Thermodynamics

Chem 211

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Chemistry New Building - 1st Floor

Ahmad Alakraa

Reference

- Thermodynamics: an engineering approach, 8th edition, Yunus A. Çengel and Michael A. Boles, **2015**, McGraw-Hill Education.

Lecture 1

Introduction and Basic concepts

Chemistry concerns with

- **Synthesizing** matter or materials "anything occupying a space and has a mass"
- **Evaluating** their properties (composition, structure, states) ⇒ (States of matter).
- **Inspecting** their reactivity "reactions" (Thermodynamics).
- **Estimating** (how fast) and changing reactions' kinetics (catalysis, inhibition) .

Thermodynamics is able to

- **Identify** whether a certain reaction/process is **possible** (or not) under a given set of conditions, **e.g.**, temperature and pressure or concentration of reactants and products. (**also,** identify the pathway)

- **Predict** the effect of different variables on the extent of a certain reaction, which is important for selecting the **optimum** conditions for maximum yield from a certain process.

- **Formulate** relationships for maximum yields obtainable from a certain reaction, where, we identify how far a particular reaction will proceed before reaching an **equilibrium**.

History

- Although the principles of **thermodynamics** have been in existence since the creation of the universe, **thermodynamics** did not emerge as a science until the construction of the first successful atmospheric **steam engines** (were very slow and inefficient) in England by **Thomas Savery** in **1697** and **Thomas Newcomen** in **1712**.

- The first and second laws of **thermodynamics** emerged simultaneously in the **1850s**, primarily out of the works of **William Rankine**, **Rudolph Clausius**, and **Lord Kelvin** (formerly William Thomson).

- The term **thermodynamics** was first used in a publication by **Lord Kelvin** in **1849**.

Power generation: stages

- **Early discovery of fire** (several million years ago):
  - gave warmth (دفء), nourishment (تغذية) and ability to craft (حرفة) objects out of stone (حجر) and metal.
  - Fire alone would not have allowed humans to survive

- **Tools manufacturing** (around 3000 BC):
  - knives (سكاكين), spearheads (رأس الحربة), wheels (عجلات); levers (العتلات) and pulleys (البكرات) (can lift heavier loads than any elephant).
  - Tools improved slowly;
    - ✓ Wheelbarrows (عربات اليد) evolved into horse drawn carts
    - ✓ Stones for grinding grain became windmills (طواحين الهواء).

Power generation: stages

Insufficient Power

- **Machines driven by animals, water and wind:**
  - Few horses can be hitched to a cart at one time.
  - A finite number of sites with running water,
  - Winds are unreliable.

- **Steam engine:** (a little over 300 years ago, 1712)
  - A device that operates continuously, producing motion (work), as long as heat is supplied to it
  - Gases expand when heated and exert tremendous pressures that can be exploited to drive power plants, aircraft and automobiles.
  - The generated power depends on the amount of heat that is produced by burning fuel, capturing solar radiation, or splitting atoms in nuclear reactions.

Questions

- What is the relation between heat and work?
- How much work can be obtained if a given amount of fuel is burned?
- Can the performance of engines be improved?

Thermodynamics was the science that grew from efforts to answer these questions

Thermodynamics

- is the science of **energy**.
- concerns with studying energy and its transformations.
- studies **equilibrium properties** in which temperature is an important variable.

- **Energy**: the ability to cause **changes**
- "**Thermodynamics**" stems from the Greek words **therme** (heat) and **dynamics** (power), which is most descriptive of the early efforts to convert heat into power.
- Today the same name is broadly interpreted to include all aspects of energy and energy transformations including power generation, refrigeration, and relationships among the properties of matter.

Thermochemistry

- A branch of **thermodynamics** which focuses on the study of **heat** given off or absorbed in a chemical reaction and relationship involved.

  - helps to determine if a particular reaction will occur or not.
  - If occurred, will it release or absorb energy?
  - estimates how much energy a reaction will release or absorb (**determines** if this Rx is economically feasible)
  - does not predict **how fast** a reaction will occur.

Thermodynamics: a quantitative subject

- concerns with **macroscopic** aspects of the interaction of matter with energy in its various forms.

- allows to derive relations between the **values** (**quantity**) of numerous physical quantities.
  - Some physical quantities, e.g., **mole fraction**, are dimensionless; their value is a pure number.
  - Most quantities, however, are not dimensionless and their values must include one or more **units**.

Thermodynamics: laws

- Thermodynamics is contained implicitly (ضمنياً) within two apparently simple statements called the "First and Second Laws of Thermodynamics".

- These two laws deals with energy-the first, explicitly, and the second, implicitly.

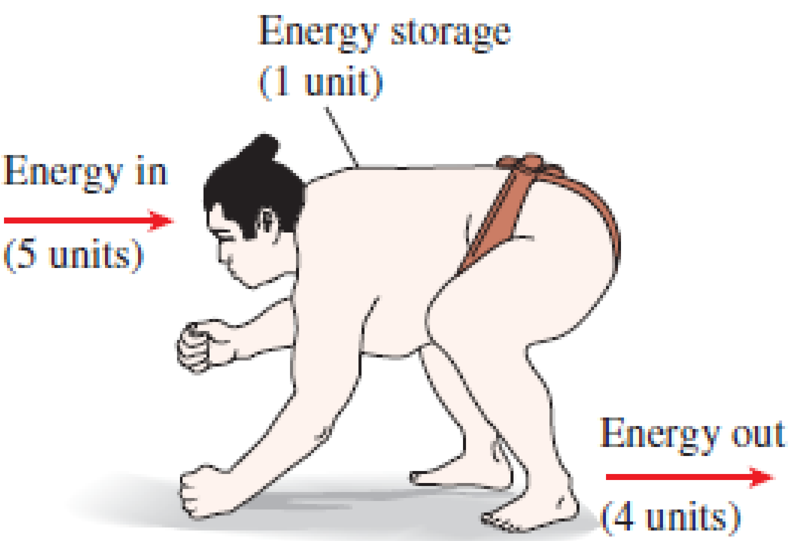
- We have no energy meters, no device we can stick into a system to record its energy.

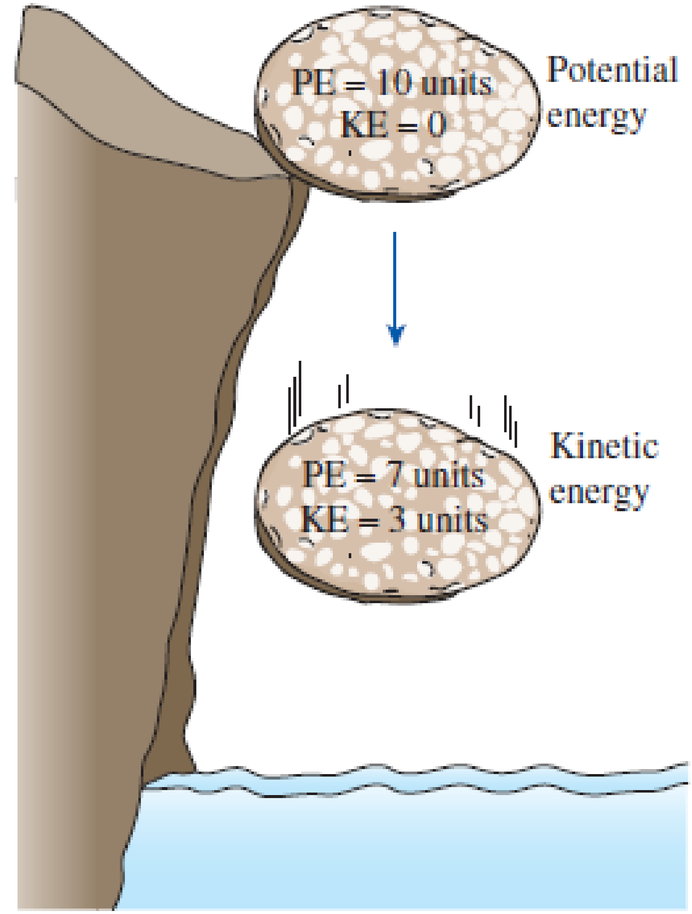
- Every form of energy is known only as a function of other variables.

First Law of Thermodynamics

Principle of Energy Conservation

- During an interaction, energy can change from one form to another but the total amount of energy remains constant.
- Energy cannot be created or destroyed.





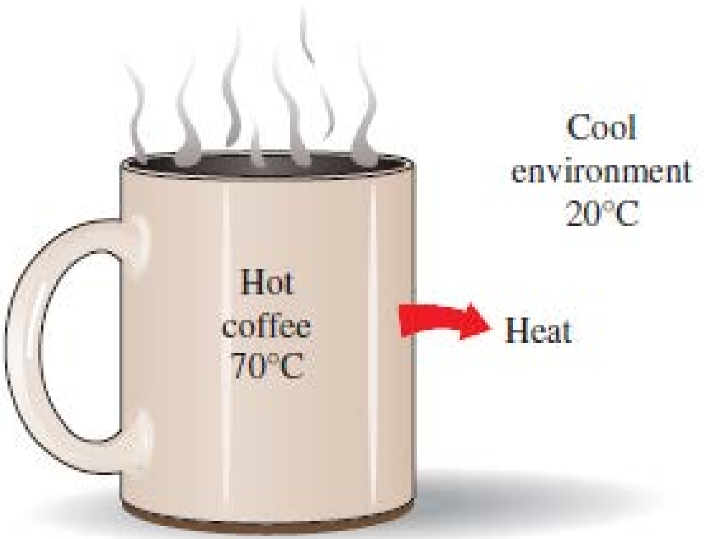
Energy is conserved

You don't get something for nothing

Second Law of Thermodynamics

Energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy.

- Even within the framework of energy conservation, you can not have it just any way you might like it.
- If you think things are going to be perfect, forget it.



Heat flows in the direction of decreasing T

The high-T energy of the coffee is degraded (transformed into a less useful form at a lower T) once it is transferred to the surrounding air.

A cup of hot coffee left on a table eventually cools, but a cup of cool coffee in the same room never gets hot by itself

Classical Thermodynamics, CT

- is a **macroscopic** (observable) approach (easy/direct) of studying thermodynamics that do not require a knowledge of the behavior of **individual particles** composing a substance.
  - e.g., P (gas) in a container is the result of **momentum transfer** between the molecules and the walls of the container.
  - **no need** to know the behavior of gas particles to determine the P in the container.
  - It would be sufficient to attach a **pressure gage** to the container.

Statistical Thermodynamics, ST

- is a microscopic (deals with unobservable events occurs at the atomic or molecular level) approach based on the average behavior of large groups of individual particles.
  - **e.g.**, **KE** of a large object can be converted into **heat** (where it increased **KE** of the atoms and molecules that comprise the warmed objects) by the effects of **friction**.
  - i.e., visible (macroscopic) mechanical motions are converted into invisible (microscopic) mechanical motions.

Classical vs. Statistical

To understand the behavior of a system and the changes taking place therein, either the classical or the statistical approach is used.

- The classical macroscopic approach does the analysis based on the quantity of the matter; it does not consider the matter at the molecular level.
- The statistical microscopic approach does the analysis at the molecular level and then the behavior of all the molecules is **added** together to determine the behavior of a system.
- Hence in **ST**, a **large** number of **variables** are required to describe the system whereas in the case of **CT**, these variables are comparatively **smaller**.

Classical vs. Statistical

- Properties like kinetic energy, velocity and momentum of molecules are required in the case of **ST** while properties like pressure, volume and temperature are needed to describe a system of **CT**.

- **CT** is based more upon experimental observations whereas **ST** is based upon the average behavior of a group of particles.

- The **statistical analysis** of any system is much more complex than the classical analysis. This means that the level of mathematics and computations in both approaches is also very different.

Thermodynamics: applications

- All activities in nature involve some interaction between energy and matter

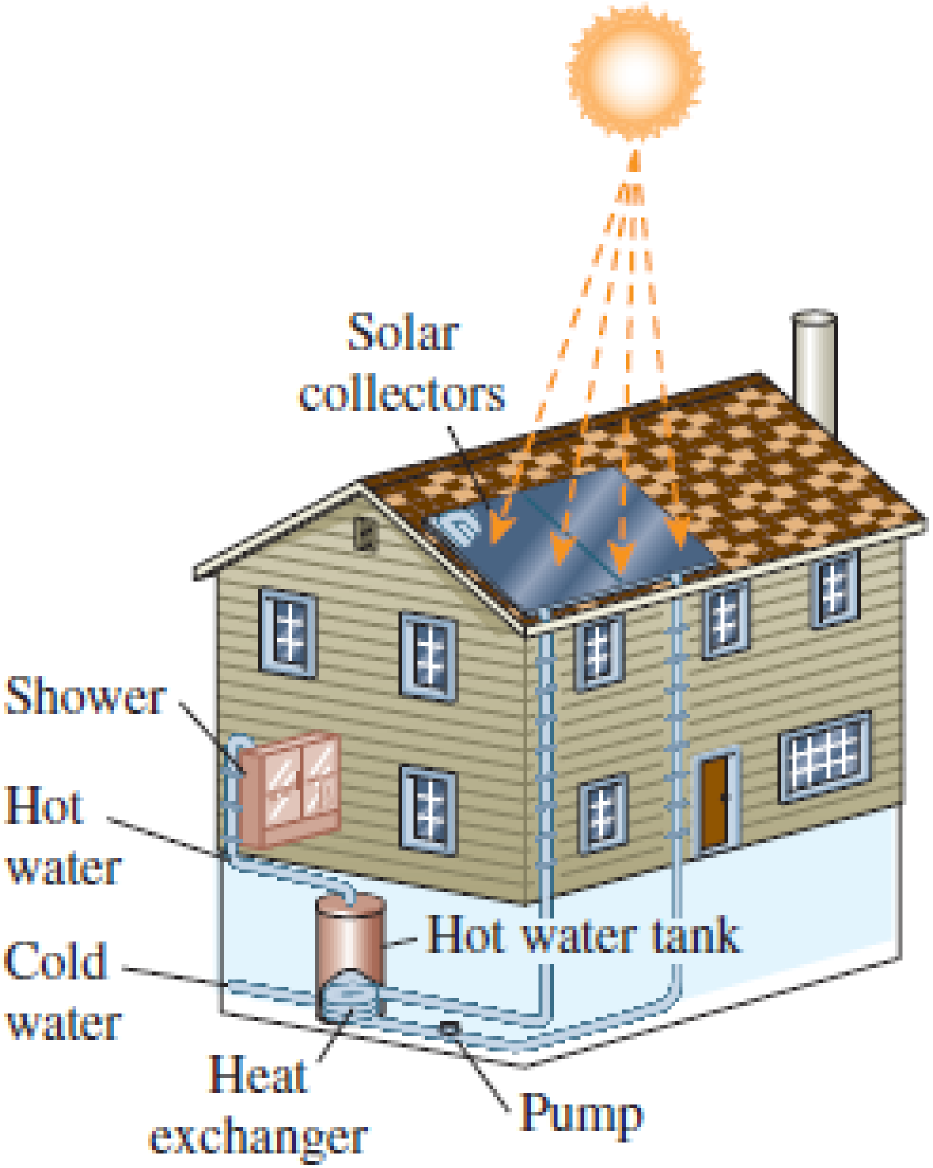
- The body **heat** generated is constantly rejected to the environment.
- The human **comfort** is closely tied to the **rate** of this metabolic heat rejection.
- We try to control this heat transfer rate by adjusting our clothing to the environmental conditions.

- The **heart** is constantly pumping blood to all parts of the human body.
- Various energy conversions occur in trillions of body cells.

Thermodynamics: applications

- The energy-efficient home is designed on the basis of minimizing heat loss in winter and heat gain in summer.

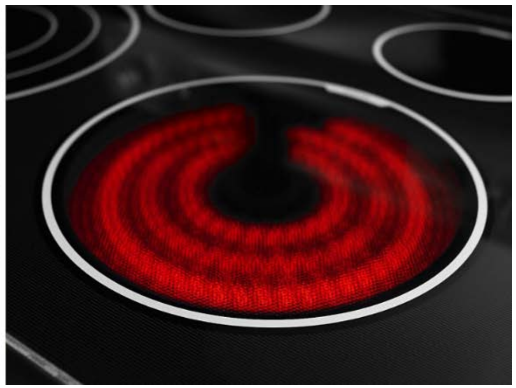
Solar hot water system



- Computer and TV

- Iron

- Refrigerator

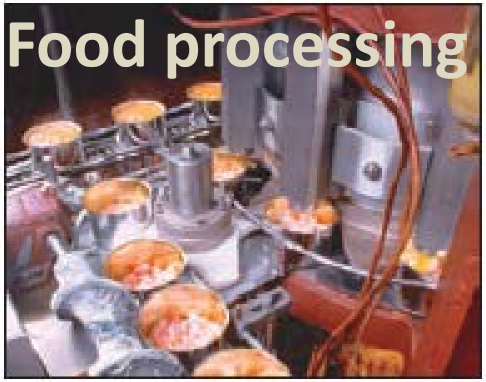


- Electric/gas range
- Humidifier
- Water heater
- Shower
- air-conditioning

- Pressure cooker

household utensils أواني
and appliances الأجهزة

Thermodynamics: design and analysis



Units of measurements

SI system

French Système International d'Unités.

7 SI Base UNITS

from which all other units are derived

Dimension	Unit	Unit Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Electrical Current	ampere	A
Amount of light	candela	cd
Amount of matter	mole	mol

Recognize the capital and small letters

Standard prefixes in SI Base units

Multiple	Prefix
10^{24}	yotta, Y
10^{21}	zetta, Z
10^{18}	exa, E
10^{15}	peta, P
10^{12}	tera, T
10^{9}	giga, G
10^{6}	mega, M
10^{3}	kilo, k
10^{2}	hecto, h
10^{1}	deka, da
10^{-1}	deci, d
10^{-2}	centi, c
10^{-3}	milli, m
10^{-6}	micro, μ
10^{-9}	nano, n
10^{-12}	pico, p
10^{-15}	femto, f
10^{-18}	atto, a
10^{-21}	zepto, z
10^{-24}	yocto, y

Other Derived SI Units

Physical quantity	Symbol (s)	Name of SI unit	Derived Unit	Definition
Frequency	v, f	Hertz	Hz	s^{-1}
Force	F	Newton	N	$kg\ m\ s^{-2} = J\ m^{-1}$
Energy	E, H,V, etc	Joule	J	$N\ m = kg\ m^{2}\ s^{-2}$
Pressure	P	Pascal	Pa	$N\ m^{-2} = kg\ m^{-1}s^{-2}$
Power	p	Watt	W	$J\ s^{-1} = kg\ m^{2}\ s^{-3}$
Charge	Q	Coulomb	C	A s
Potential	E,…etc	Volt	V	$J\ A\ s^{-1}$
Resistance	R	Ohm	Ω	$V\ A^{-1}$
Conductance	G	Siemens	S	Ω^{-1}
Capacitance	C	Farad	F	$C\ V^{-1}$

Other Units

Physical quantity	Symbol	SI unit
Area	A	m^2
Volume	V	m^3
Velocity	U, V, c	$m\ s^{-1}$
Acceleration	a, g	$m\ s^{-2}$
Weight	G,W	N
Density	p	$kg\ m^{-3}$
Volume	liter (l)	dm^3
Force	dyne (dyn)	10^{-5} N
Concentration	Molar (M)	$mol\ dm^{-3}$
Energy	Calorie (Cal)	4.18 J
Energy	Erg (erg)	10^{-7} J
Pressure	Atmosphere (atm)	1.013×10^5 Pa
Pressure	(mm Hg)	133.322 Pa
Pressure	Torr (torr)	133.322 Pa
Pressure	Bar	10^5 Pa
Pressure	Atmosphere	760 mm Hg = 76 cm Hg

Temperature

- is a physical property for the **hotness** or **coldness** of an object. It determines "direction of heat flow".

- **Heat** always flows **spontaneously** from a substance of a **higher T** to another of a **lower T**.

- The T scales are commonly **Celsius** and **Kelvin**.

- The **Celsius scale** is based on the assignment of **0 °C** to the freezing point of water and **100 °C** to its boiling point at sea level.

- The SI unit of temperature is the **Kelvin (K)**.

- Zero on the Kelvin scale is the lowest attainable temperature, –273.15 °C, referred to as absolute zero (Temperature at which the gas molecules stop to move)

- The Celsius and Kelvin scales have equal-sized units.

$$T(K) = T(°C) + 273.15$$

- The common temperature scale in the United States is the Fahrenheit scale.

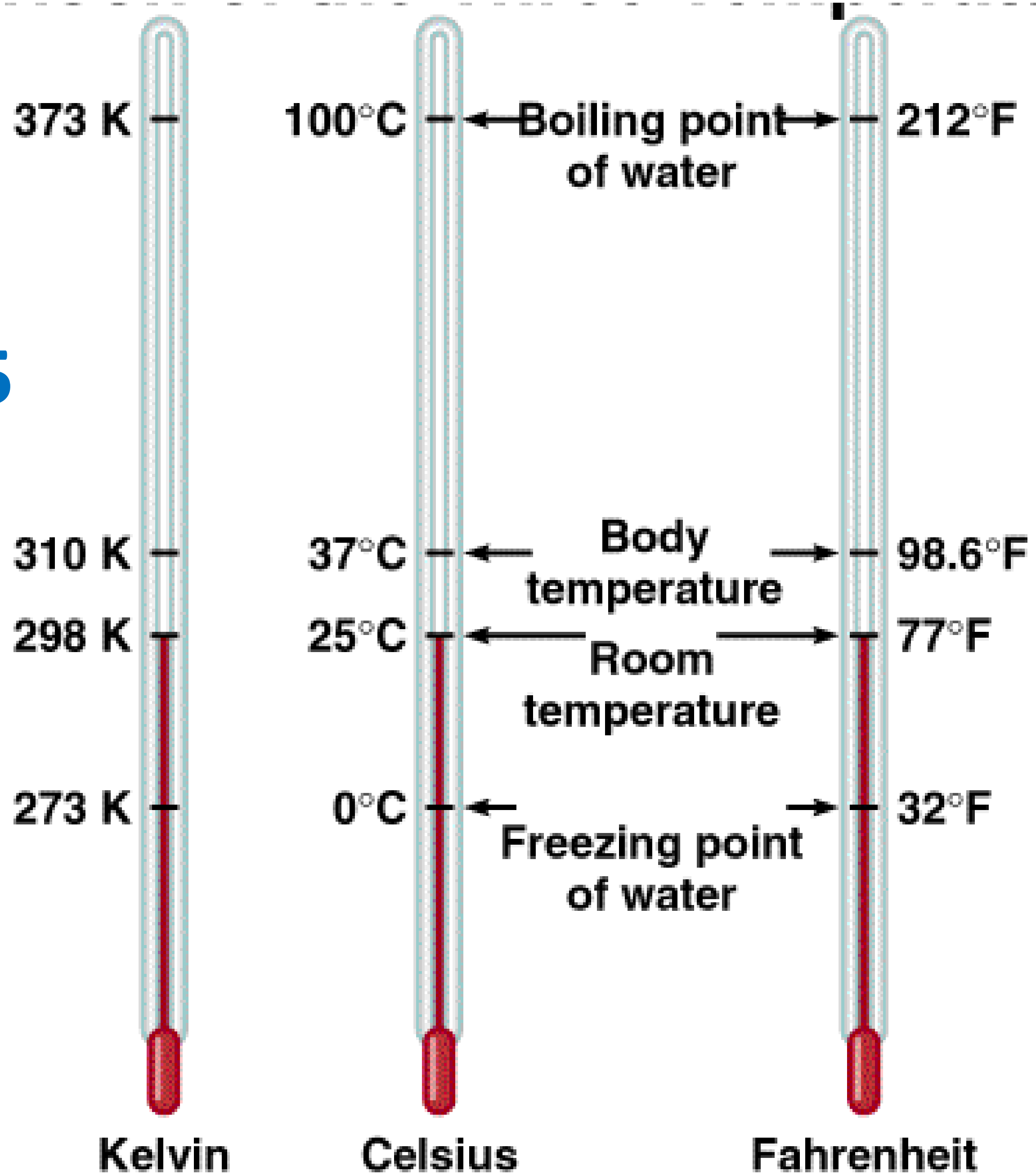
Water freezes at 32 °F and boils at 212 °F

$$^{o}F = \frac{9}{5}(\,^{o}C) + 32$$

Scales comparison

$$K = {}^{\circ}C + 273.15$$

$$^{o}C = \frac{5}{9}(\,^{o}F - 32)$$



Pressure

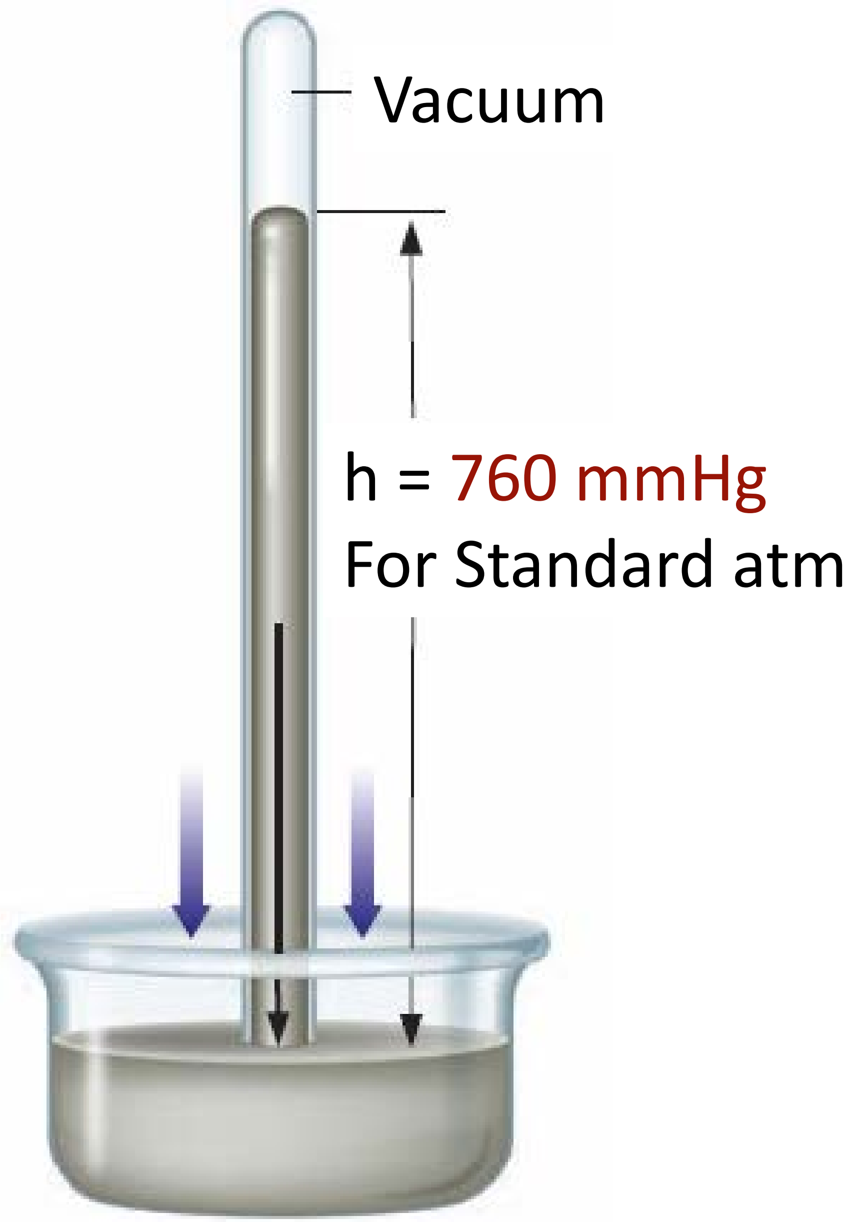
- is the normal force exerted by a fluid (gas or liquid) per unit area.
- It has the unit (N/m^2), which is called a Pascal (Pa).
- Pressure is also used on solid surfaces as synonymous to normal stress.

$$1 \text{ bar} = 10^5 \text{ Pa} = 0.1 \text{ MPa} = 100 \text{ kPa}$$

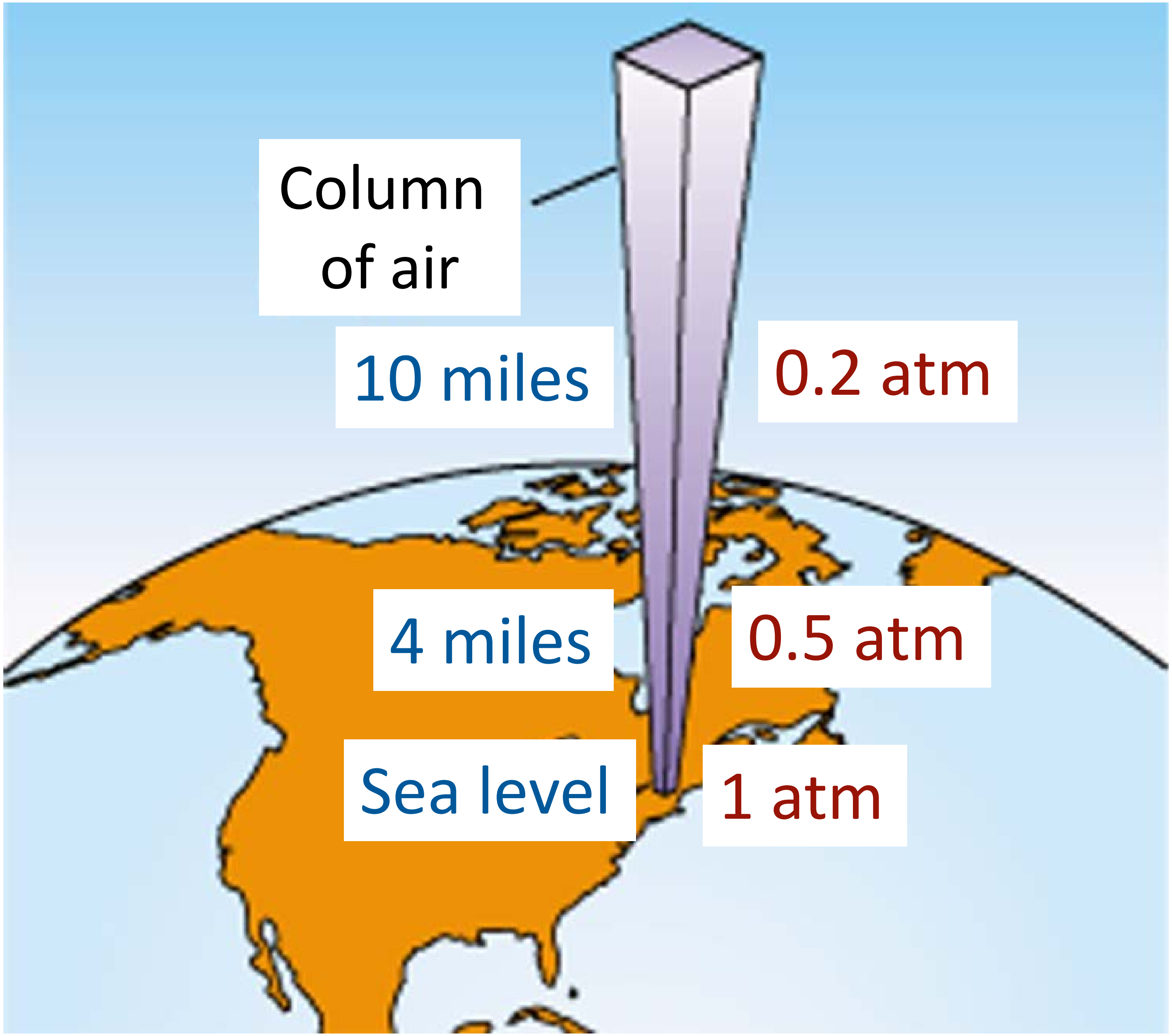
$$1 \text{ atm} = 101{,}325 \text{ Pa} = 101.325 \text{ kPa} = 1.01325 \text{ bars} = 760 \text{ mm Hg} = 760 \text{ torr}$$

Measuring P: Torricelli's barometer 1643

- Gases mix completely and exert pressure on surroundings.
- Torricelli's barometer is constructed by filling a glass tube with liquid mercury and inverting it in a dish of mercury.
- At sea level the height of this column of mercury averages 760 mm.



Pressure decreases at higher altitudes



SI system

P is measured in N m^{-2} (Pa: Pascal)

$$P\ (atm) == Length \times density \times Acceleration$$

$$0.76\ m \times 1.36 \times 10^{4}\ kg\ m^{-3} \times 9.8\ m\ s^{-2}$$

$$1.01325\ \times 10^{5}\ kg\ m^{-1} s^{-2}\ (N\ m^{-2})(Pa)$$

1 atm = 1.0325 bar = 760 mmHg

= 760 torr = 101,325 N/m^2 = 101,325 Pa

Mass vs. Weight

- **Weight** is often **incorrectly** used to express **mass**.
- Weight (**W**) is a **force**.
  - It is the gravitational force applied to a body, and its magnitude is determined from Newton's second law,

$$W\ (N) = m\,g$$

where m is the mass of the body, and g is the local gravitational acceleration (g is 9.807 m/s^2 at sea level and 45° latitude).

- The mass of a body remains the same regardless of its location in the universe. Its weight, however, changes with a change in gravitational acceleration. A body weighs less on top of a mountain since g decreases with altitude.

Work, J

a form of **energy** (force times distance)

$$W = N \times m = J$$

Calorie, Cal

The amount of energy needed to raise the temperature of 1 g of water at 14.5°C by 1°C.

$$1\ \text{cal} = 4.1868\ \text{J}$$

Feel the Unit

If you light a typical match and let it burn itself out, it yields approximately one **kJ** of energy

Power

- It is the time **rate** of energy or the rate of doing work.

- Its unit is (**J/s**) $\Rightarrow$ that is called watt (W).

- **Electrical energy** is expressed in kilowatt-hour (kWh), which is equivalent to 3600 kJ.
  - An electric appliance with a rated power of 1 kW consumes 1 kWh of electricity when running continuously for one hour.
  - Do not get confused between kW (power or rate) and kWh (energy) are often confused.

"the new wind turbine will generate **50 kW** of electricity per year"

Incorrect statement

"the new wind turbine with a power of **50 kW** will generate 438000 kWh of electricity per year"

correct statement

Energy of 50 kW for a year

$$= \frac{50\ kJ}{s} \times 1y = \frac{50\ kJ}{s} \times 365 \times 24 \times 60 \times 60\ s = 1576800000\ \text{kJ}$$

$$= 1576800000\ \text{kJ} \times \frac{1\ kWh}{3600\ kJ} = 438000\ kWh$$

Exercise

Energy production from wastewater

What is potential energy benefit of maximum energy recovery using domestic wastewater to a town of 100,000 people?

- Calculate the maximum energy production for assuming 500 L/d per capita, 300 mg/L of COD (chemical oxygen demand), and 14.7 kJ/g COD (based on wastewater solids)?
- How much is this electricity worth at $0.44/kWh?
- How many homes would this power, assuming 1.5 kW/home?

Solution

Environ. Sci. Technol. 2016, 50, 4439−4447

Calculate power in megawatts (MW)

$$P = (10^5 \text{cap}) \left(\frac{500 \text{ L}}{\text{d cap}}\right) \left(\frac{1 \text{ d}}{24 \text{ h}}\right) \left(300 \frac{\text{mg COD}}{\text{L}}\right)$$

$$\left(\frac{\text{g COD}}{10^3 \text{mg}}\right) \left(\frac{14.7 \text{ kJ}}{\text{g COD}}\right) \left(\frac{1 \text{ kWh}}{3600 \text{ kJ}}\right) \left(\frac{\text{MW}}{10^3 \text{ kW}}\right)$$

$$= 2.6 \text{ MW}$$

Cost per year

$$\text{Value}$$

$$= (2.6 \text{ MW}) \left(\frac{10^3 \text{kW}}{\text{MW}}\right) \left(\frac{24 \times 365 \text{ h}}{1 \text{ yr}}\right) \left(\frac{\$\, 0.44}{\text{kWh}}\right)$$

$$= \$10 \times 10^6 \text{yr}^{-1}$$

no. of homes

$$\text{homes} = (2.6\ \text{MW})\left(\frac{10^3\text{kW}}{\text{MW}}\right)\left(\frac{\text{home}}{1.5\ \text{kW}}\right)$$

$$= 1700\ \text{home}$$

- This assumed **100 %** energy recovery, which is hopeful but not reasonable. A recovery of 25-50 % of the energy is more logic.

Exercise

Energy production from wastewater

- A school is paying $0.12/kWh for electric power. To reduce its power bill, the school installs a wind turbine with a rated power of 30 kW. If the turbine operates 2200 hours per year at the rated power, determine the amount of electric power generated by the wind turbine and the money saved by the school per year.

Solution

Total electric energy generated per year = energy per time (power) × time

$$\text{Total Energy} = 30 \text{ kW} \times 2200 \text{ h} = 66{,}000 \text{ kWh}$$

Money save per year =

Total energy per year × unit cost

$$\text{Money saved} = 66{,}000\ \text{kWh} \times \frac{\$0.12}{\text{kWh}} = \$7920$$

Alternatively,

The annual electric energy production also could be determined in kJ by unit manipulations as

$$\text{Total Energy} = (30\ \text{kW})\,(2200\ \text{h})\left(\frac{3600\ \text{s}}{1\ \text{h}}\right)\left(\frac{1\ \text{kJ/s}}{1\ \text{kW}}\right) = 2.38 \times 10^{8}\ \text{kJ} = 66{,}000\ \text{kWh}$$

Energy the capacity to do work or to produce heat

Law of energy's conservation: energy can be **converted** from one form to another but can neither be **created** nor **destroyed**.

Basic forms of Energy

Potential Energy

energy due to position or composition.

e.g., attractive and repulsive forces

Kinetic Energy

energy due motion of an object of a mass m and a velocity υ.

$$K.E. = \frac{1}{2} m \upsilon^2$$

Potential Energy

- Any type of stored energy: Chemical, nuclear, gravitational, mechanical.

Kinetic Energy

- is found in movement, e.g., a flying airplane; or vibrating atoms (if they are hot or transmitting sound waves).
- Electricity is the kinetic energy of flowing electrons between atoms.

Energy Conversion/Transformation

- Energy may transfer between systems in three basic forms:
  - → Mass
  - → Heat, q
  - → Work, w

Mechanical work

- When a force acts upon an object to cause a displacement of the object, it is said that work was done upon the object

$$W = F \cdot d = m \cdot g \cdot h \quad (J)$$

(force) . (distance) = (mass). (acceleration) .(height)

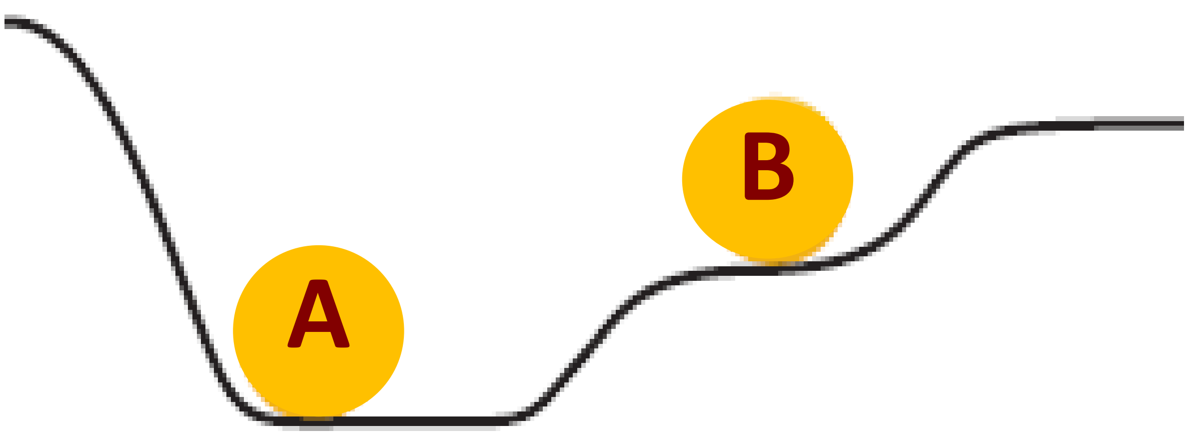
$$= P \cdot A \cdot h = P \cdot V$$

(pressure) . (area).(height) (pressure) . (volume)

$PE_A > PE_B$

Initial

PE, $_{A\ lost}$ = PE, $_{B\ gained}$ (work) + Frictional Energy (Heat)



$PE_A < PE_B$

Final

- If A rolls down, part of PE_A converts to KE_A.
- Part of KE_A is lost as frictional heating
- Upon collision with B, the other part transfers to B (PE_B increases) i.e. ,work was done by ball A on B.
- Ball A lost specific (fixed) amount of its potential energy $PE_{A,\ lost}$.
- The amount of energy transferred in the form of work or heat may vary based on the conditions (e.g., surface roughness),

$PE_{A,\ lost}$ (fixed)=

$PE_{B,\ gained}$ (work, variable) +

Frictional Energy (Heat, variable)

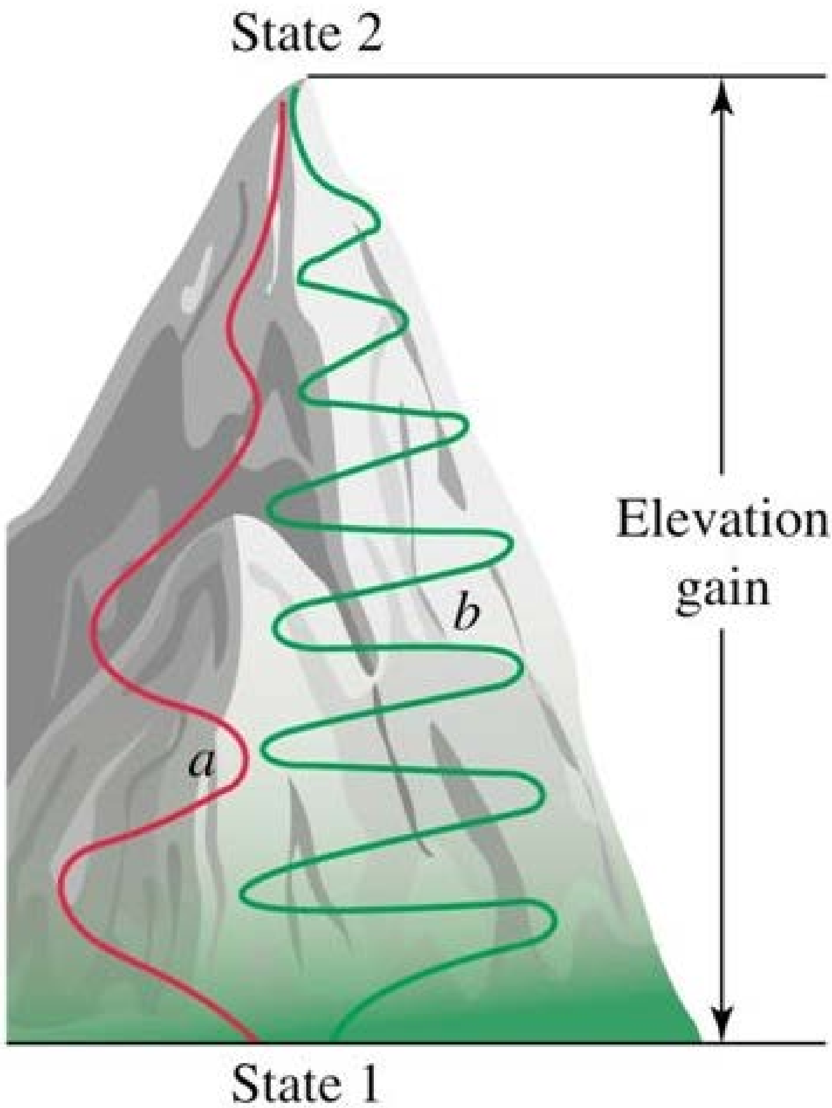
Temperature, Heat, and Work

- Temperature is a property reflecting the random motions of particles in a substance.
- Heat is a form of energy. It involves the energy transfer between two objects due to a temperature difference.
- Work is the force acting over a distance.

State (path-independent) functions

System's properties that depend only on the system's present (initial and final) state not on the system's past or future (pathway)

State (path-independent) functions



- ✓ A change in state functions is independent of the particular pathway taken between the two states.

- ✓ ΔE is a state function; however, work and heat are both non-state functions (depend on the pathway) .

State/Non-state functions

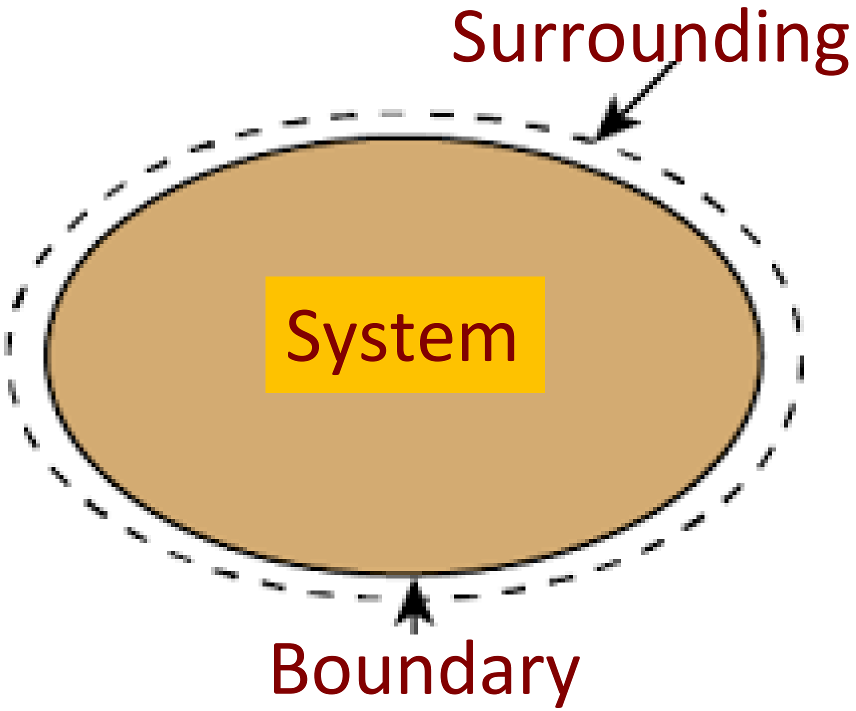
- **State property (Functions):** Functions which depend on the initial and final states of the system, not on the path it takes. (e.g., Internal energy, Temperature, Volume, Pressure).

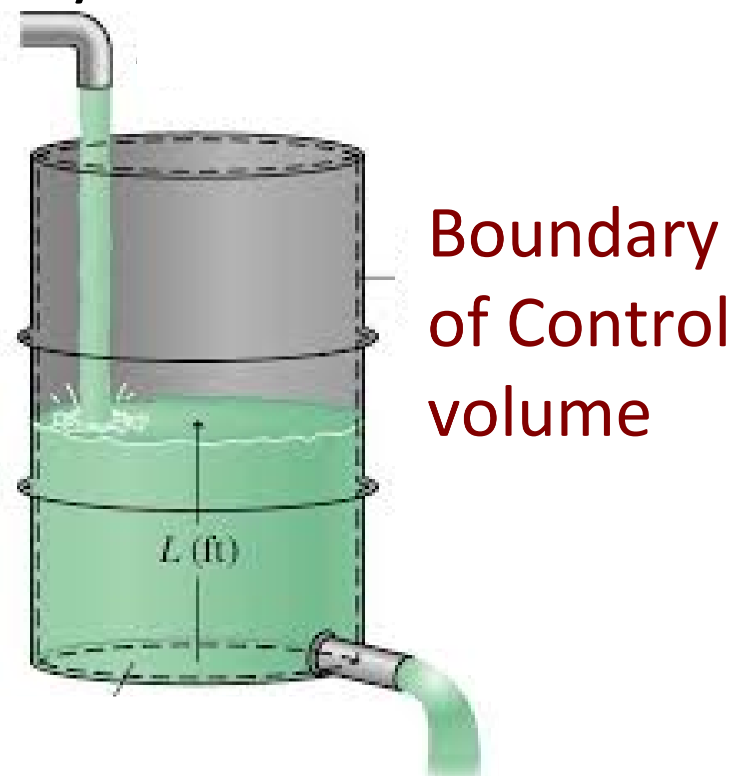
- **Path or non-State property (Functions):** Functions which depend not only on the initial and final states of the system, but also on the path it takes. (e.g., **Heat** and **Work**; written dq or dw. Never written **Δq** or **Δw**).

Thermodynamics is largely concerned with relations between state functions which characterize systems.

System/Surroundings

- **System**: volume of interest (reaction vessel, test tube, biological cell, atmosphere, etc.)
- **Surroundings**: volume outside a system



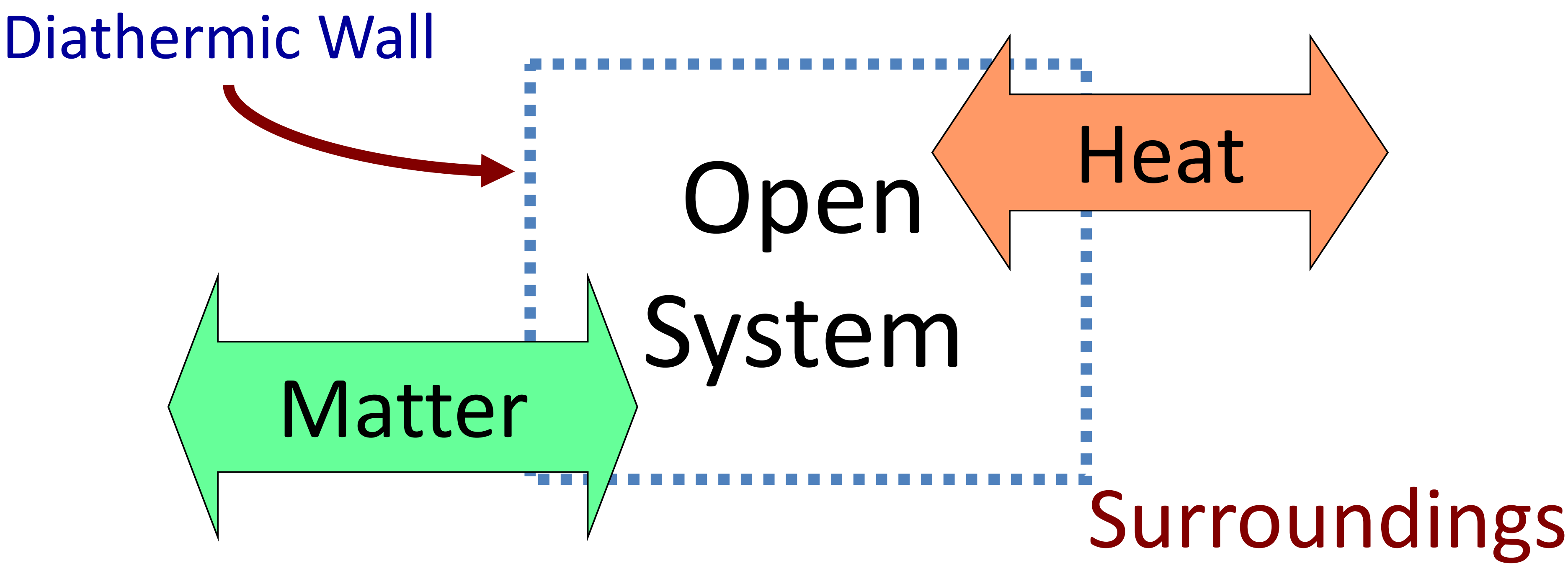


- Mathematically speaking, the **boundary** (fixed or movable) has zero thickness, and thus it can neither contain any mass nor occupy any volume in space.

Open (control volume) systems

A system permitting the heat (Energy) and mass transfer between system & surroundings

- **Diathermic Walls:** Walls permitting energy transfer as heat (such as steel and glass) ('dia' is the Greek word for "through").



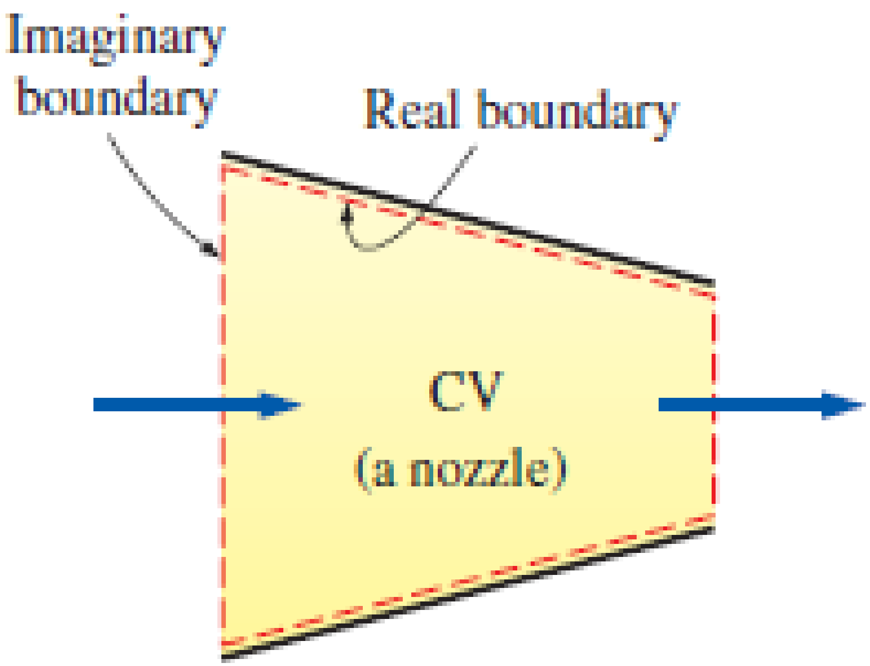
Open (control volume) systems

- usually encloses a device that involves mass flow such as a water heater, a car radiator, compressor, turbine, or nozzle.

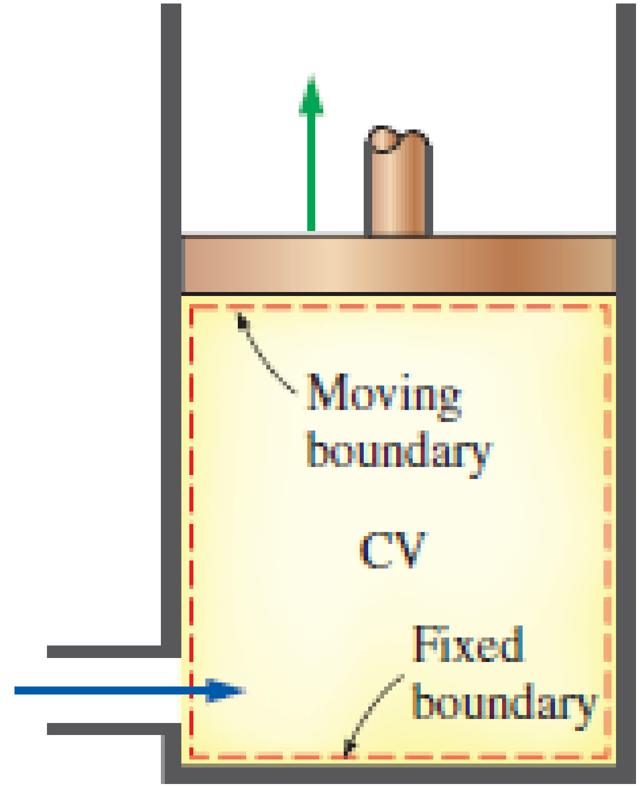
- Flow of air through a nozzle is a good example for the **control volume** would be the region within the nozzle.

- The boundaries of a control volume are called a **control surface**, and they can be real or imaginary.
  - In the case of a nozzle, the inner surface of the nozzle forms the real part of the boundary, and the entrance and exit areas form the imaginary part, since there are no physical surfaces there.

Open Systems



A control volume with real and imaginary boundaries



A control volume with fixed and moving boundaries as well as real and imaginary boundaries

Control volume systems can involve heat, work, and mass interaction.

Example

Electric water heater

> How much heat must we transfer to the water in the tank in order to supply a steady stream of hot water?

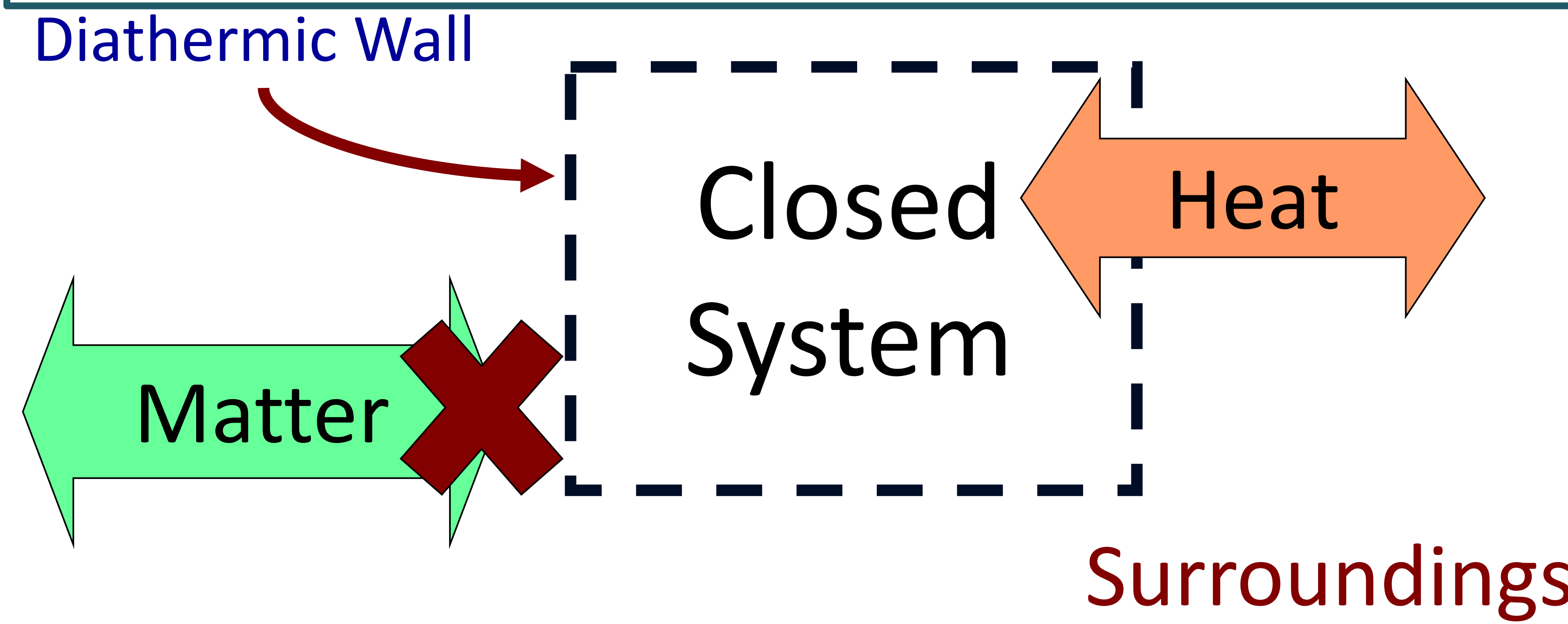
Analysis

- Since hot water will leave the tank and be replaced by cold water, it is more convenient to choose a fixed volume (not mass) as our system for the analysis.

- This fixed volume will be the interior surfaces of the tank while the hot and cold water streams are the mass leaving and entering the control volume at two locations.

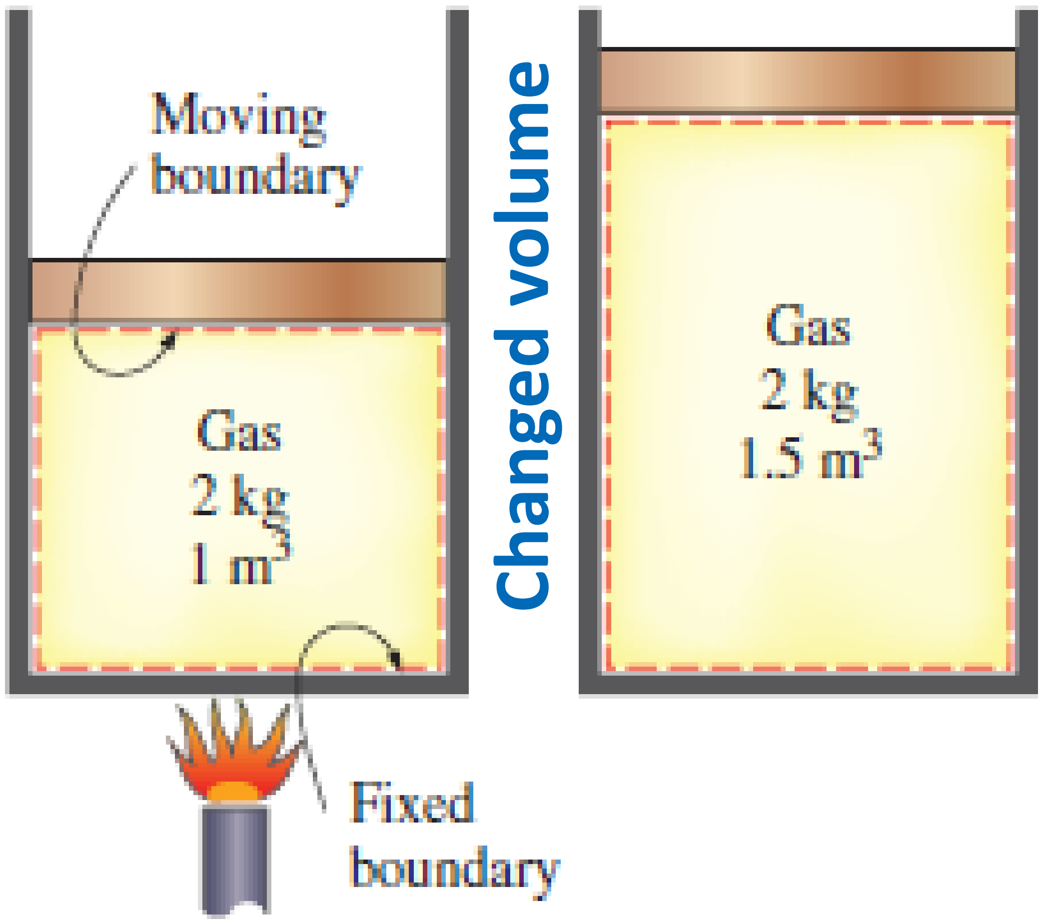
Closed (or control mass) systems

- consists of a fixed amount of mass, and no mass can cross its boundary.
- permits the exchange of heat and work but not mass between system & surroundings



A closed system with a moving boundary

- The volume of a closed system does not have to be fixed.
- If, as a special case, energy is not allowed to cross the boundary, that system is called an isolated system.

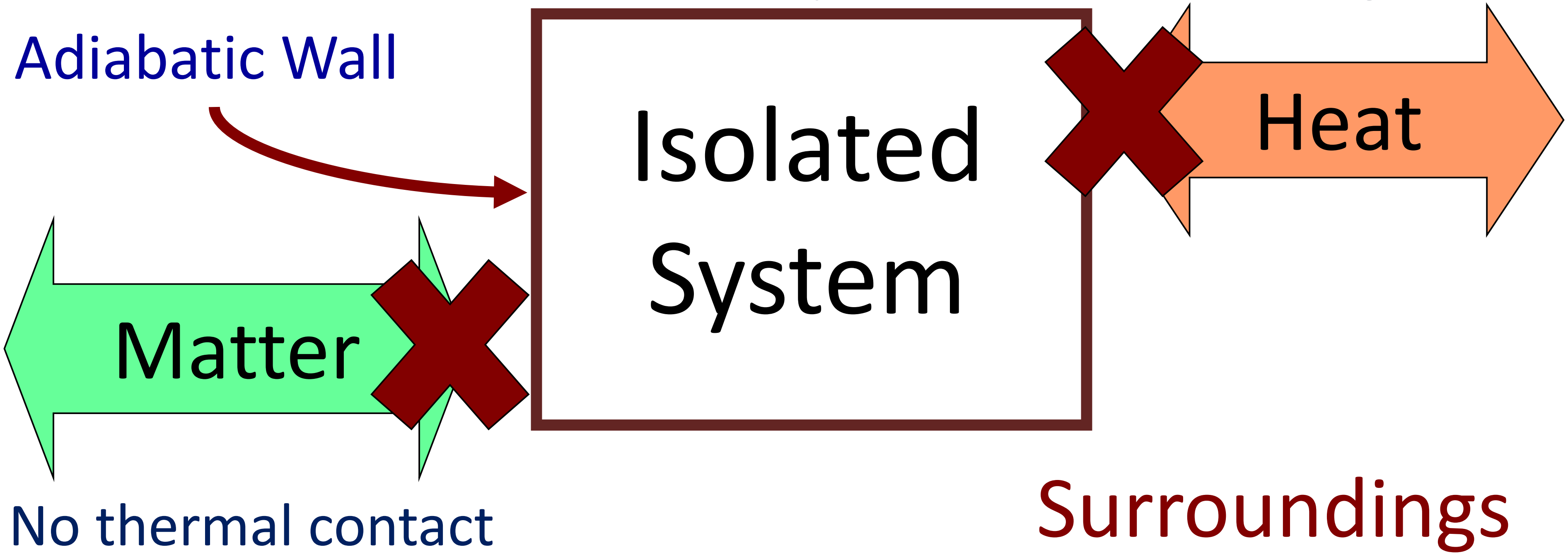


Isolated Systems

A system permitting neither the heat (Energy) nor mass transfer between system & surroundings

- **Adiabatic Walls**: Walls that DO NOT permit energy transfer as heat.

No change in internal energy ($\Delta E=0$) if no work is done between system and surrounding



Systems

homogeneous

- The system has the same properties throughout its extension (a **single** phase)

heterogeneous

- The system is composed of a **number** of homogeneous parts (called **phases**)

Phase

- is a homogeneous, physically distinct, and mechanically separable portion of any heterogeneous system.

General conventions

Work

Flow of energy (work or heat) is viewed from the system's perspective.

- If the system does work on the surroundings, then work (w) is negative.
- If the surroundings does work on the system, then work (w) is positive.

Heat

- If the system loses heat to the surroundings, then heat (q) is negative.
- If the system gains heat from the surroundings, then heat (q) is positive.

Chemical-Heat Energy Transformations

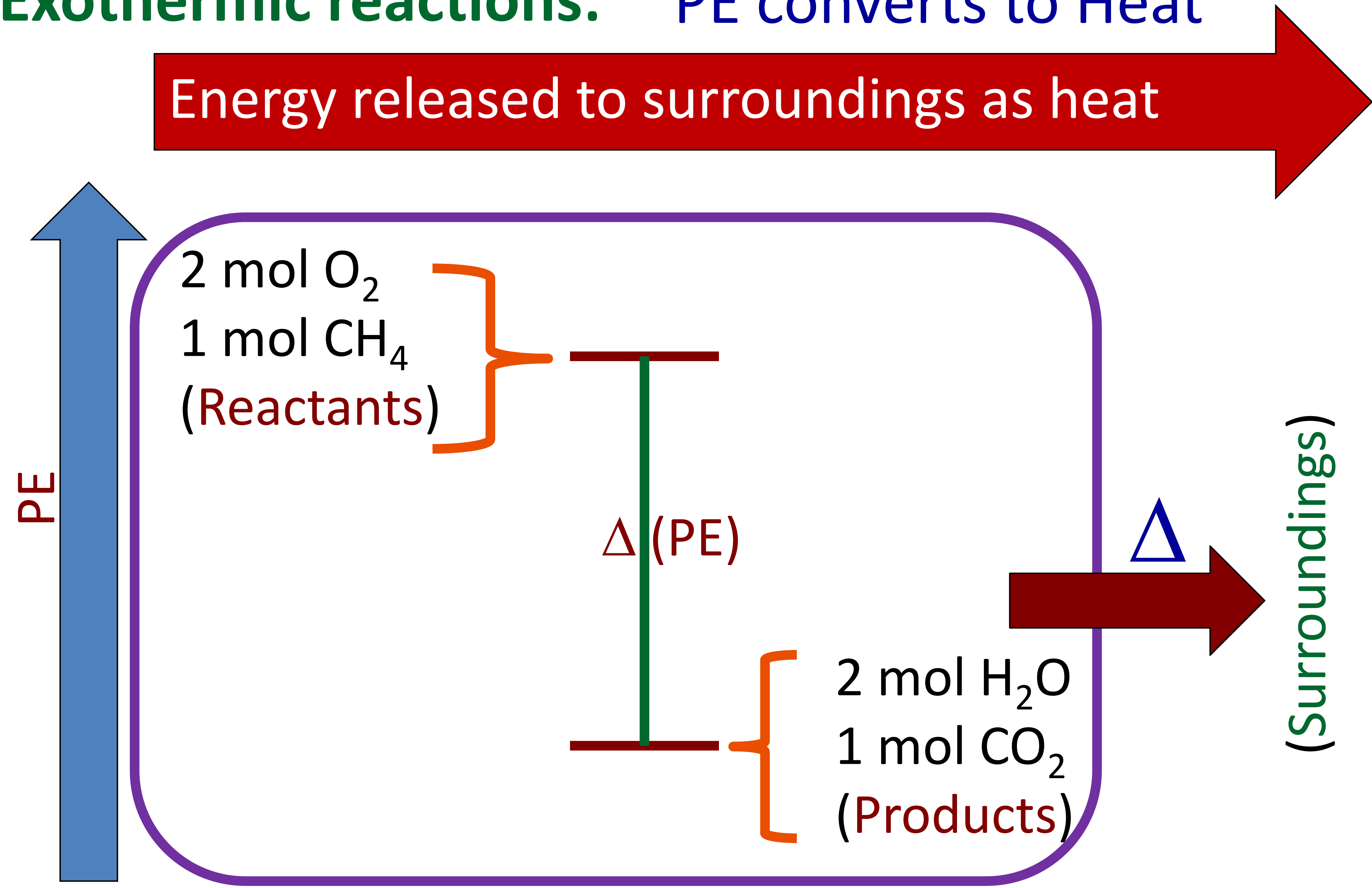
- The combustion of methane: heating homes

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\,(g) + \text{energy (heat)}$$

- Exothermic Reactions: reactions result in the evolution of heat.

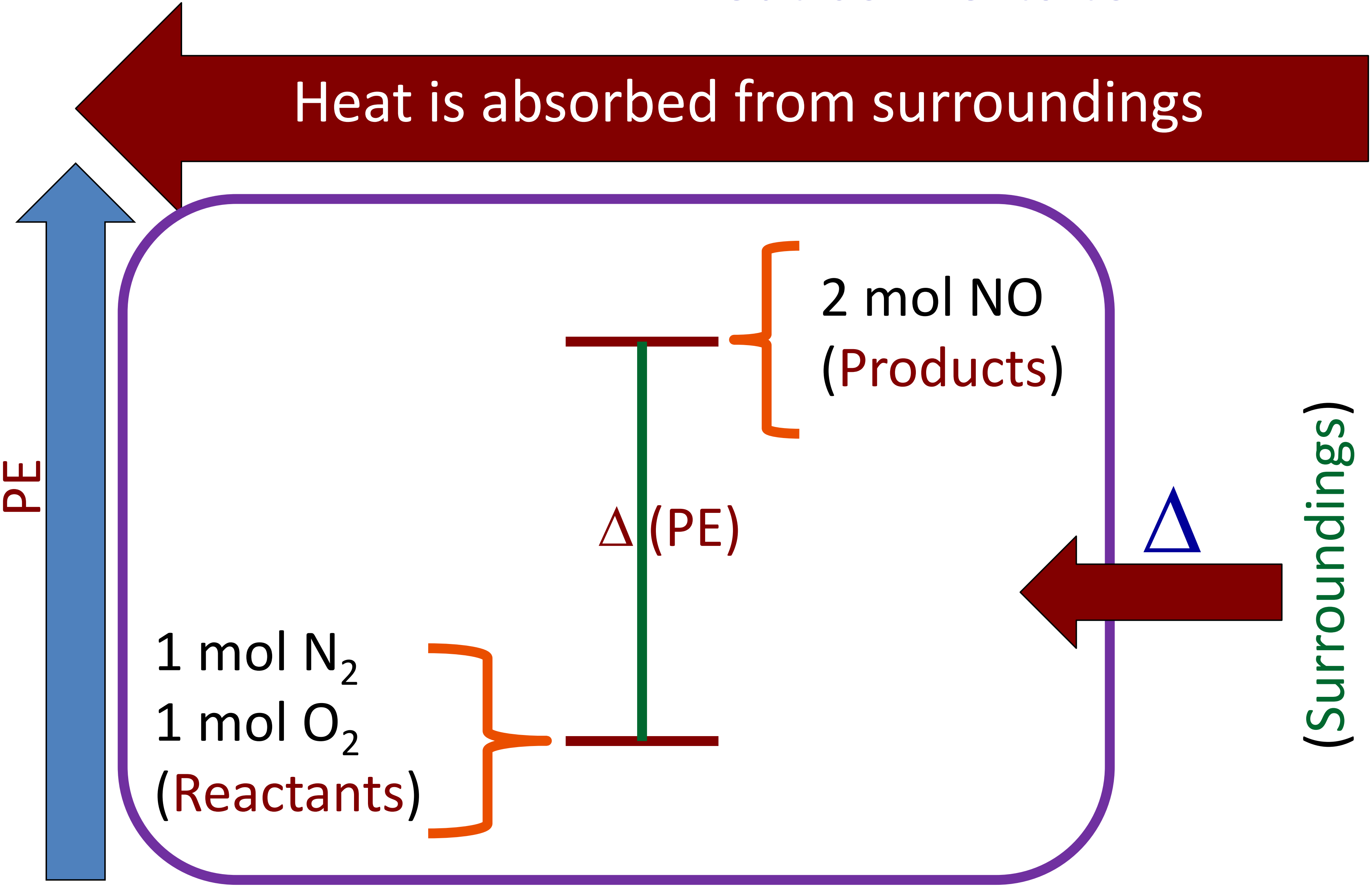
- Endothermic Reactions: reactions that absorb energy from the surroundings.

Exothermic reactions: PE converts to Heat



$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O\ (g) + \textbf{energy}\ (heat)$$

Endothermic reactions: Heat converts to PE



$$N_2(g) + O_2(g) + \textbf{energy (heat)} \rightarrow 2NO\ (g)$$

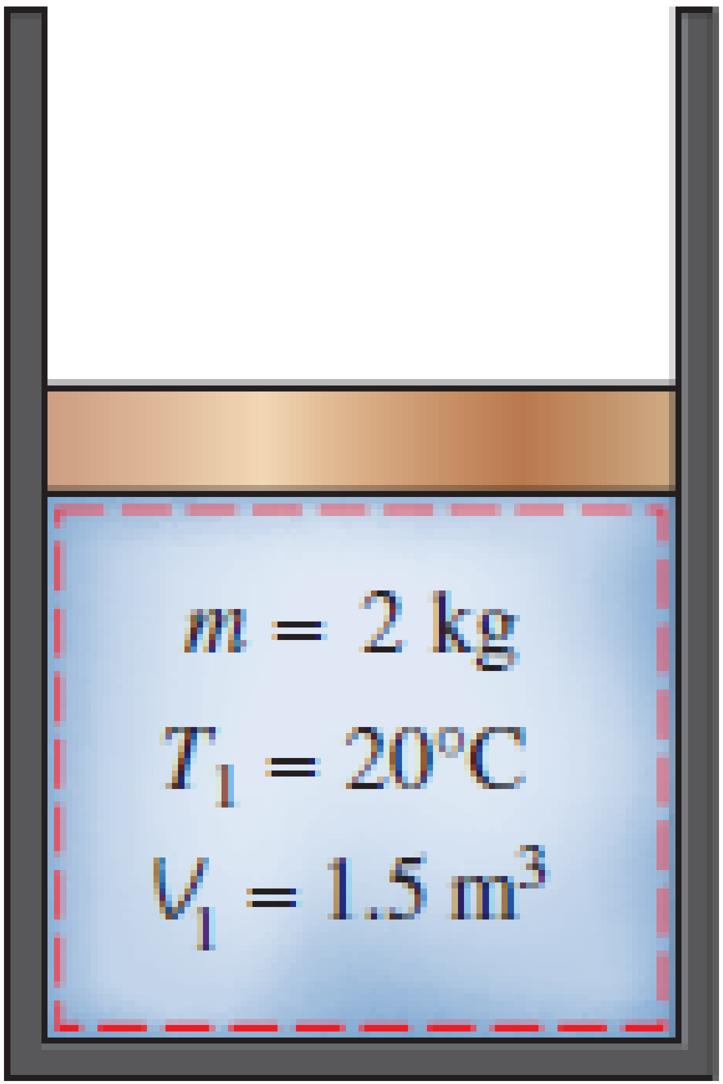
State

- is a **condition** describing a system maintained at **equilibrium** when all properties (variables) (measured or calculated) throughout the entire system are fixed (unchanged).
- If the value of even one property changes, the state will change to a different one.

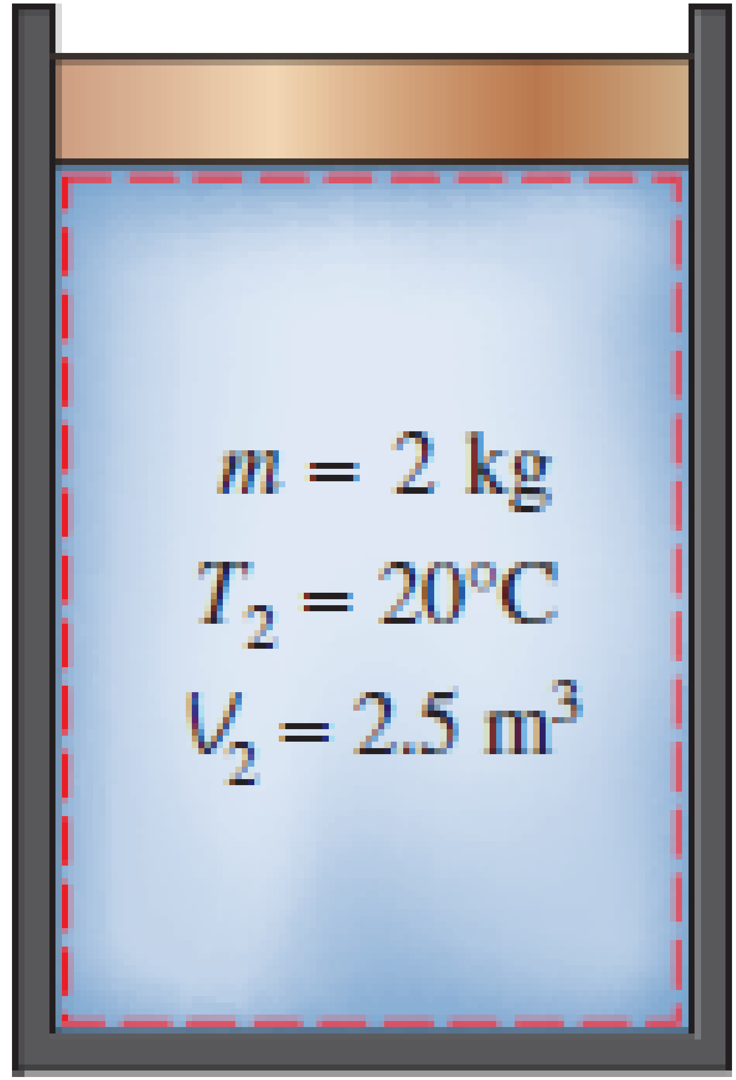
Property

any characteristic of a system

- **External**: macroscopic velocities, or position coordinates in an external field.
- **Internal** (Intensive/extensive): P, V, m, etc., of all substances in the system.



State 1



State 2

Extensive/Intensive Properties

- **Extensive property (Functions):** functions which depend on the mass of the material or the system's size (e.g., total mass, total volumes, total momentum, Internal energy, Volume)
- **Intensive Property (Functions):** functions which are independent of the mass of the material (e.g., Pressure, Temperature, Density, Molar quantities).
  - Includes extensive properties per unit mass (specific properties), e.g., specific volume (v=V/m) and specific total energy (e = E/m).

Generally, **uppercase letters** are used to denote extensive properties (with mass *m* being a major exception), and **lowercase letters** are used for intensive properties (with pressure *P* and temperature *T* being the obvious exceptions).

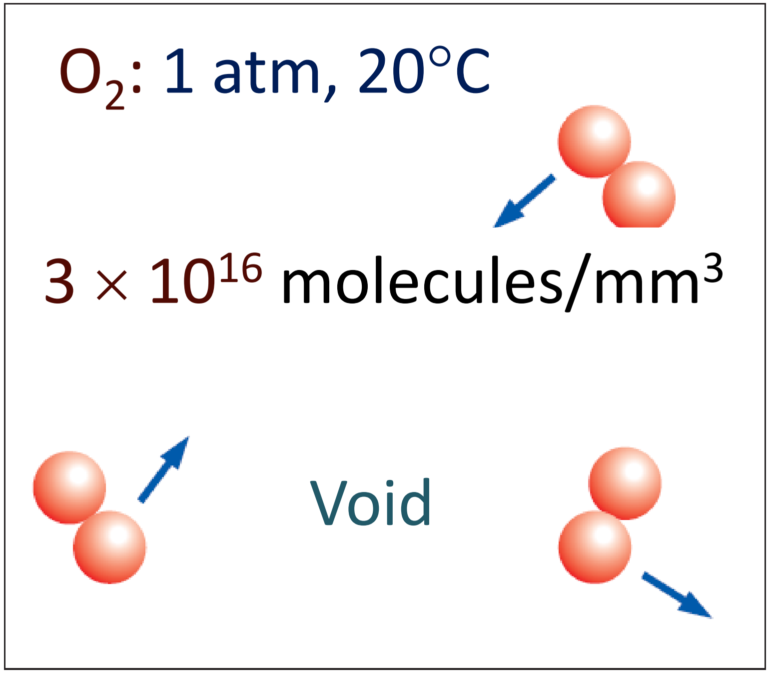
Continuum

"Matter is made up of atoms that are widely spaced in the gas phase. Yet it is very convenient to disregard the atomic nature of a substance and view it as a **continuous**, homogeneous matter with no holes, that is, a continuum"

- This allows treating properties as **point functions** assuming the variation of properties continually in space with no jump discontinuities.
- This idealization is valid as long as the size of the system we deal with is large relative to the space between the molecules (as most practical problems).
- This continuum idealization is implicit in many statements we make, such as "the density of water in a glass is the same at any point."

- Consider a container filled with oxygen at atmospheric conditions. The diameter of the oxygen molecule is about 3×10^{-10} m and its mass is 5.3×10^{-26} kg.

- The *mean free path* of oxygen at 1 atm pressure and 20°C is 6.3×10^{-8} m. That is, an oxygen molecule travels, on average, a distance of 6.3×10^{-8} m (about 200 times of its diameter) before it collides with another molecule.



The continuum model is applicable as long as the characteristic length of the system (e.g., its diameter) is much larger than the *mean free path* of the molecules.

Equilibrium

A state of balance

- Driving forces (**potential**) are balanced in all directions within the system.
- No change in all of its **intensive** properties with time.
- Thermodynamics deals with **equilibrium** states.
- There are many types of equilibrium (thermal, mechanical, phase, chemical), and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied.

- **Thermal** equilibrium indicates keeping the temperature the same throughout the entire system, i.e., the system involves no temperature differential, which is the driving force for heat flow.
- **Mechanical** equilibrium indicates no change in pressure at any point of the system with time.
- **Phase** equilibrium (If a system involves two phases), indicates that the mass of each phase reaches an equilibrium level and stays there.
- **Chemical** equilibrium indicates no change in the chemical composition of the system with time, that is, no chemical reactions occur.

The state postulate

"The state of a simple compressible system is completely specified by two independent, intensive properties."

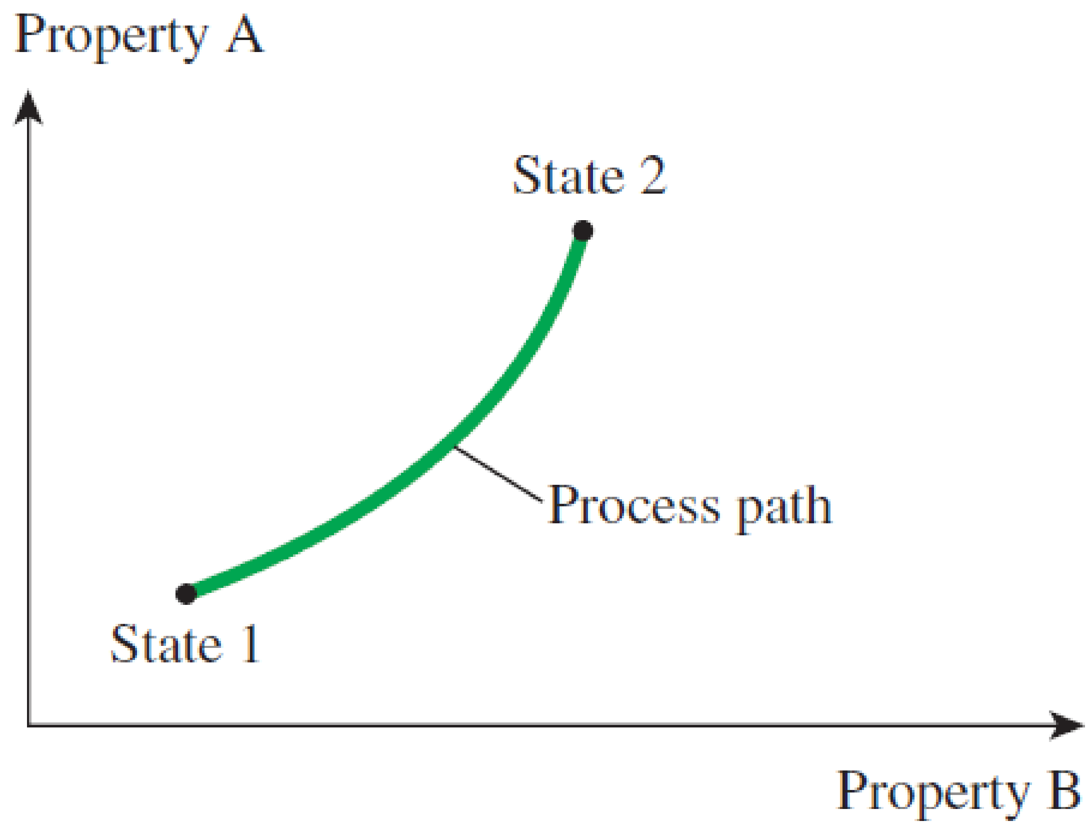
- "simple compressible", i.e., in absence of electrical, magnetic and gravitational fields, motion, and surface tension effects.
- "independent": as temperature and specific volume, which are always independent, and together they can fix the state of a simple compressible system.
  - Temperature and pressure, however, are independent properties for single-phase systems, but are dependent properties for multiphase systems (e.g., a mixture of gas & liquid, the boiling T depends on P).

- Once these two properties are specified, the rest of the properties assume certain values automatically.

Process

Any change that a system undergoes from one **equilibrium** state to another

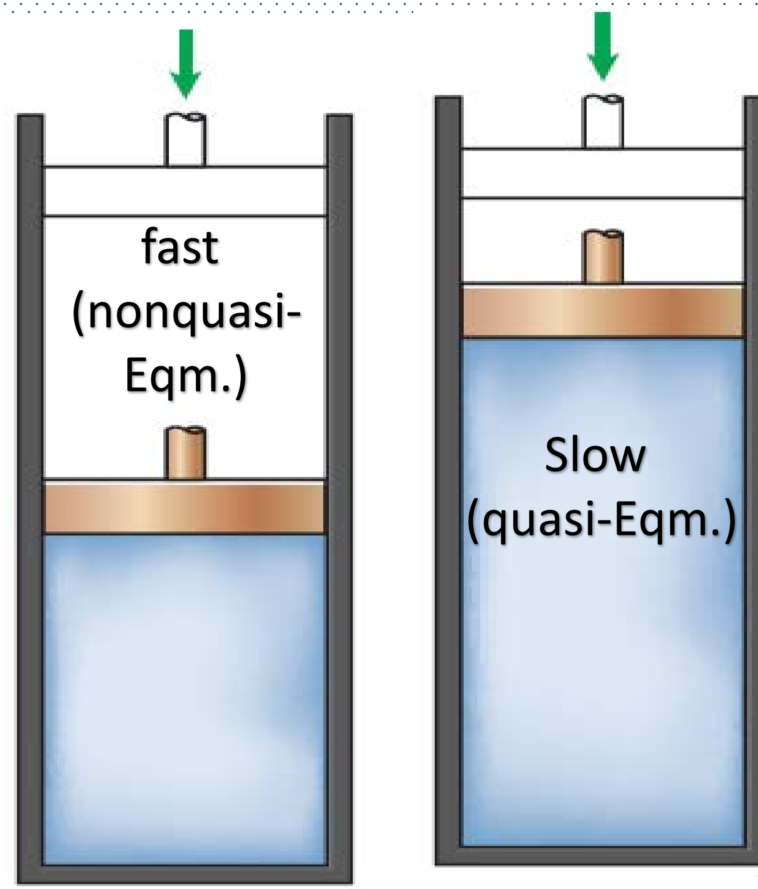
- The series of states through which a system passes during a process is called the path of the process.
- To describe a process completely, one should specify the initial and final states of the process, as well as the path it follows, and the interactions with the surroundings.



Quasi-static (quasi-equilibrium) process

- A process proceeding in such a manner that the system remains infinitesimally متناهي الصغر close to an equilibrium state at all times.

- It can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.



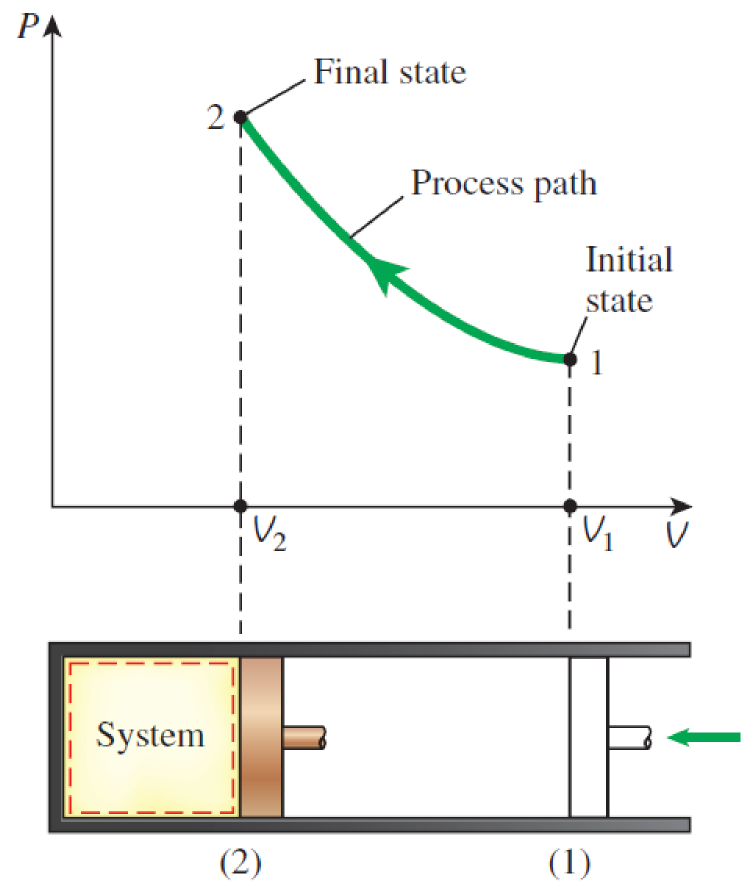
- If a process (e.g., the expansion of a gas) is running and the system is subjected to external influence (e.g., pressure) encountering (exactly) the force driving the expansion so that the system is passing by a series of equilibrium states, this process is called "**quasi-static process**".

- These processes are imaginary, easy to analyze and considered limiting for natural process:
  - (work-producing devices deliver the most work when they operate on quasi-equilibrium processes, **hence**, actual processes are compared to them).
- Other forces as friction may act against this idealization.

Process diagram

- A process path indicates a series of equilibrium states through which the system passes during a process and has significance for quasi-equilibrium processes only.

- For nonquasi-equilibrium processes, we are not able to characterize the entire system by a single state, and thus we cannot speak of a process path for a system as a whole.
- A nonquasi-equilibrium process is denoted by a dashed line between the initial and final states instead of a solid line.



Processes: Types

- The prefix **iso-** is often used to designate a process for which a particular property remains constant

- An **isothermal** process is a process during which the temperature T remains constant.

- An **isobaric** process is a process during which the pressure P remains constant.

- An **isochoric** (or **isometric**) process is a process during which the specific volume **v** remains constant.

Cycle

$$\oint dU = 0$$

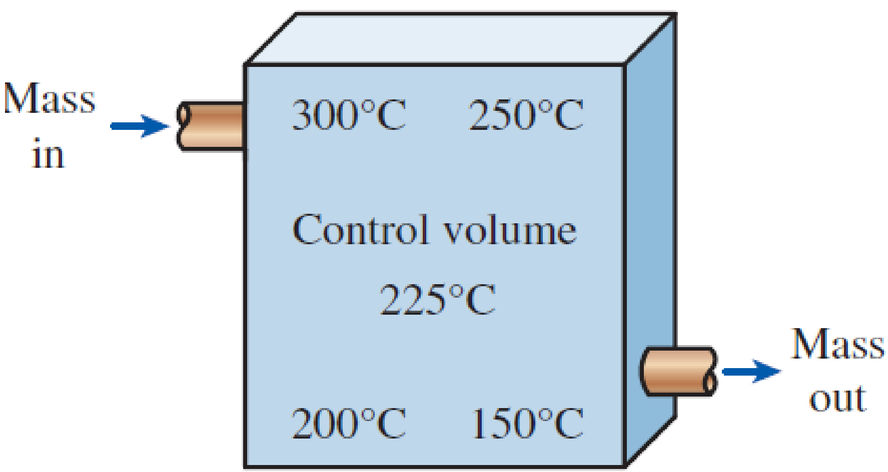
- A system is said to have undergone a cycle if it returns to its initial state at the end of the process. That is, for a cycle the initial and final states are identical.

- **"Steady"** implies no change with time. The opposite of steady is unsteady, or transient.
- **"Uniform"** implies no change with location over a specified region.

Steady-flow process

as in turbines, pumps, boilers, condensers, heat exchangers or refrigeration systems

- A process during which a fluid flows through a **control volume** steadily, i.e., the fluid properties can change from point to point within the control volume, but at any fixed point they remain the same during the entire process.



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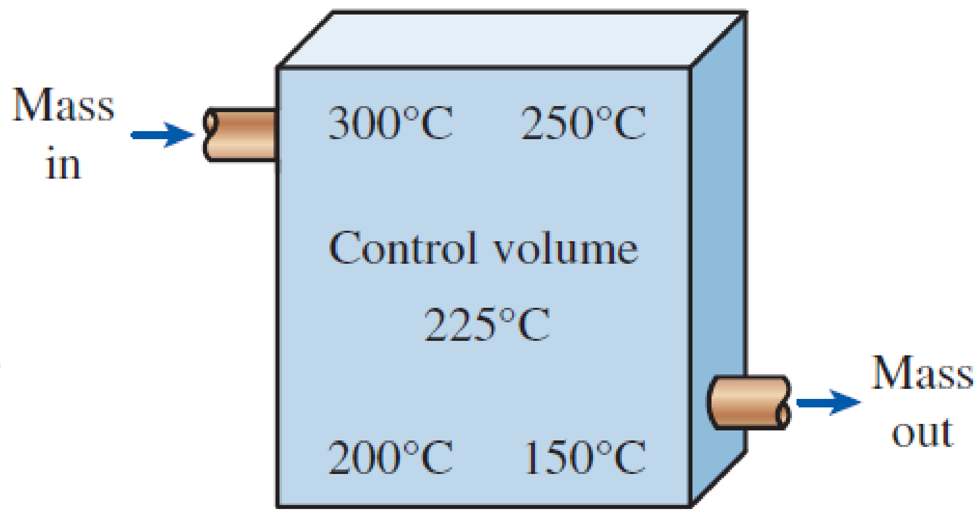

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Volume *V*, mass *m*, and total energy content *E* of the control volume remain **constant** during a steady-flow process.

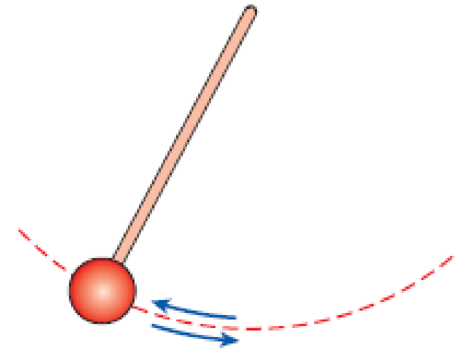
Reversible/irreversible processes

"Once a cup of hot coffee cools, it will not heat up by retrieving the heat it lost from the surroundings."

irreversible

Reversible

- "a process that can be reversed without leaving any trace on the surroundings".
- both the system and the surroundings are returned to their initial states at the end of the reverse process.
- This is possible only if the net heat and net work exchange between the system and the surroundings is zero for the combined (original and reverse) process.



Frictionless pendulum

A system passes through a series of equilibrium states during a reversible process.

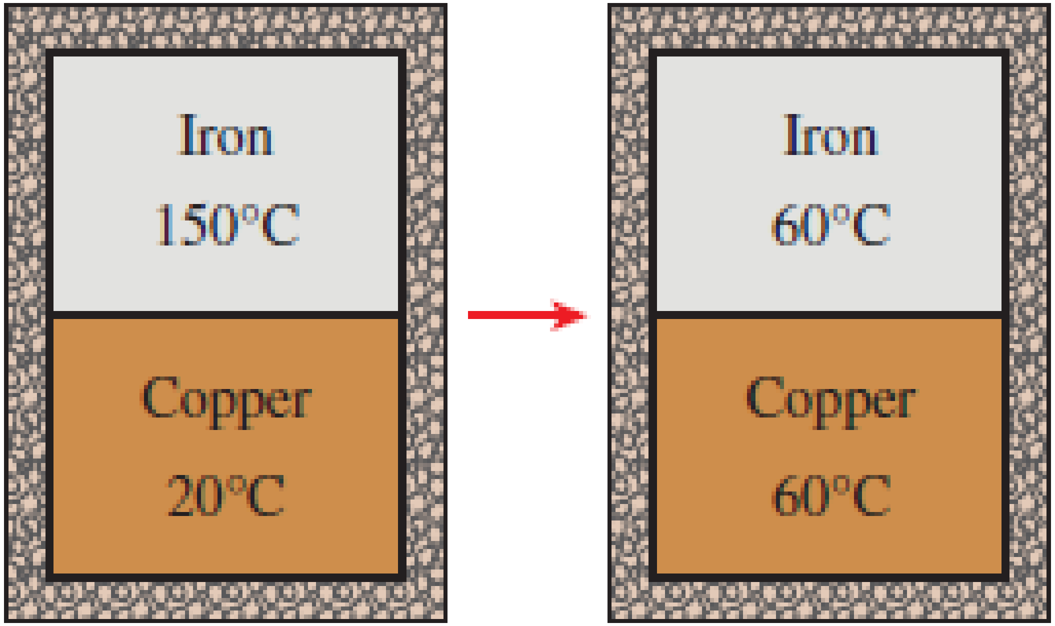
Quasistatic vs. reversible

- **Quasistatic**: the process is so slow, that the system is always in (or very close to) an equilibrium state.
- **Reversible**: the process goes the other way as soon as you reverse the applied conditions.
- Quasistatic and reversible are not the same thing. For example you can mix two gases very slowly (quasistatic) but you can't reverse that easily.
  - The reason is that the entropy between the starting point and the endpoint has increased and that's a main characteristic of an irreversible process.

- https://www.khanacademy.org/science/physics/thermodynamics/laws-of-thermodynamics/v/quasistatic-and-reversible-processes

Temperature and heat transfer

- Temperature is a property measuring the degree of "hotness" or "coldness" of a substance.
- A cup of hot coffee left on the table eventually cools off and a cold drink eventually warms up (attaining a thermal equilibrium is driving).



"Two bodies reaching thermal equilibrium after being brought into contact in an isolated enclosure"

0^{th} law of thermodynamics

R H Fowler / 1931

If two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other

If the third body with a thermometer

Two bodies are in thermal equilibrium if both have the same temperature reading even if they are not in contact

- The 0^{th} law was recognized more than half a century after the formulation of the 1^{st} & 2^{nd} laws of thermodynamics.
- "Zeroth" since it should have preceded the first and the second laws of thermodynamics.