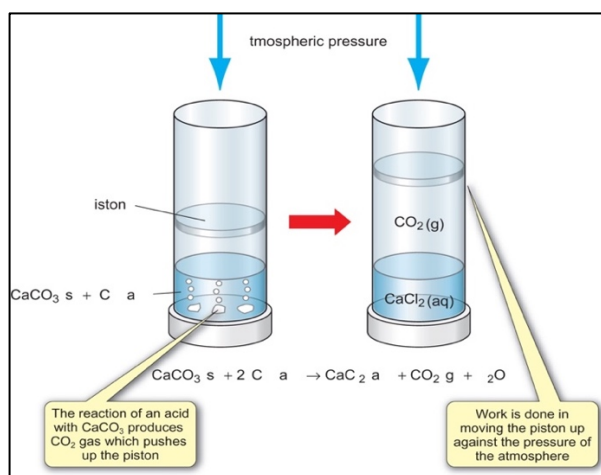
The state of a system is changed by the supply or removal of energy in the form of heat or work. In molecular terms, heating is the transfer of energy that makes use of disorderly, apparently random, molecular motion in the surroundings. In contrast, work is the transfer of energy that makes use of organized motion in the surroundings.



Therefore, when energy is transferred to the surroundings as heat, the transfer stimulates random motion of the atoms in the surroundings. On the other hand, when a system does work, it stimulates orderly motion in the surroundings.

Expansion Work

Expansion work is the work that arising from a change in volume. This type of work includes the work done by a gas as it expands and drives back the atmosphere. Many chemical reactions result in the generation of gases or consumption of gases (for instance, the thermal decomposition of calcium carbonate as illustrated in [Figure](#)), and the thermodynamic characteristics of a reaction depend on the work it can do. The term ‘expansion work’ also includes work associated with negative changes of volume.

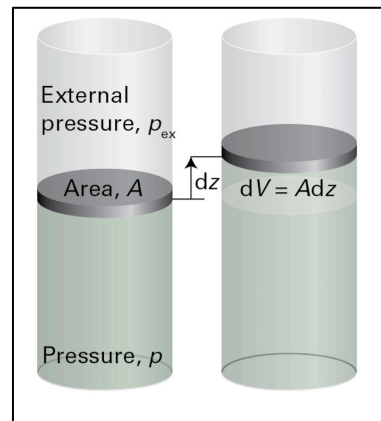


(a) The general expression for work

The calculation of expansion work starts from the definition used in physics, which states that the work required to move an object a distance ds (dz) against an opposing force.

$$w = - \int_{v_i}^{v_f} P_{ex} dv$$

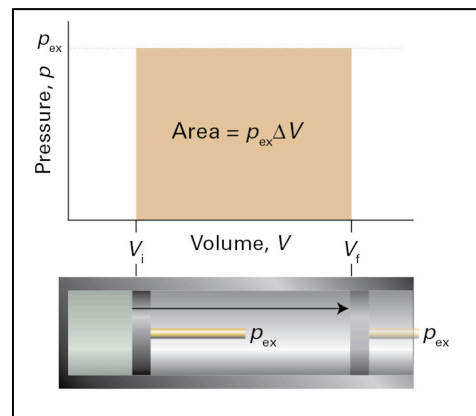
The negative sign tells us that, when the system moves an object against an opposing force, the internal energy of the system doing the work will decrease.



(b) Expansion against constant pressure

Suppose that the external pressure is constant throughout the expansion. For example, the piston may be pressed on by the atmosphere, which exerts the same pressure throughout the expansion.

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



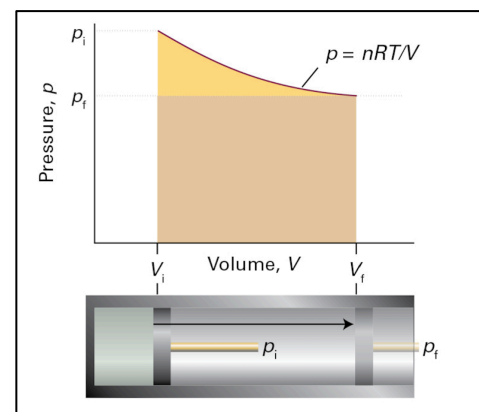
(c) Reversible expansion:

A reversible change or process means that a process which can be reversed in direction at any stage. The main idea of reversible expansion work is the system in equilibrium. $P = P_{ex}$

(d) Isothermal reversible expansion

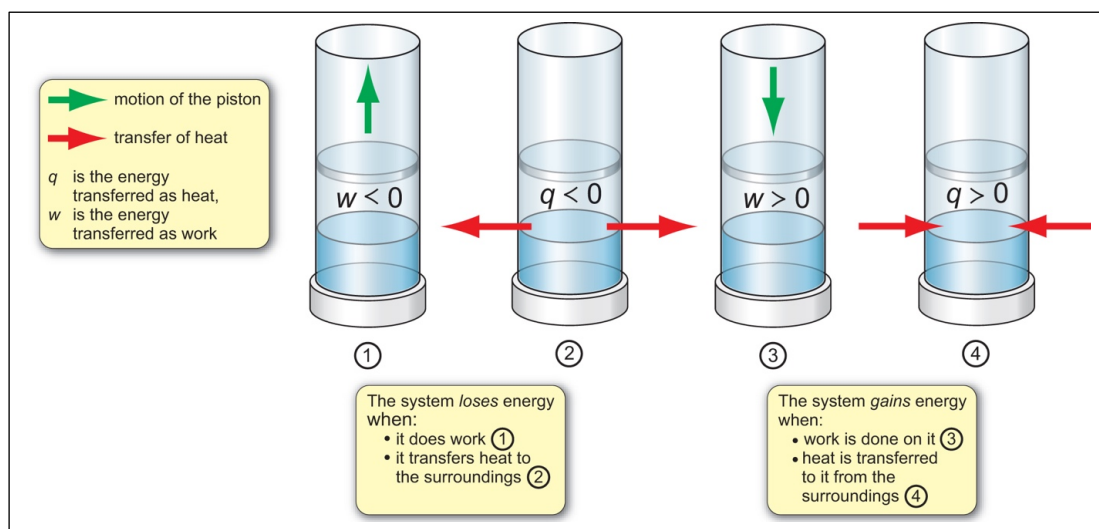
The expansion is made isothermal by keeping the system in thermal contact with its surroundings (a constant temperature bath).

$$w = -nRT \ln \frac{v_f}{v_i}$$



Note:

- Energy gained (heat absorbed by or work done on) a system is **positive**;
- Energy lost (heat released from or work done by) a system is **negative**.



➤ **Energy** is the capacity to do work.

SI Units: Joule, J which is equal to $1\text{Nm} = 1\text{ Kg.m}^2. \text{s}^{-2}$

Power is the rate of supplying energy. Its unit is the **Watt, $1\text{W} = 1\text{ J. s}^{-1}$**

There are many forms that energy can take. Some of these forms are thermal, mechanical, kinetic, potential, electric, magnetic, chemical, and nuclear. When you sum all of the forms of energy acting within a system you will obtain the system's total energy.

There are two types of energy that make up the energy of a system:

1. **Macroscopic forms:** are those which can be influenced by external effects such as gravity, magnetism electricity and surface tension.

- a. **Kinetic Energy, K_E :** is the energy that the body possesses as a result of its motion.

$$K_E = \frac{1}{2}mv^2 \quad \text{where, } m = \text{mass, } v = \text{velocity Unit: Joule}$$

- b. **Potential Energy, P_E :** is the energy that body possesses as a result of its position.

$$P_E = mgh \quad \text{where } m:\text{mass, } g:\text{acceleration of gravity, } h:\text{height}$$

2. **Microscopic forms:** are those related to the molecular structure of a system. The sum of microscopic energies is called **internal energy**.

➤ **Heat** is the energy that transferred from one system to another as a result of thermal interactions.

There are two main processes in the energy transferring as heat:

1. **An exothermic process** is a process that releases energy as heat into the surroundings. All combustion reactions are exothermic.
2. **An endothermic process** is a process in which energy taken in from the surroundings.

Question:

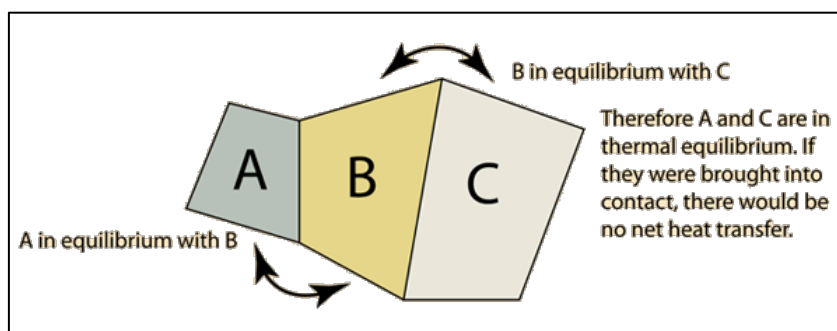
1. Calculate the energy transferred as work, when **1 mol** of a gas expands from a volume of **5 dm³** to **10 dm³** against a constant pressure of **760 torr**.
2. When a sample of 1.0 mol of Ar, regarded as a perfect gas, undergoes an isothermal reversible expansion at 20.0°C from 10.0 dm³ to 30 dm³. Calculate the work done.
3. A chemical reaction takes place in a container of cross-section area 75.0 cm². As a result of the reaction, a piston is pushed out through 25.0 cm against an external pressure of 150 kPa. Calculate the work done by the system.

THEMODYNAMICS

Laws of Thermodynamics

1. Zeroth law of thermodynamics

If two bodies are in thermal equilibrium with a third body, they are in thermal (thermodynamics) equilibrium with each other.



2. First law of Thermodynamics

the first law can be state as " Energy can be transferred or transformed but cannot be created or destroyed".

The internal energy of an isolated system is constant.

Mathematical formula:

$$\Delta U = q + w$$

where ΔU : the change in internal energy
 q : energy transferred as heat
 w : work done on/by the system

➤ Internal Energy

The internal energy is the total energy of a system. It is the sum of potential and kinetic energy of the atoms, ions or molecules of the system.

The internal energy is a state function, so it depends only on the initial and final states of a system.

$$\Delta U = U_f - U_i$$

$$\text{Unit: Joule, } J = \text{Kg.m}^2.\text{s}^{-2}$$

The internal energy of a system is an extensive property (depends on the amount of a substance). While the Molar Internal energy is an intensive property. The Molar internal energy is the internal energy divided by the amount of substance in a system.

|

$$U_m = \frac{U}{n}$$

Unit: kJ/mol

➤ **There are two ways that the value of expansion work can be zero:**

1. Free expansion: free expansion work when $P = 0$, so $w = 0$

No expansion work is done because the gases expand into a vacuum. From the first law of thermodynamics

$$\Delta U = q + w$$

Therefore, $\Delta U = q_P$ Heat supplied to the system at constant pressure

2. Reactions at constant volume:

$$w = -P_{ex} \Delta v \quad \text{because of at constant volume } \Delta v = 0$$

so, $w = 0$

$$\Delta U = q + w$$

Therefore, $\Delta U = q_v$ Heat supplied to the system at constant volume

➤ **Enthalpy**

Enthalpy can be defined as a thermodynamic property, its value is the sum of internal energy plus the product of the pressure and volume of the system.

$$H = U + pV$$

The Enthalpy change, ΔH : is the heat transferred at constant pressure by a chemical reaction or a process.

Because of the internal energy, pressure and volume are state function, therefore the enthalpy is a state function. In addition, it depends on the amount of a substance, so it is an extensive property.

Q/ How to prove that enthalpy change is equal to the transferred heat at constant pressure?

$$\Delta H = q_P$$

➤ **Heat capacities**

Heat capacity is the heat needed to raise the temperature of a substance by 1K.

Unit: J/K

Mathematical formula:

$$C = \frac{q}{\Delta T}$$

where **c**: the heat capacity

q: quantity of heat supplied

ΔT : change in temperature

Heat capacity is an extensive property but can be an intensive property when:

1. **Specific heat capacity**, C_s , which is the heat capacity of a sample divided by the mass.

$$C_s = \frac{C}{m}, \quad \text{so,} \quad C_s = \frac{q}{m \Delta T} \quad \text{Unit: } \frac{J}{K \cdot kg}$$

2. **Molar heat capacity**, C_m , which is the heat capacity of a sample divided by the amount of substance.

$$C_m = \frac{C}{n} \quad \text{so,} \quad C_m = \frac{q}{n \Delta T} \quad \text{Unit: } \frac{J}{K \cdot mol}$$

➤ **Isochoric and Isobaric Heat Capacities:**

1. Heat capacity at constant pressure (isobaric): is the heat capacity that recorded at constant pressure.

$$C_P = \frac{q_P}{\Delta T} \quad \text{so,} \quad q_P = C_P \Delta T$$

The heat capacity at constant pressure is used to relate the change in enthalpy to the change in temperature. Therefore, from the definition of the change in enthalpy, we proved that $\Delta H = q_P$

So,

$$\Delta H = C_P \Delta T$$

$$C_P = \frac{\Delta H}{\Delta T}$$

The heat capacity at constant pressure is the analogue of heat capacity at constant volume, and both of them are *extensive properties*. **The molar heat capacity at constant pressure**, $C_{p,m}$, is the heat capacity per mole of substance; it is an *intensive property*.

2. Heat capacity at constant volume (Isochoric heat capacity): is the heat capacity that recorded at constant volume

$$C_v = \frac{q_v}{\Delta T} \quad \text{so,} \quad q_v = C_v \Delta T$$

From the first law of thermodynamic we proved that there is no expansion work is done at constant volume, therefore: $\Delta U = q_v$

$$C_v = \frac{\Delta U}{\Delta T}$$

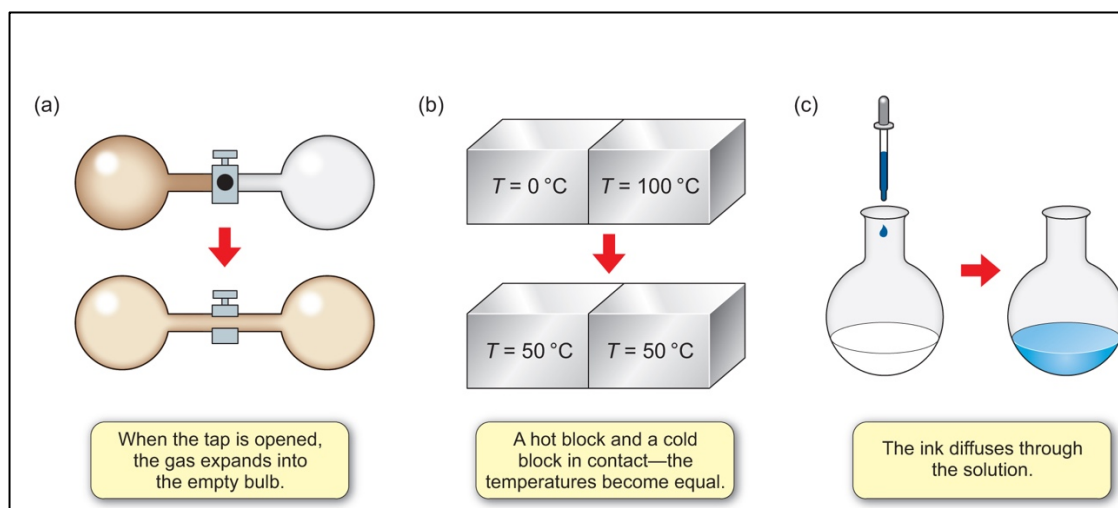
The molar heat capacity at constant volume, $C_{v,m}$, is the heat capacity per mole of substance.

THEMODYNAMICS

Laws of Thermodynamics

3. The Second law of thermodynamics: what are spontaneous processes

A spontaneous process is a process that occurs naturally without any external intervention. As shown in the figures below, when the tap in figure (a) is opened, gas flows into an evacuated vessel until the pressure is equal on both sides. The same thing that happens when a block of hot metal is placed against a cold one, as in figure (b), it very unlikely that it will get hotter while cold one cools down. Heat will be transferred until both blocks are the same temperature.



➤ Entropy and the second law of Thermodynamics

The main use of Entropy is in predicting the direction of chemical (or any other) change. This is summarized in the Second Law of Thermodynamic. The second law can be stated in a number of ways, but the most straightforward is:

Spontaneous processes are those that increase the total entropy of the Universe

Since the entropy is related to disorder, the second law shows that spontaneous processes are those that lead to an increase in disorder of the Universe. The total entropy change for a process is made up of the changes for the system and the surroundings. The Second law can therefore be expressed as:

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0 \quad \text{spontaneous process}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} < 0 \quad \text{non-spontaneous process}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} = 0 \quad \text{process is at equilibrium}$$

➤ The definitions of Entropy

Entropy is a measure of the randomness or disorder in a system. There are two approaches, one classical and one molecular. They turn out to be equivalent, but each one enriches the other:

a. The thermodynamics definitions of entropy

The thermodynamic definition of entropy concentrates on the change in entropy, ΔS , that occurs as a result of a physical or chemical change. As illustrated before, heat stimulates random motion in the surroundings. On the other hand, work stimulates uniform motion of atoms in the surroundings and so does not change their entropy.

$$\Delta S = \frac{q_{rev}}{T}$$

Entropy change (JK⁻¹)

Quantity of heat added reversibly (J)

temperature (K)

according to the above equation, when the energy transferred as heat is expressed in joules, J, and the temperature in kelvin, so the units of entropy are (J/K). entropy is an extensive property. Molar entropy is the entropy divided by the amount of substance, $S_m = S/n$, units are J/K.mol.

b. The statistical definitions of entropy

The entry point into the molecular interpretation of the Second law of thermodynamics is Boltzmann's formula.

$$S = k_B \ln W$$

W is the number of ways (microstates) of arranging the molecules and their energy in the system. The larger the number of arrangements, the less ordered the system, the larger the entropy.

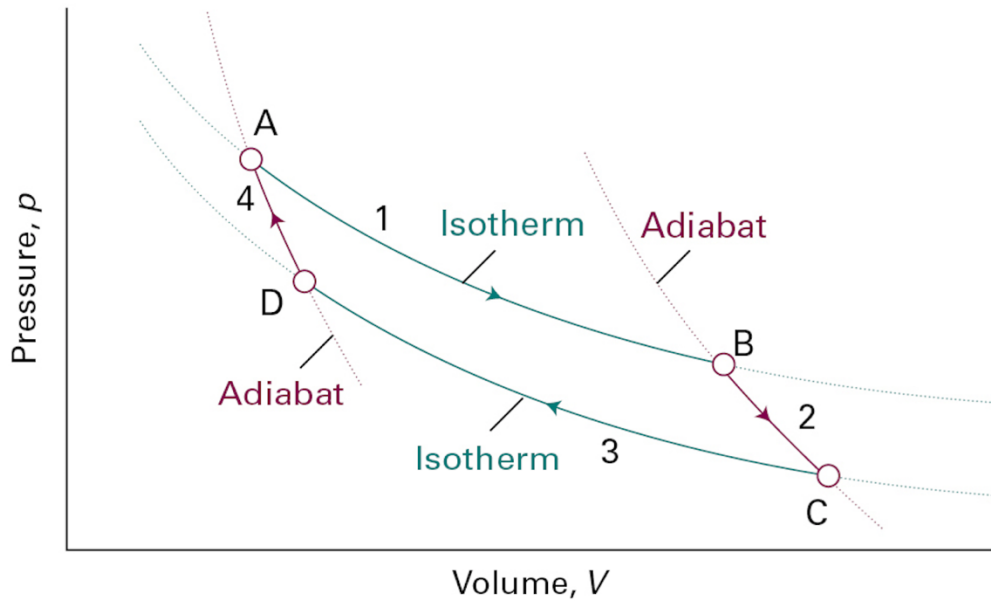
➤ **The Entropy as a state function**

Entropy is a state function

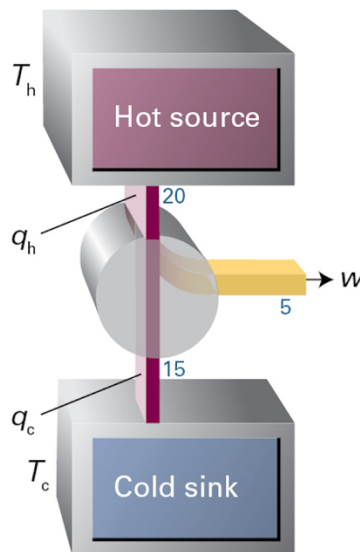
- A.** The first step is to prove that Entropy is a state function and $\Delta S = q_{\text{rev}} / T$ is independent on the path that taken between the initial and final states by Carnot Cycle. It is the most efficient heat engine cycle. It's a theoretical thermodynamic cycle named by the French engineer Carnot.

Carnot cycle consists of four reversible stages or processes:

1. Reversible isothermal expansion from A to B at T_h ; the entropy change is q_h/T_h , where q_h is the energy supplied to the system as heat from the hot source.
2. Reversible adiabatic expansion from B to C. no energy leaves the system as heat, so the change in entropy is zero. In the course of this expansion, the temperature falls from T_h to T_c the temperature of the cold sink.
3. Reversible isothermal compression from C to D at T_c . Energy is released as heat to the cold sink; the change in entropy of the system is q_c/T_c ; in this expression q_c is negative.
4. Reversible adiabatic compression from D to A. no energy enters the system as heat, so the change in entropy is zero. The temperature rises from T_c to T_h .



- B.** The second step is to show that $\Delta S = q_{rev} / T$ can be applied to any material, not just a perfect gas. And this will be by finding the **Efficiency** of the heat engine. The efficiency of a heat engine relates how much useful work is output for a given amount of heat energy input.



Heat engine is basically a device that converts heat energy into mechanical work. Heat naturally flows from hot to cold reservoir. The system can absorb some of the heat energy and use it to convert it to mechanical work.

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from hot source}} = \frac{|w|}{|q_h|}$$

The work in this case is equal to the difference between the heat energy of hot source and cold source.

$$w = |q_h| - |q_c|$$

While the efficiency of Carnot cycle will be

$$\eta_c = 1 - \frac{T_c}{T_h}$$

➤ **Entropy changes accompanying specific processes:**

We now see how to calculate the entropy changes that accompanying a variety of basic processes:

(a) Expansion

The change in Entropy of a perfect gas that expands isothermally from V_i to V_f is

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

Entropy change for the isothermal expansion of a perfect gas

Because S is a state function, the value of ΔS is independent of the path between the initial and final states, so this expression applies whether the change of state occurs reversible or irreversible.

(b) Phase transitions

Entropy changes during of phase-fusion (melting), vaporization, sublimation provide straightforward applications of of equation $\Delta S = q/T$. At the normal temperature of phase change, the reversible heat change at constant pressure is the enthalpy change so that $q_{rev} = \Delta H$

$$\Delta_{vap}S = S_{(vapour)} - S_{(liquid)} \quad \text{and} \quad q_{rev} = \Delta_{vap}H$$

$$\Delta_{fus}S = S_{(liquid)} - S_{(solid)} \quad \text{and} \quad q_{rev} = \Delta_{fus}H$$

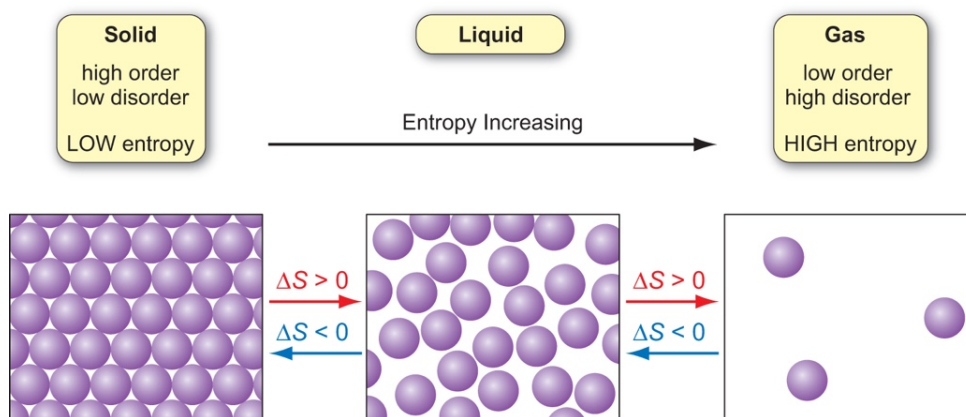
therefore,

$$\Delta_{vap}S = \frac{\Delta_{vap}H^\circ}{T_b}$$

$$\Delta_{fus}S = \frac{\Delta_{fus}H^\circ}{T_m}$$

where $\Delta_{vap}H^\circ$ and $\Delta_{fus}H^\circ$ are the standard enthalpy changes of vaporization and fusion at the boiling point and melting point, T_b and T_m , respectively. The entropy changes for the reverse processes- condensation and freezing- have the opposite sign but the same magnitude as those for vaporization and fusion.

$\Delta_{vap}H^\circ$ and $\Delta_{fus}H$ have positive values since vaporization and fusion are endothermic processes and an input of energy required. This is consistent with the idea of entropy as a measure of disorder. A vapor is more disordered- and so has higher entropy than liquid as illustrated in the figure below:

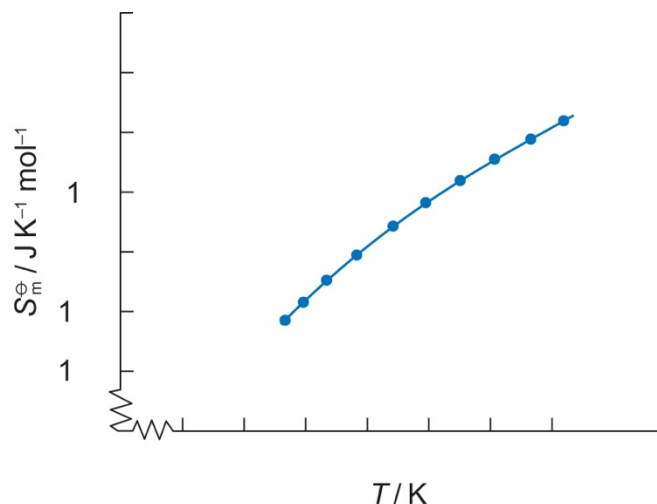


(c) Heating – how the entropy of a system changes with temperature:

As the temperature increases, matter generally becomes more disordered. The entropy of a system will increase with temperature.

The difference between the entropy of 1 mol of a substance (its molar entropy) at two temperatures is given by the equation below. When S_{Ti} is the molar entropy of a substance at an initial temperature T_i and S_{Tf} , is the molar entropy at the final temperature T_f .

$$S_{Tf} = S_{Ti} + C_p \ln \frac{T_f}{T_i}$$



Questions

1. A heat engine absorbs 2500J of heat and discards 2100J of heat. Calculate the work performed by this engine and its thermal efficiency.
2. A jet engine releases 5000 J of energy per cycle and performs 800J of work. (a) how much heat is absorbed by this engine per cycle? (b) what is the thermal efficiency? (c) how much work can this engine perform in 50 cycles? (d) if the engine completes each cycle in 0.20 seconds, what is the power rating of this engine?
3. 8000 J of heat energy is absorbed per cycle by a diesel engine that is 15% efficient. (a) How much work does it perform per cycle? (b) how much energy does it expel to the environment per cycle?
4. An engine has a heat input of 175 kW and a work output of 21 kW. (a) what is the thermal efficiency? (b) at what rate is heat discarded into the environment?
5. A Carnot engine takes in 4500J of heat energy from a reservoir at 800K. (a) how much energy will be released to a cold reservoir at 300K? (b) how much work is performed by this engine? (c) what is the efficiency?

THERMODYNAMICS

Laws of Thermodynamics

4. The Third law of Thermodynamics

Entropy is related to disorder, so a perfectly ordered system has zero entropy. Such a system would be a perfect solid crystal at absolute zero of temperature so that there is no disorder of any type. A perfect crystal is one with all the atoms, ions, or molecules aligned perfectly and with no defects. At 0K, all molecules will be in their ground state. There is only one way of arranging the molecules, so $W=1$ in the Boltzmann formula and hence $S=0$.

(a) The Nernst heat theorem

The experimental observation that turn out to be consistent with the view that entropy of a regular array of molecules is zero at $T=0$. So, it is summarized as *“The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $\Delta S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.* This conclusion is summarized by the **Third law of Thermodynamics:**

The entropy of all perfect crystalline substances at zero kelvin is zero.

(b) Third-law entropies

Entropies reported on the basis that $S(0) = 0$ are called Third-law entropies (and commonly just ‘entropies’). When the substance is in its standard state at the temperature T , the standard (Third-law) entropy is denoted S^\ominus . The standard entropy S^\ominus_{298} , of a substance is the entropy of 1 mol at 298K and 1 bar pressure. The units are $J K^{-1}mol^{-1}$.

➤ Standard entropy change of reaction

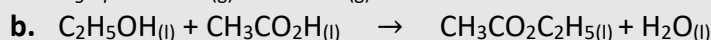
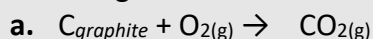
The standard entropy change of a reaction is defined as the difference between the molar entropies of the pure, separated products and pure, separated reactants. For values at 298K

$$\Delta_r S_{298}^\ominus = \underbrace{\sum \nu_i S_{298}^\ominus (\text{products})}_{\substack{\text{The sum of} \\ \text{the standard} \\ \text{entropies of all} \\ \text{of the products}}} - \underbrace{\sum \nu_i S_{298}^\ominus (\text{reactants})}_{\substack{\text{The sum of} \\ \text{the standard} \\ \text{entropies of all} \\ \text{of the reactants}}}$$

Since S_{298}^\ominus , refers to one mole of a substance, it must be multiplied by the stoichiometric coefficient, ν_i , in the balanced equation for the reaction.

Example

Calculate the standard entropy change of a reaction at 298K for each of the following reactions:



➤ Reactions at other temperatures

The entropy change at other temperature can be calculated by using the equation below to find the standard entropies of the reactants and products at other temperatures. The standard entropy change of reaction at temperature T, given by:

$$\Delta_r S_T^\ominus = \Delta_r S_{298}^\ominus + \Delta C_p \ln \frac{T}{298 \text{ K}}$$

Standard entropy change of reaction at temperature, T

Standard entropy change of reaction at 298 K

Temperature of reaction

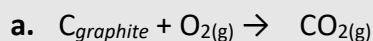
The molar heat capacity change for the reaction (the difference between products and reactants)

The above equation enables the calculation of entropy changes for reactions at any temperature as long as heat capacity data are available. ΔC_p is the difference in molar heat capacities of the products and reactants given by this equation:

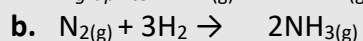
$$\Delta C_p = \sum v_i C_p (\text{products}) - \sum v_i C_p (\text{reactants})$$

Example

The entropy changes at 298K for the following reactions are as shown. Calculate $\Delta_r S$ for each reaction at 1023 K.



$$\Delta_r S^\circ_{298} = +2.96 \text{ JK}^{-1}\text{mol}^{-1}$$

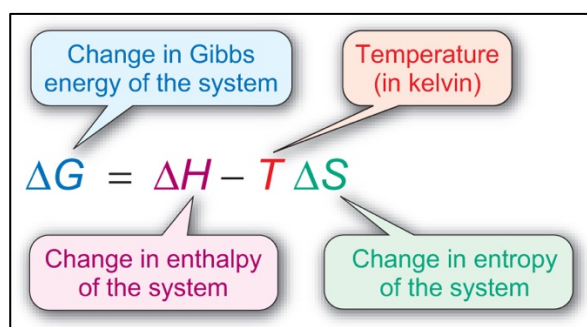


$$\Delta_r S^\circ_{298} = -198.7 \text{ JK}^{-1}\text{mol}^{-1}$$

➤ **Gibbs free energy**

Total entropy change and Gibbs energy change

The sign of total entropy change for a reaction indicates whether or not it will be spontaneous. The Gibbs energy change, ΔG , combines changes in enthalpy and entropy into a single state function that describes the spontaneity of a process at constant temperature and pressure and uses only properties of the system.



Since the enthalpy and entropy are state functions, Gibbs energy must also be a state function. The requirement for a change to be spontaneous is $\Delta S > 0$. Since $\Delta G = -T\Delta S$. Therefore, the key relationships are summarized as follows:

- If $\Delta G < 0$ the reaction or process is spontaneous
- If $\Delta G > 0$ the reaction or process is non-spontaneous
- If $\Delta G = 0$ the reaction or process is at equilibrium

Processes that have $\Delta G < 0$ are spontaneous because they increase the entropy of the Universe and thus obey the Second law. The Gibbs energy just gives a convenient way of applying the Second Law while considering properties only of the system.

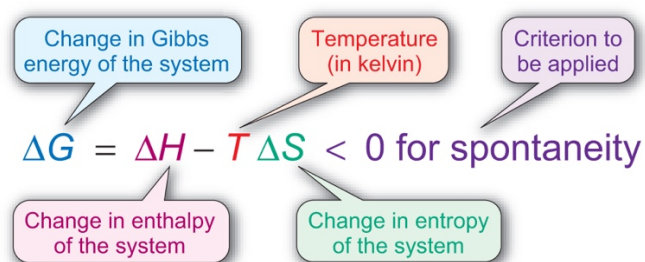
Example

Calculate the change in Gibbs energy when 1.00 mol of ice melts at: (a) 0°C (b) 10 °C (c) -10 °C. Comment on the results of each temperature.

($\Delta_{fus}H^\circ(\text{H}_2\text{O}) = +6.01 \text{ kJ mol}^{-1}$ and $\Delta_{fus}S^\circ(\text{H}_2\text{O}) = +22.0 \text{ J K}^{-1} \text{ mol}^{-1}$)

➤ Gibbs energy: the balance between enthalpy change and entropy change

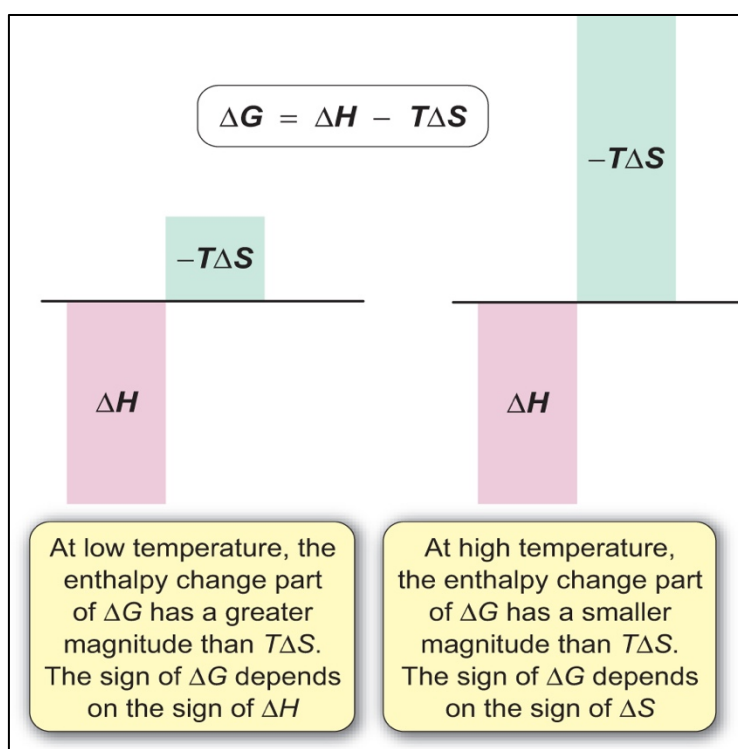
If we look again in detail to the equation of the definition of Gibbs energy, as below,



the Gibbs energy change must be negative for a process to be spontaneous at constant temperature and pressure. But for the contributions of enthalpy and entropy changes:

- $\Delta H < 0$ (negative, exothermic change) makes a favorable contribution to spontaneity.
- $\Delta H > 0$ (positive, endothermic change) makes an unfavorable contribution to spontaneity.
- $\Delta S < 0$ (negative, entropy decreases) makes an unfavorable contribution to spontaneity.
- $\Delta S > 0$ (positive, entropy increases) makes a favorable contribution to spontaneity.

The contribution of ΔS works in the opposite way to that of ΔH because of the minus sign in the $(-T\Delta S)$ term. The temperature determines the relative importance of these two contributions.



An exothermic reaction that also has an increase in entropy will be spontaneous at all temperatures, since both contributions lead to a negative value for ΔG . An endothermic reaction that also has a decrease of entropy will be non-spontaneous at all temperatures, since both contributions lead to a positive value for ΔG . As illustrated in the table below:

Reaction	Value of ΔH	Value of ΔS	Value of ΔG	Spontaneity
Endothermic	Positive, > 0	Negative, < 0	Positive for all T	Never spontaneous
Endothermic	Positive, > 0	Positive, > 0	Positive at low T, Negative at high T	Becomes spontaneous on heating
Exothermic	Negative, < 0	Positive, > 0	Negative for all T	Always spontaneous
Exothermic	Negative, < 0	Negative, < 0	Positive at high T; Negative at low T	Becomes spontaneous on cooling

➤ **Helmholtz Free Energy**

Helmholtz energy, A, is a thermodynamics property that determine the the criteria of spontaneous change.

$$dA_{T,v} \leq 0 = \text{spontaneous}$$

Helmholtz energy is independent on the path of the reaction or the process, so it's a state function. Moreover, it is an extensive property.

➤ **The Helmholtz and Gibbs energies**

Consider a system in thermal equilibrium with its surroundings at a temperature T . When a change in the systems occurs and there is a transfer of energy as heat between the system and the surroundings, the ***Clausius inequality*** (the expression ***Clausius inequality*** proves to be of great importance for the discussion of the spontaneity of chemical reactions) reads

$$dS - \frac{dq}{T} \geq 0$$

we can develop this inequality in two ways according to the conditions (of constant volume or constant pressure)

(a) Consider heating at constant volume and temperature. Then in the absence of additional (non-expansion) work, we can write $dq_v = dU$, consequently

$$dS - \frac{dU}{T} \geq 0$$

$$dA_{T,v} \leq 0 = \text{spontaneous}$$

(b) Consider heating at constant pressure and temperature. When energy transferred as heat at constant pressure, and there is no work other than expansion work, we can write $dq_p = dH$, consequently

$$dS - \frac{dH}{T} \geq 0$$

$$dG_{T,p} \leq 0 = \text{spontaneous}$$

➤ **Maximum work**

The change in the Helmholtz function is equal to the maximum work accompanying a process at constant temperature:

$$dw_{max} = dA \quad \text{Maximum work (constant T)}$$

As a result, A is sometimes called the 'maximum work function' or the 'work function'.

➤ **Maximum non-expansion work**

The analogue of the maximum work interpretation of ΔA , and the origin of the name 'free energy' can be found for ΔG . In the following equation, we show that at constant temperature and pressure, the maximum additional (non-expansion) work, $w_{add,max}$ is given by the change in Gibbs energy:

$$w_{add,max} = \Delta G \quad \text{Maximum non-expansion work (constant T and p)}$$

This expression is particularly useful for assessing the electrical work that may be produced by fuel cells and electrochemical cells.