# Basic Concepts of Thermodynamics

Part II

# Highlights

- To understand thermodynamics, it is imperative to define a **system and its surroundings**. Those two concepts are the basis for describing and doing calculations on any energy exchange process.
- A primary goal of the study of thermodynamics is to determine the quantity of **heat exchanged** between a system and its surroundings.
- **The system is the part of the universe being studied**, while the **surroundings are the rest of the universe** that interacts with the system.

# Highlights

- A system and its surroundings can be as large as the solar system or as small as the contents of a beaker in a chemistry laboratory. The type of system one is dealing with can have very important implications because the type of system dictates certain conditions and **laws of thermodynamics** associated with that system.

- The thermodynamic state of a system is defined by specifying values of a **set of measurable properties** enough to determine all other properties. For fluid systems, **typical properties are pressure, volume, and temperature**. More complex systems may require the specification of more unusual properties.

# Highlights

- **The microscopic description of a system is the complete description of each particle**, by example, the microscopic description of a gas would be the list of the state of each molecule: position and velocity.

- **The macroscopic description, which is in terms of a few properties** is thus far more accessible and useable for engineering applications, although it is **restricted to equilibrium states**. For a given macroscopic system, there are many microscopic states.

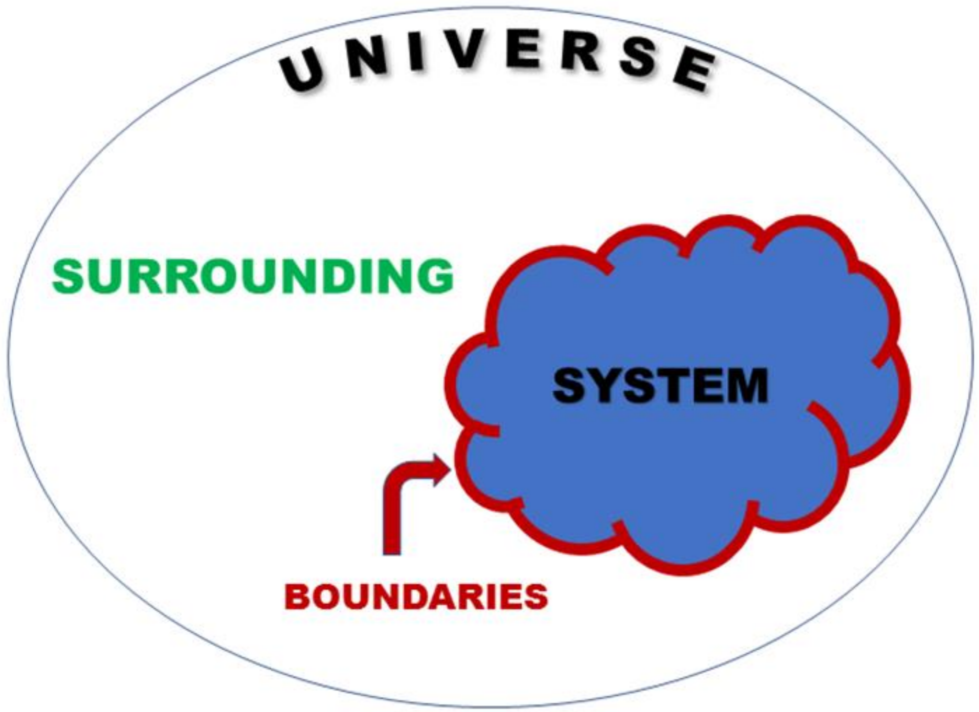
# Highlights

- **The properties of matter that do not depend on the size or quantity of matter** in any way are referred to as **intensive properties** of matter. Temperatures, density, color, melting and boiling point, etc., all are intensive properties as they will not change with a change in size or quantity of matter.

- **There are properties** such as length, mass, volume, weight, etc. that **depend on the quantity or size of the matter**, these properties are called an **extensive property** of matter, and their value changes if the size or quantity of matter changes.

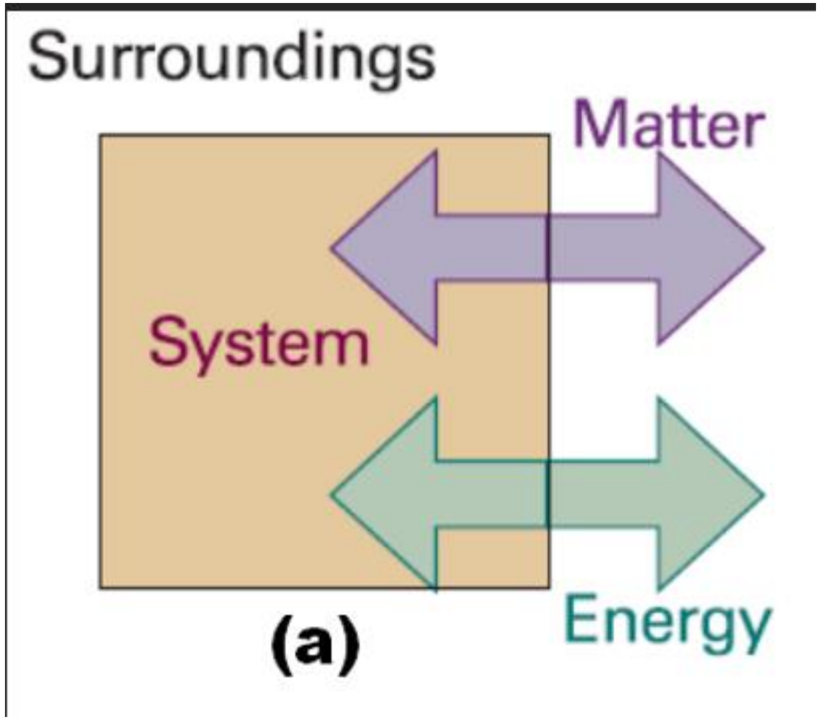
# Defining the Universe (system and surrounding)

- For Thermodynamics, **the universe** is divided into two, the **system** and its **surroundings**.
- **The system is the part of the world** in which we **have a special interest**. It may be as simple as a free body or as complex as an entire chemical refinery.
- **The surroundings comprise the region outside the system** and are where we **make our measurements**. The type of system depends on the characteristics of the **boundary that divides** it from the surroundings



# Boundaries and types of the systems

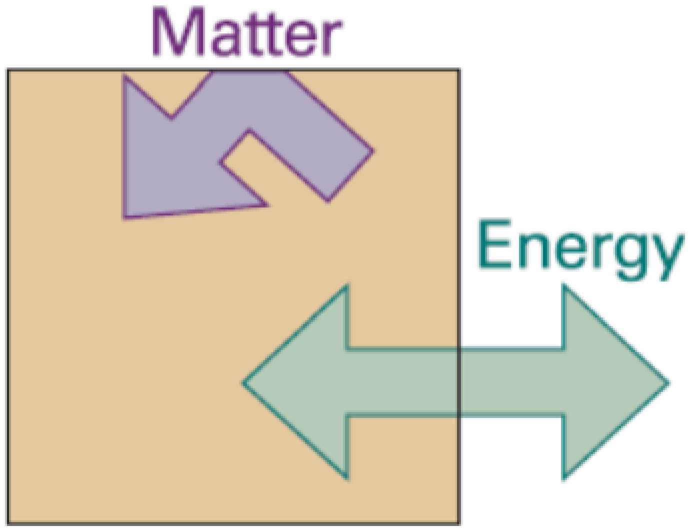
If **matter can be transferred** through the boundary between the system and its surroundings, it is classified as **open**.



# Boundaries and types of the systems

**If the matter cannot pass through the boundary** the system is classified as **closed**. Both **open and closed systems can exchange energy with their surroundings**.

For example, a closed system can expand and thereby raise the weight in the surroundings. **It may also transfer energy** to them if they are at a lower temperature.



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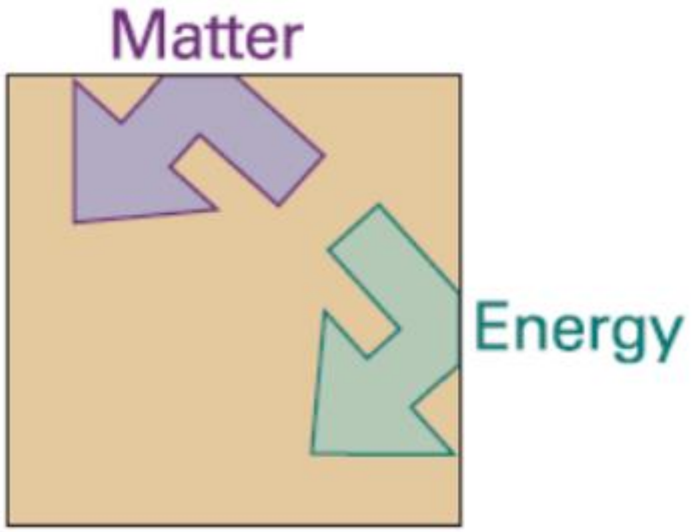
# Boundaries and types of the systems

**An isolated system is a closed** system that has neither mechanical nor thermal contact with its surroundings.

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# Boundaries and types of the systems

- The composition of the matter inside the system may be fixed or may be changing through chemical or nuclear reactions. The shape or volume of the system being analyzed is not necessarily constant, as when a gas in a cylinder is compressed by a piston or a balloon is inflated.

# Describing Systems and Their Behavior

- Engineers are interested in studying systems and how they interact with their surroundings.

- In this lesson, we introduce several terms and concepts used to describe systems and how they behave.

- In molecular terms, **heating is the transfer of energy** that makes use of **disorderly molecular motion**.

# Describing Systems and Their Behavior

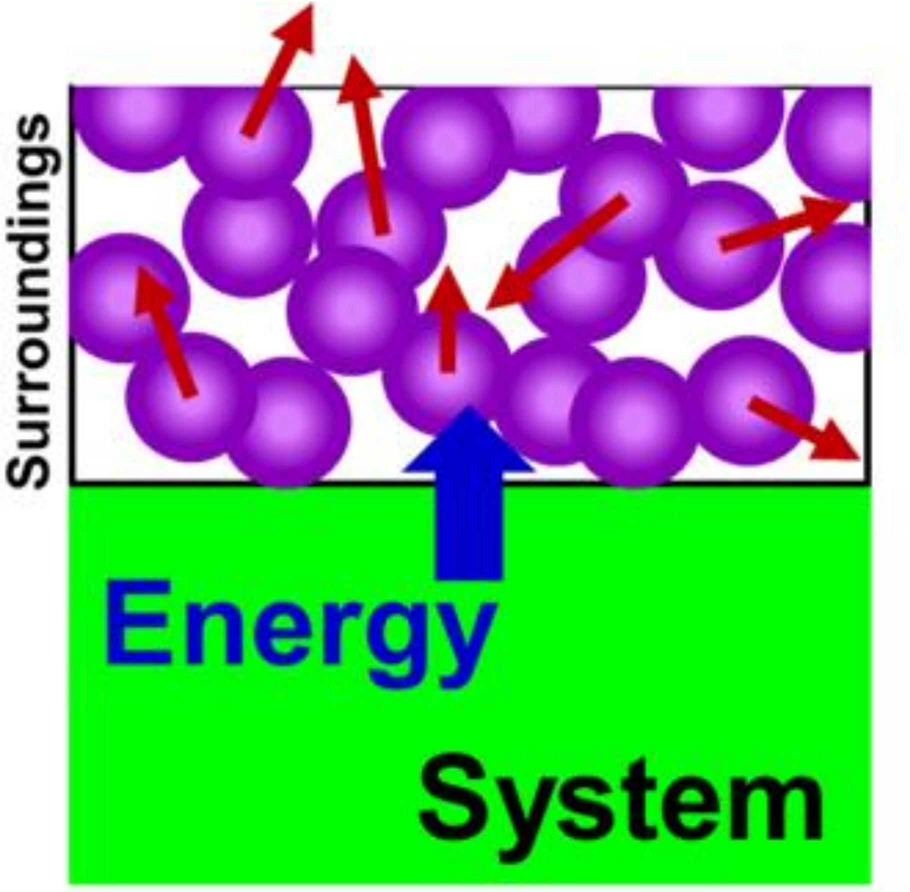
- The disorderly motion of molecules is called **thermal motion**.

- The **thermal motion** of the molecules in the **hot surroundings** stimulates the molecules in the cooler system to move more vigorously and, as a result, **the energy of the system is increased**.

- When a **system heats its surroundings**, molecules of the **system stimulate the thermal motion** of the molecules in the **surroundings**.

# Describing Systems and Their Behavior

- When energy is transferred to the surroundings as heat, the transfer stimulates the random motion of the atoms in the surroundings.



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# Describing Systems and Their Behavior

- In contrast, **work is the transfer of energy** that makes use of **organized motion**.

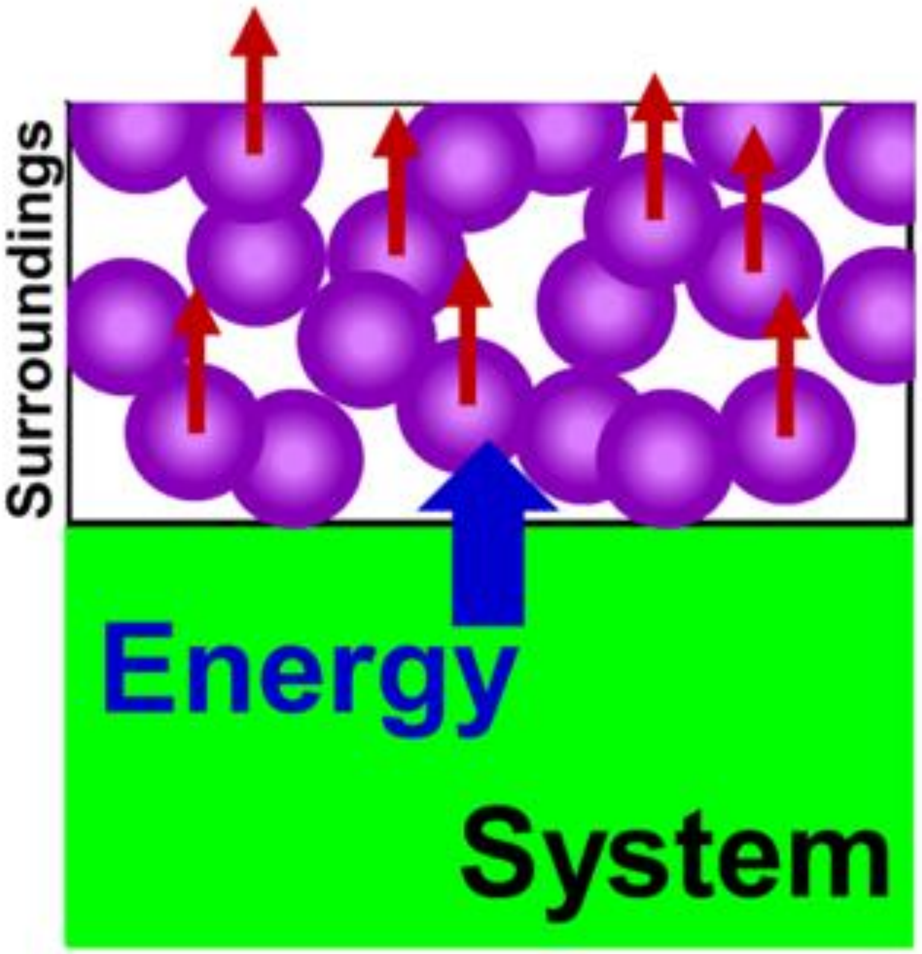
- When a weight is raised or lowered, its atoms move in an organized manner (up or down).

- The atoms in a spring move in an orderly manner when it is wound; the electrons in an electric current move in an orderly direction when it flows.

# Describing Systems and Their Behavior

When a system does work, it stimulates orderly motion in the surroundings.

When a system does work it causes atoms or electrons in its surroundings to move in an organized way. Likewise, when work is done on a system, molecules in the surroundings are used to transfer energy to it in an organized way, as the atoms in weight are lowered or a current of electrons is passed.



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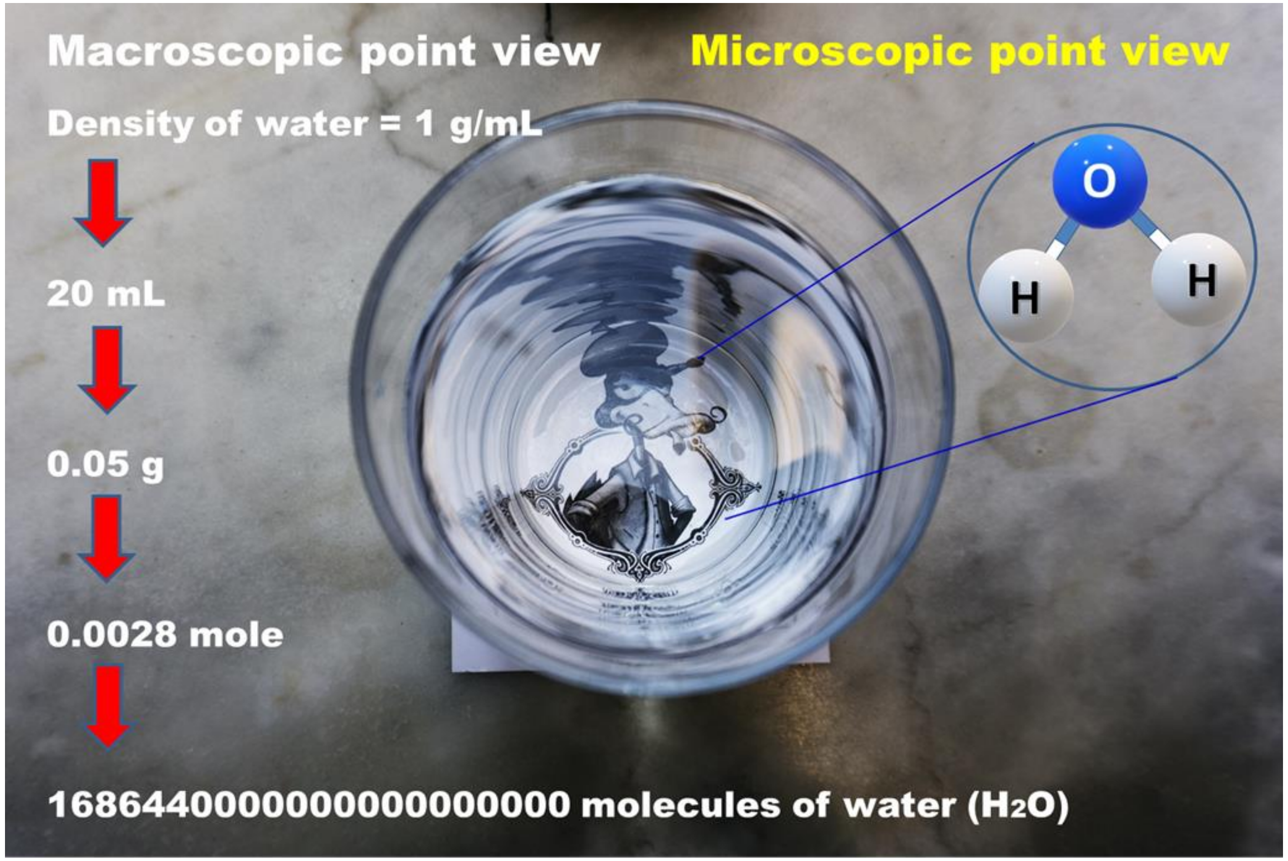
# Macroscopic and Microscopic points of view in Thermodynamics

- Systems can be studied from a macroscopic or a microscopic point of view. The macroscopic approach to thermodynamics is concerned with gross or overall behavior. This is sometimes called classical thermodynamics.

- No model of the structure of matter at the molecular, atomic, and subatomic levels is directly used in classical thermodynamics. Although the behavior of systems is affected by molecular structure, classical thermodynamics allows important aspects of system behavior to be evaluated from observations of the overall system.

# Macroscopic and Microscopic points of view in Thermodynamics



# Macroscopic and Microscopic points of view in Thermodynamics

- For the great majority of engineering applications, classical thermodynamics provides a considerably more direct approach to analysis and design.

- For this reason, the macroscopic viewpoint is the one adopted in this course. When it serves to promote understanding, however, concepts are interpreted from the microscopic point of view.

# Properties and states of the systems

- To describe a system and predict its behavior requires knowledge of its properties and how those are related.

- A **property is a macroscopic characteristic** of a system such as mass, volume, energy, pressure, and temperature to which a numerical value can be assigned at a given time without knowledge of the previous behavior of the system.

- Thermodynamics also deals with quantities that are not properties, such as mass flow rates and energy transfers by work and heat.

# Properties and states of the systems

- The word **state** refers to the **condition of a system** as **described** by its **properties**.
- Since there are normal relations among the properties of a system, the **state** often can be **specified** by **providing the values of a subset of the properties**. All other properties can be determined in terms of these few.

# Properties and states of the systems

- The physical state of a substance sample is defined by its physical properties.

- Two samples of a substance that have the same physical properties are in the same state.

- The state of a pure gas, for example, is specified by its volume, $V$, amount of substance (number of moles), $n$, pressure, $p$, and temperature, $T$.

# Properties and states of the systems

- When any of the properties of a system change, the state changes, and the system is said to have undergone a process.

- A process is a transformation from one state to another. However, if a system exhibits the same values of its properties at two different times, it is in the same state at these times.

- It is important to notice that regardless of the path when a system moves from state 1 to state 2, the properties of state 2 will always be the same.

# Properties and states of the systems

- A system is said to be in a **steady state** if **none** of its **properties changes with time**.

- A **thermodynamic cycle** is a sequence of processes that **begins and ends in the same state**.

- After a cycle, all properties have the same values they had at the beginning.

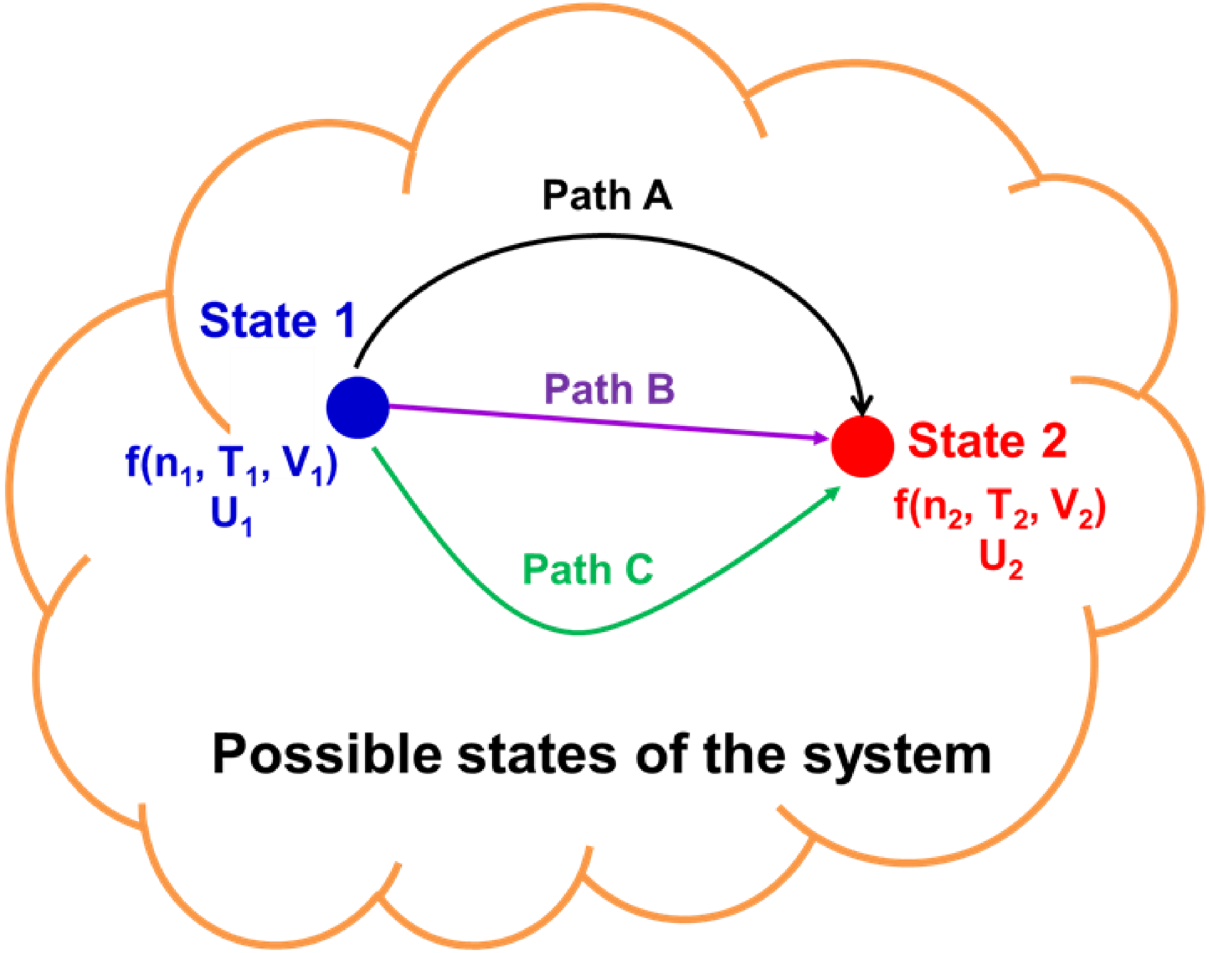
# Properties and states of the systems

- Consequently, over the cycle the system experiences no net change of state.

- Cycles that are repeated periodically play prominent roles in many areas of application.

- For example, steam circulating through an electrical power plant executes a cycle.

# Properties and states of the systems



# Properties and states of the systems

- In thermodynamics, **the total energy of a system is called its internal energy**, U. The internal energy is the total kinetic and potential energy of the molecules in the system. We denote by ΔU the change in internal energy when a system changes from an initial state i with internal energy $U_i$ to a final state f of internal energy $U_f$

$$\Delta U = U_f - U_i$$

# Properties and states of the systems

- **The internal energy is a state function** in the sense that its value depends only on the current state of the system and is **independent of how that state has been prepared**.

- In other words, it is a **function of the properties that determine the current state of the system**. Changing any one of the state variables, such as the pressure, results in a change in internal energy.

# Properties and states of the systems

- At a given state, each property has a definite value that can be assigned without knowledge of how the system arrived at that state.

- Therefore, a change in the value of a property as a system is moved from one state to another is determined solely by the two involved states and is independent of the way the change of state occurred.

- That is, the change is independent of the details of the process.

# Properties and states of the systems

- Conversely, if the value of a quantity is independent of the process that moved the system between two states, then that quantity is the change in a property.

- This provides a test for determining whether a quantity is a property: A quantity is a property if its change in value between two states is independent of the process.

- It follows that if the value of a quantity depends on the details of the process, and not solely on the involved states, that quantity cannot be a property.

# Extensive and Intensive Properties

- Thermodynamic properties can be placed in two general classes: extensive and intensive.

- A **property is called extensive if its value for an overall system is the sum of its values for the parts into which the system is divided**. Mass, volume, energy, and several other properties introduced later are extensive.

# Extensive and Intensive Properties

- **Extensive properties depend on the size or extent of a system**.

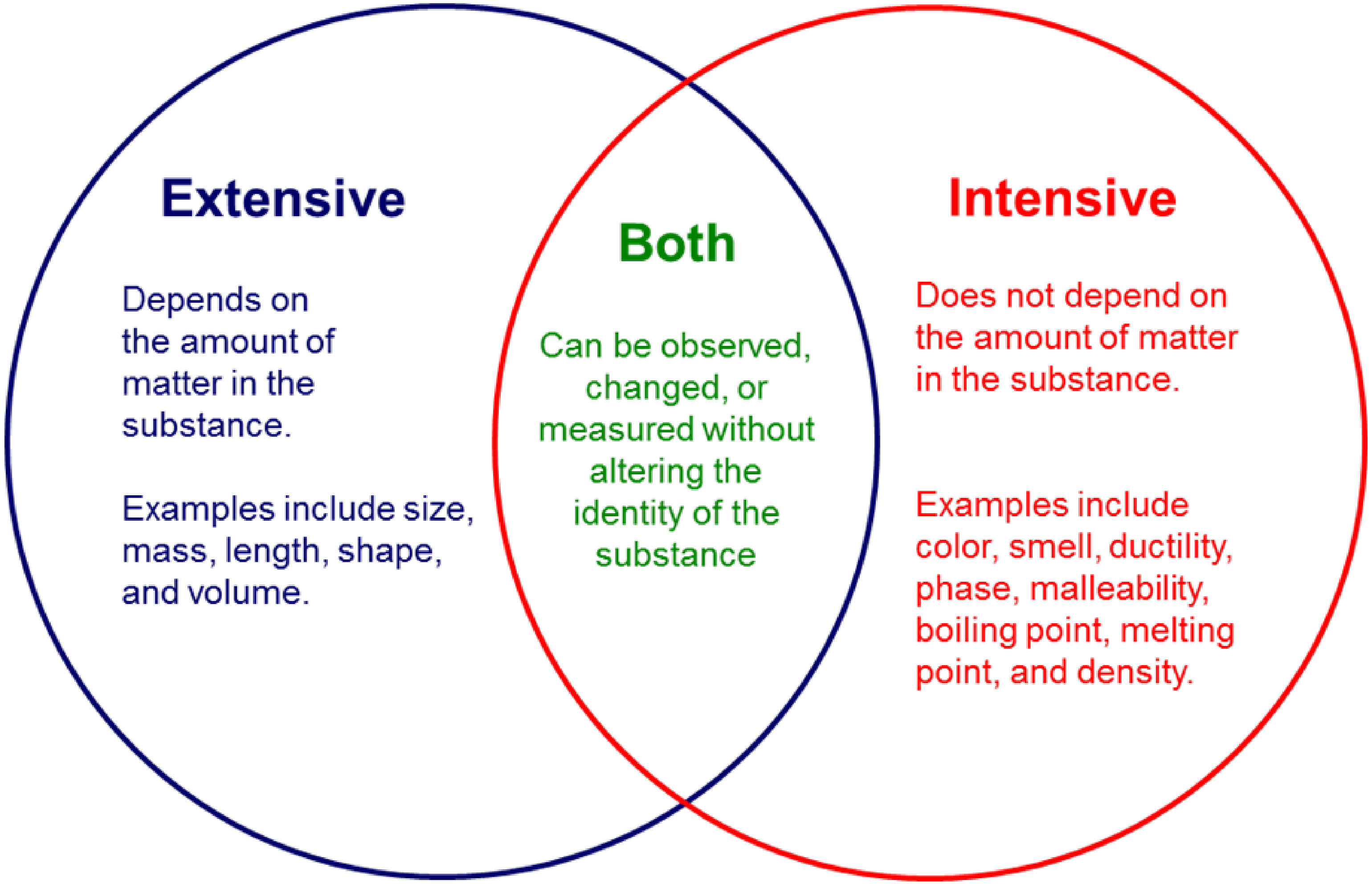
- The extensive properties of a system can change with time, and many thermodynamic analyses consist mainly of carefully accounting for changes in extensive properties such as mass and energy as a system interacts with its surroundings.

# Extensive and Intensive Properties

- **Intensive properties are not additive in the sense previously considered**. Their values are independent of the size or extent of a system and may vary from place to place within the system at any moment.

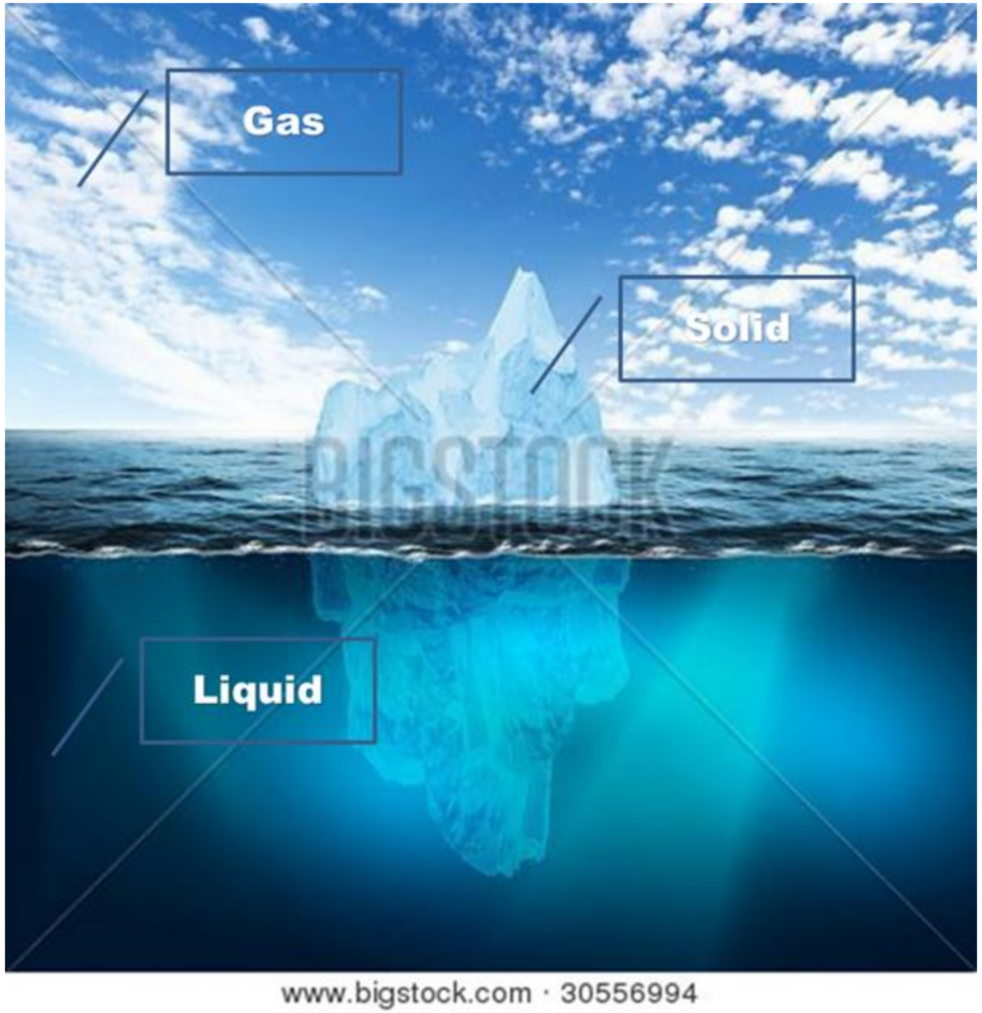
- Thus, intensive properties may be functions of both position and time, whereas extensive properties vary at most with time. Specific volume, pressure, and temperature are important intensive properties

# Extensive and Intensive Properties



# Properties of Pure Substances

- A phase of a substance is a form of matter that is uniform throughout in chemical composition and physical state.
- Homogeneity in physical structure means by example, that the matter is in a state.



# Phase and Pure Substances

- Thus, we speak of solid, liquid, and gas phases of a substance, and its various solid phases, such as the white and black allotropes of phosphorus.

- A pure substance is uniform and invariable in chemical composition.

- A pure substance can exist in more than one phase, but its chemical composition must be the same in each phase.

# Phase and Pure Substances

- For example, if liquid water and water vapor form (steam) a system with two phases, the system can be regarded as a pure substance because each phase has the same composition.

- A system can contain one or more phases. For example, a system of liquid water and water vapor contains two phases.

- When more than one phase is present, the phases are separated by phase boundaries (interface). Note that gases say oxygen and nitrogen, can be mixed in any proportion to form a single gas phase.

# Phase and Pure Substances

- Certain liquids, such as alcohol and water, can be mixed to form a single liquid phase. But liquids such as oil and water, which are not miscible, form two liquid phases.

- A uniform mixture of gases can be regarded as a pure substance provided it remains a gas and does not react chemically.

- Changes in composition due to chemical reactions are considered in advance.

# Phase and Pure Substances

- A system consisting of air can be regarded as a pure substance as long as it is a mixture of gases; but if a liquid phase should form on cooling, the liquid would have a different composition from the gas phase, and the system would no longer be considered a pure substance.

# Thermodynamics Equilibrium

- **Classical thermodynamics places primary emphasis on equilibrium states and changes from one equilibrium state to another**.

- Thus, the concept of equilibrium is fundamental. In mechanics, equilibrium means a condition of balance maintained by an equality of opposing forces.

# Thermodynamics Equilibrium

- In thermodynamics, the concept is more far-reaching, including not only a balance of forces but also a balance of other influences.

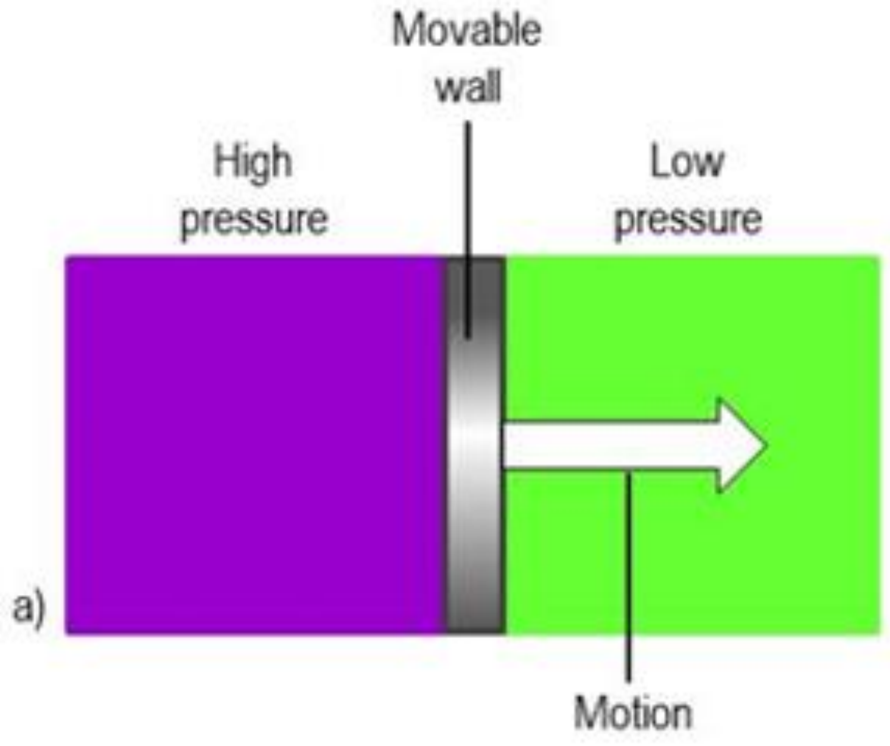
- Each kind of influence refers to an aspect of thermodynamic, or complete, equilibrium. Accordingly, several types of equilibrium must exist individually to fulfill the condition of complete equilibrium; among these are mechanical, thermal, phase, and chemical equilibrium.

# Thermodynamics Equilibrium

- If there are no changes, we conclude that the system is in equilibrium now it was isolated. The system can be said to be in an equilibrium state.

# Thermodynamics Equilibrium

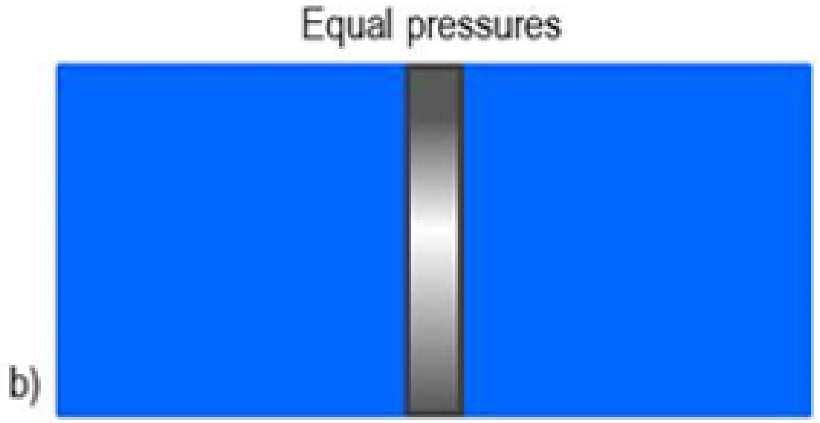
If two gases are in separate containers that share a common movable wall, the gas that has the higher pressure will tend to compress the gas that has a lower pressure. The pressure of the high-pressure gas will fall as it expands and that of the low-pressure gas will rise as it is compressed.



# Thermodynamics Equilibrium

if the two pressures are identical, the wall will not move. The latter condition is one of mechanical equilibrium between the two regions.

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.



# Two types of boundary that can separate the objects

- A boundary is diathermic (thermally conducting) if a change of state is observed when two objects at different temperatures are brought into contact.

- A metal container has diathermic walls.

- A boundary is adiabatic (thermally insulating) if no change occurs even though the two objects have different temperatures.

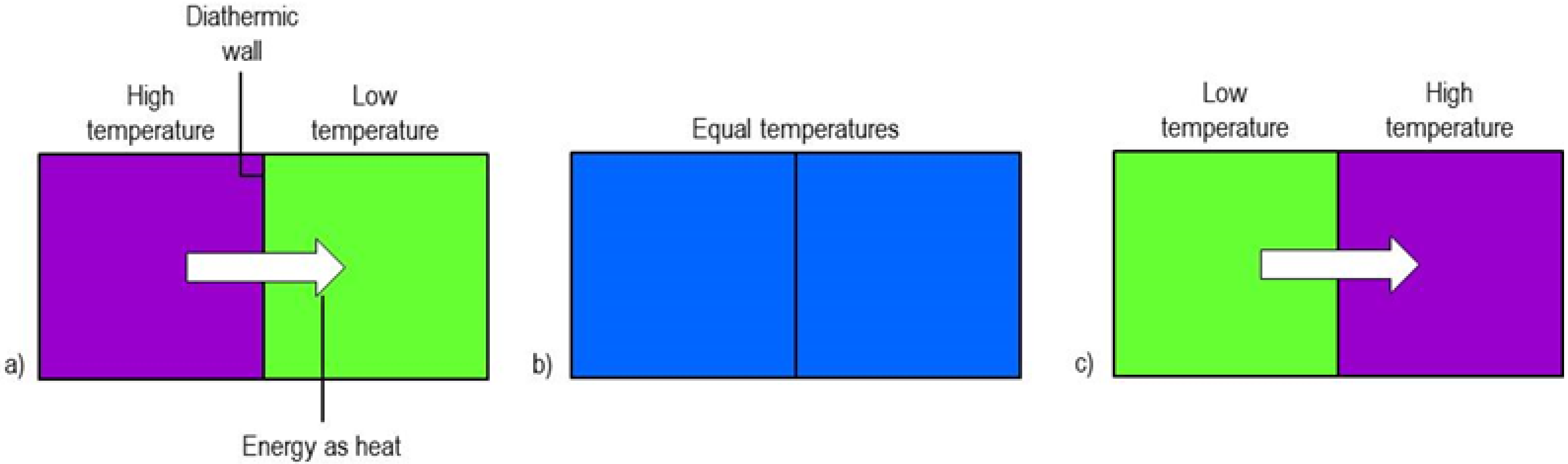
- A vacuum flask approximates an adiabatic container.

# Thermodynamics Equilibrium

- When a system is isolated, it does not interact with its surroundings; however, its state can change because of spontaneous events occurring internally as its intensive properties, such as temperature and pressure, tend toward uniform values.

- When all such changes cease, the system is in equilibrium. Hence, for a system to be in equilibrium it must be a single phase or consist of several phases that do not tend to change their conditions when the overall system is isolated from its surroundings.

# Energy flows as heat




At equilibrium, the temperature is uniform throughout the system.

# Measuring Mass

- A substance is a distinct, pure form of matter. The amount of substance, n (more colloquially number of moles), in a sample is reported in terms of the mole (mol).

- 1 mol is the amount of substance that contains as many objects (atoms, molecules, ions, or other specified entities) as there are atoms in exactly 12 g of carbon-12. This number is found experimentally to be approximately $6.02 \times 10^{23}$.

# Measuring Mass

- If a sample contains N entities, the amount of substance it contains is $n = N/N_A$
- where $N_A$ is the Avogadro constant: $N_A = 6.02 \times 10^{23}\ \text{mol}^{-1}$. Note that $N_A$ is a quantity with units, not a pure number.

# Measuring Mass

- A molar property, $X_m$, is the value of an extensive property, $X$, of the sample divided by the amount of substance present in the sample: $X_m = X/n$.

- A molar property is intensive.

- An example is the molar volume, $V_m$, the volume of a sample divided by the amount of substance in the sample (the volume per mole).

# Measuring Mass

- The one exception to the notation $X_m$ is the molar mass, which is denoted M. The molar mass of an element is the mass per mole of its atoms. The molar mass of a molecular compound is the mass per mole of molecules

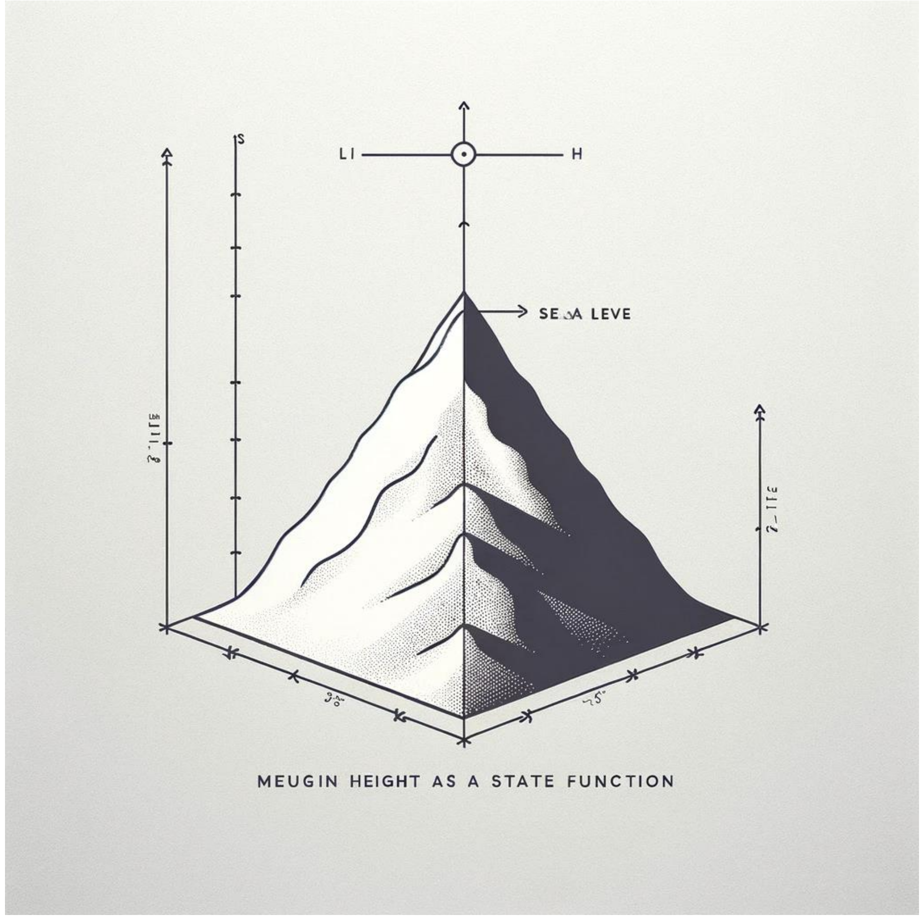
# Measuring Mass

- The molar concentration ("molarity") of a solute in a solution is the amount of substance of the solute divided by the volume of the solution.

- Molar concentration is usually expressed in moles per cubic decimeter (mol $dm^{-3}$ or mol $L^{-1}$; 1 $dm^3$ is identical to 1 L).

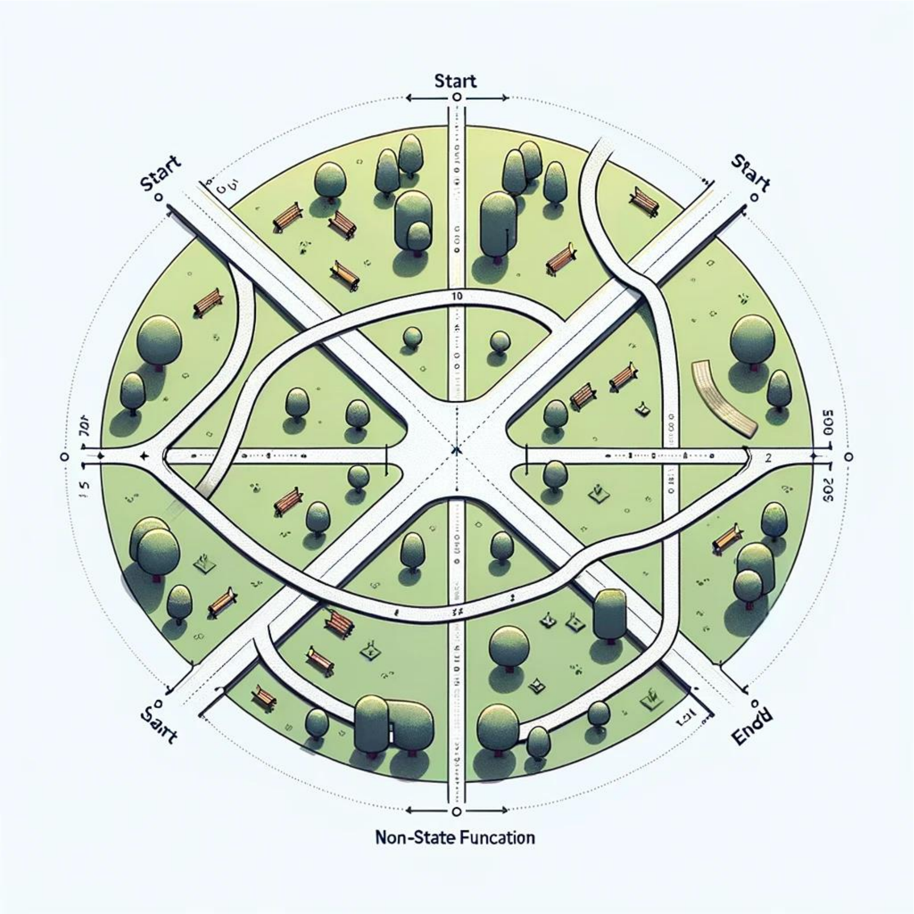
# State Function Example: Height of a Mountain

- Height of a Mountain is an example of a state function. The height of a mountain above sea level is a specific value that doesn't depend on the path you took to measure it. Whether you climb the mountain from the north face, or the south face, or measure it using satellite data, the height of the mountain relative to sea level remains the same.



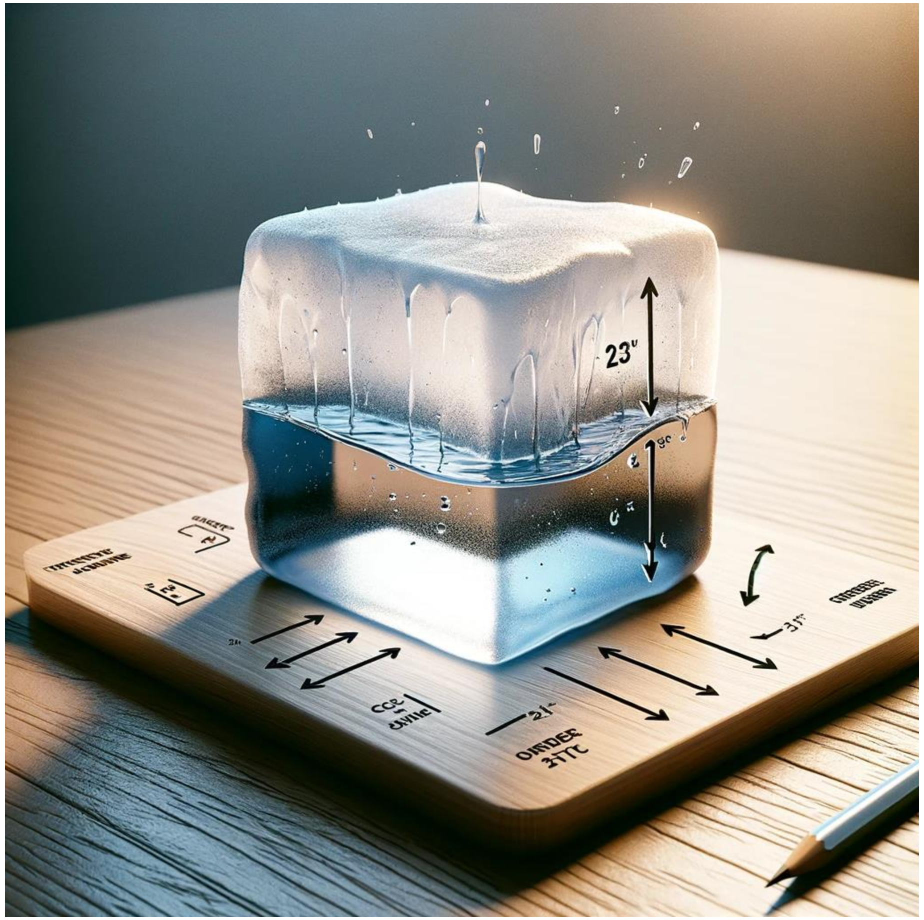
# Non-State Function Example: Path of a Walk

- Path of a Walk is a perfect example of a non-state function. Consider two people starting at the same point and ending at the same point but taking different routes. The total distance each person travels depends on the specific path they took, not just the start and endpoints.



# Transfer heat: An ice cube melting into water

The illustration represents the concept of disorder through the melting of an ice cube into water. This transition from a solid (more ordered state) to a liquid (more disordered state) visually demonstrates an increase in disorder



# Molarity Calculation Example: NaCl in Water

- Assume we are dissolving 5.85 grams of NaCl (table salt) in water to make a total volume of 250 mL (0.25 L) of solution.

Step 1: Calculate Moles of NaCl

- To calculate the moles of NaCl, we first determine the molar mass of NaCl. The molar mass of Na (Sodium) is 22.99 g/mol, and the molar mass of Cl (Chlorine) is 35.45 g/mol. Therefore, the molar mass of NaCl is 58.44 g/mol. Using the formula:
- n = mass / molar mass
- where the mass of NaCl is 5.85 grams, we find:
- n = 5.85 / 58.44

# Molarity Calculation Example: NaCl in Water

- Assume we are dissolving 5.85 grams of NaCl (table salt) in water to make a total volume of 250 mL (0.25 L) of solution.

Step 2: Calculate Molarity

- Molarity (M) is defined as the number of moles of solute per liter of solution. The formula for molarity is:
- M = moles of solute/volume of solution in liters
- Using the moles of NaCl calculated in Step 1 and the volume of the solution (0.25 L), we calculate the molarity.

# Molarity Calculation Example: NaCl in Water

- Assume we are dissolving 5.85 grams of NaCl (table salt) in water to make a total volume of 250 mL (0.25 L) of solution.

Calculations:

- - Moles of NaCl: 0.1001 moles
- - Molarity of the solution: 0.4004 M

# Molar Volume Calculation Example: $CO_2$ Gas

Given: A 44.8-liter container is filled with $CO_2$ gas at standard temperature and pressure (STP).

Step 1: Identify the Molar Volume at STP

- The molar volume of an ideal gas at STP is 22.4 L/mol. This value applies to $CO_2$ or any ideal gas under STP conditions.

# Molar Volume Calculation Example: $CO_2$ Gas

Step 2: Calculate Moles of $CO_2$ at STP

- Using the given volume of $CO_2$ and the molar volume at STP, the calculation is as follows:
- Moles of $CO_2$ = Volume of $CO_2$ / Molar Volume at STP = 44.8 L / 22.4 L/mol = 2.0 moles

# Molecular theory of gases