

## Basic Concepts of Thermodynamics

Every science has its own unique vocabulary associated with it. Precise definition of basic concepts forms a sound foundation for development of a science and prevents possible misunderstandings. Careful study of these concepts is essential for a good understanding of topics in thermodynamics.

### Thermodynamics and Energy

Thermodynamics can be defined as the study of energy, energy transformations and its relation to matter. The analysis of thermal systems is achieved through the application of the governing conservation equations, namely *Conservation of Mass*, *Conservation of Energy* (1st law of thermodynamics), the 2nd law of thermodynamics and the property relations. Energy can be viewed as the ability to cause changes.

First law of thermodynamics: one of the most fundamental laws of nature is the conservation of energy principle. It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant.

Second law of thermodynamics: energy has quality as well as quantity, and actual processes occur in the direction of decreasing quality of energy.

Whenever there is an interaction between energy and matter, thermodynamics is involved. Some examples include heating and air-conditioning systems, refrigerators, water heaters, etc.

### Dimensions and Units

Any physical quantity can be characterized by dimensions. The arbitrary magnitudes assigned to the dimensions are called units. There are two types of dimensions, *primary* or *fundamental* and *secondary* or *derived* dimensions.

Primary dimensions are: mass, *m*; length, *L*; time, *t*; temperature, *T*

Secondary dimensions are the ones that can be derived from primary dimensions such as: velocity ( $m/s$ ), pressure ( $Pa = kg/m.s^2$ ).

There are two unit systems currently available SI (International System) and USCS (United States Customary System) or English system. We, however, will use SI units exclusively in this course. The SI units are based on decimal relationship between units. The prefixes used to express the multiples of the various units are listed in Table 1-1.

Table 1: Standard prefixes in SI units.

MULTIPLE	$10^{12}$	$10^9$	$10^6$	$10^3$	$10^{-2}$	$10^{-3}$	$10^{-6}$	$10^{-9}$	$10^{-12}$
PREFIX	tetra, T	giga, G	mega, M	kilo, k	centi, c	mili, m	micro, $\mu$	nano, n	pico, p

**Important note:** in engineering all equations must be dimensionally homogenous. This means that every term in an equation must have the same units. It can be used as a sanity check for your solution.

### Example 1: Unit Conversion

The heat dissipation rate density of an electronic device is reported as  $10.72 \text{ mW/mm}^2$  by the manufacturer. Convert this to  $\text{W/m}^2$ .

$$10.72 \frac{\text{mW}}{\text{mm}^2} \times \left( \frac{1000\text{mm}}{1\text{m}} \right)^2 \times \frac{1\text{W}}{1000\text{mW}} = 10720 \frac{\text{W}}{\text{m}^2}$$

### Closed and Open Systems

A *system* is defined as a quantity of matter or a region in space chosen for study. The mass or region outside the system is called the *surroundings*.

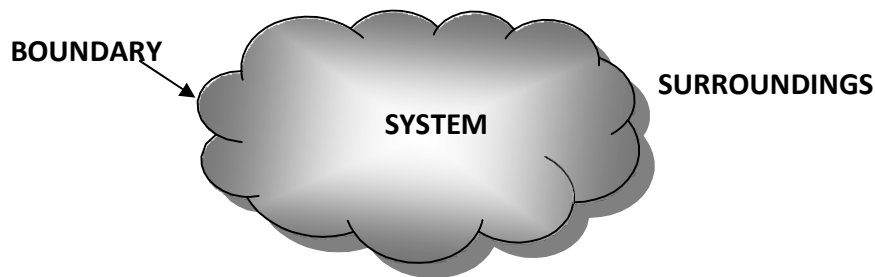


Fig. 1: System, surroundings, and boundary

**Boundary:** the real or imaginary surface that separates the system from its surroundings. The boundaries of a system can be fixed or movable. Mathematically, the boundary has zero thickness, no mass, and no volume.

**Closed system or control mass:** consists of a fixed amount of mass, and no mass can cross its boundary. But, energy in the form of heat or work, can cross the boundary, and the volume of a closed system does not have to be fixed.

**Open system or control volume:** is a properly selected region in space. It usually encloses a device that involves mass flow such as a compressor. Both mass and energy can cross the boundary of a control volume.

**Important note:** some thermodynamics relations that are applicable to closed and open systems are different. Thus, it is extremely important to recognize the type of system we have before start analyzing it.

**Isolated system:** A closed system that does not communicate with the surroundings by any means.

**Rigid system:** A closed system that communicates with the surroundings by heat only.

Adiabatic system: A closed or open system that does not exchange energy with the surroundings by heat.

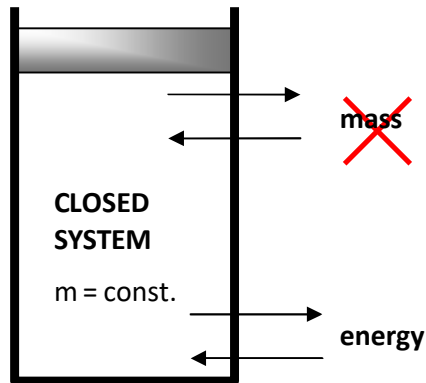


Fig. 2: Closed system, mass cannot cross the boundaries, but energy can.

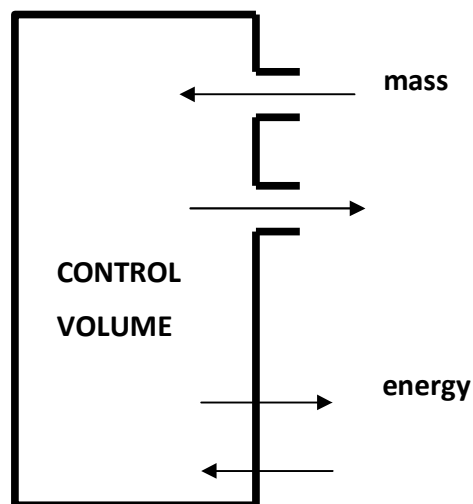


Fig. 3: Control volume, both mass and energy can cross the boundaries.

## Energy

In thermodynamics, we deal with change of the total energy only. Thus, the total energy of a system can be assigned a value of zero at some reference point. Total energy of a system has two groups: *macroscopic* and *microscopic*.

Macroscopic forms of energy: forms of energy that a system possesses as a whole with respect to some outside reference frame, such as kinetic and potential energy. The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity, and surface tension.

- ◆ Kinetic energy: energy that a system possesses as a result of its relative motion relative to some reference frame, KE

$$KE = \frac{mV^2}{2} \quad (kJ)$$

where V is the velocity of the system in (m/s).

- ◆ Potential energy: is the energy that a system possesses as a result of its elevation in a gravitational field, PE

$$PE = mgz \quad (kJ)$$

where g is the gravitational acceleration and z is the elevation of the center of gravity of the system relative to some arbitrary reference plane.

Microscopic forms of energy: are those related to molecular structure of a system. They are independent of outside reference frames. The sum of microscopic energy is called the *internal energy, U*.

The total energy of a system consists of the kinetic, potential, and internal energies:

$$E = U + KE + PE = U + \frac{mV^2}{2} + mgz \quad (kJ)$$

where the contributions of magnetic, electric, nuclear energy are neglected. Internal energy is related to the molecular structure and the degree of molecular activity and it may be viewed as the sum of the kinetic and potential energies of molecules.

- ◆ The sum of translational, vibrational, and rotational energies of molecules is the kinetic energy of molecules, and it is also called the *sensible energy*. At higher temperatures, system will have higher sensible energy.
- ◆ Internal energy associated with the phase of a system is called *latent heat*. The intermolecular forces are strongest in solids and weakest in gases.
- ◆ The internal energy associated with the atomic bonds in a molecule is called *chemical or bond energy*. The tremendous amount of energy associated with the bonds within the nucleolus of atom itself is called *atomic energy*.

Energy interactions with a closed system can occur via *heat transfer* and *work*.

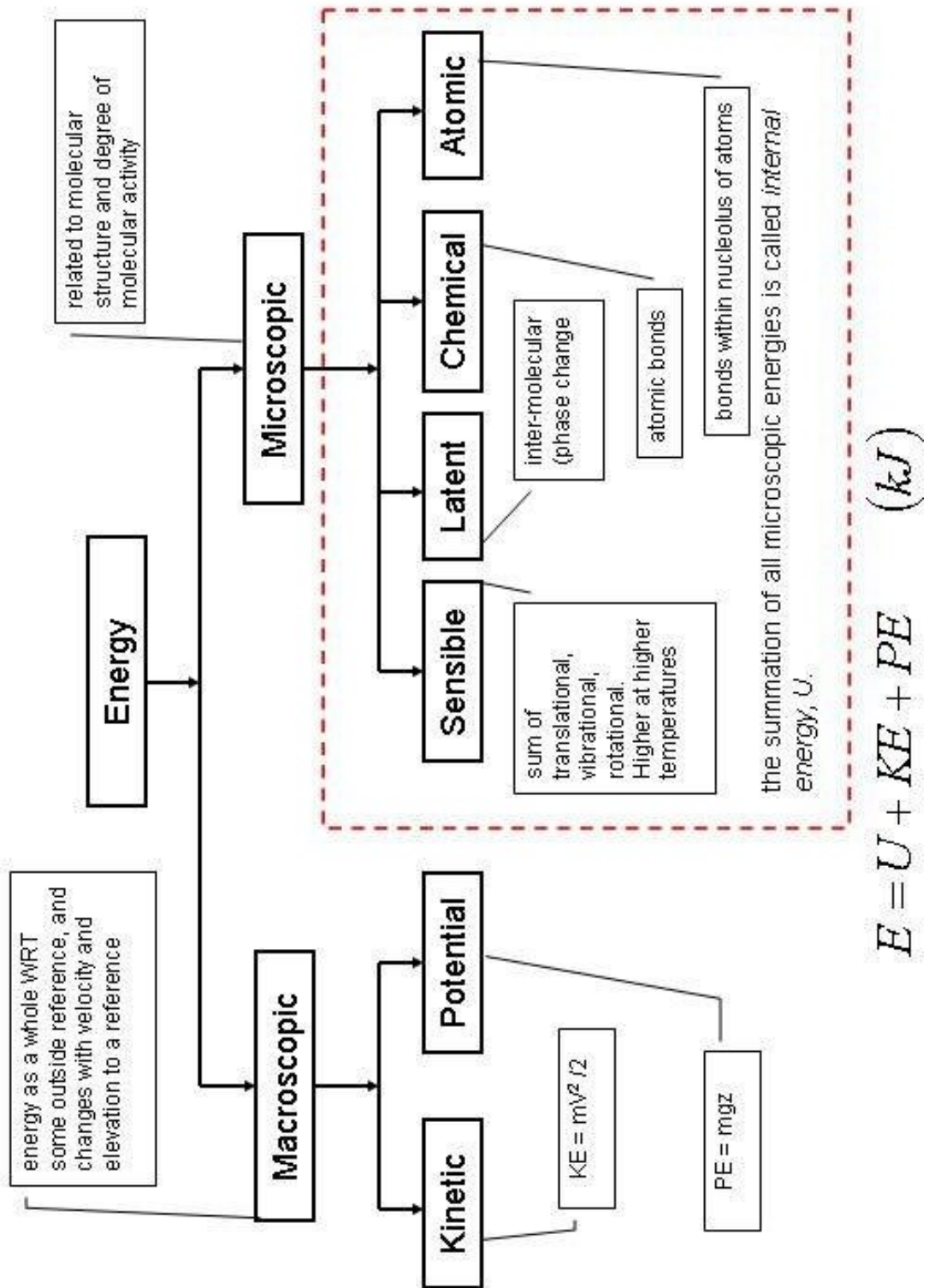


Fig. 1-4: Forms of energy.

## Properties of a System

Any characteristic of a system is called a *property*. In classical thermodynamics, the substance is assumed to be a *continuum*, homogenous matter with no microscopic holes. This assumption holds as long as the volumes, and length scales are large with respect to the intermolecular spacing.

Intensive properties: are those that are independent of the size (mass) of a system, such as temperature, pressure, and density. They are not additive.

Extensive properties: values that are dependant on size of the system such as mass, volume, and total energy U. They are additive.

- ◆ Generally, uppercase letters are used to denote extensive properties (except mass  $m$ ), and lower case letters are used for intensive properties (except pressure  $P$ , temperature  $T$ ).
- ◆ Extensive properties per unit mass are called specific properties, e.g. specific volume ( $v=V/m$ ).

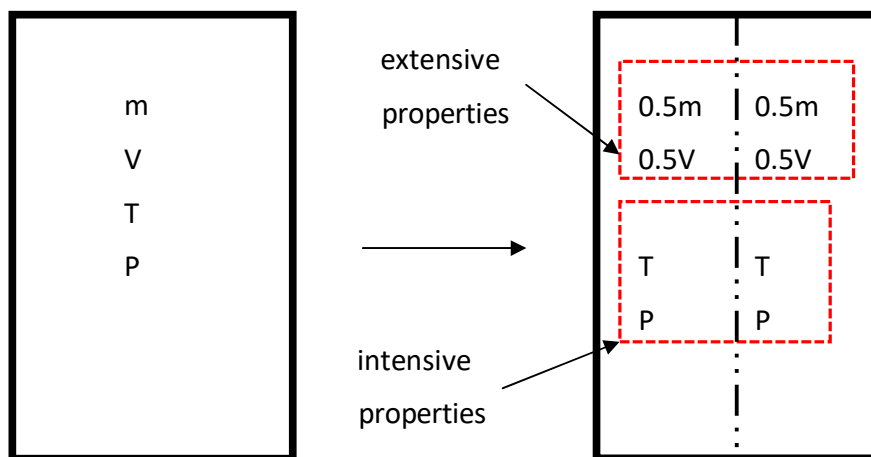


Fig. 1-5: Intensive and extensive properties of a system.

## State and Equilibrium

At a given *state*, all the properties of a system have fixed values. Thus, if the value of even one property changes, the state will change to different one.

In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system. A system in equilibrium experiences no changes when it is isolated from its surroundings.

- ◆ Thermal equilibrium: when the temperature is the same throughout the entire system.

- ◆ Mechanical equilibrium: when there is no change in pressure at any point of the system. However, the pressure may vary within the system due to gravitational effects.
- ◆ Phase equilibrium: in a two phase system, when the mass of each phase reaches an equilibrium level.
- ◆ Chemical equilibrium: when the chemical composition of a system does not change with time, i.e., no chemical reactions occur.

## Processes and Cycles

Any change a system undergoes from one equilibrium state to another is called a *process*, and the series of states through which a system passes during a process is called a *path*.

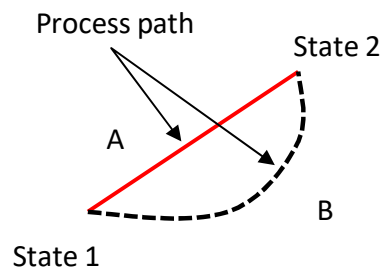


Fig. 6: To specify a process, initial and final states and path must be specified.

Quasi-equilibrium process: can be viewed as a sufficiently slow process that allows the system to adjust itself internally and remains infinitesimally close to an equilibrium state at all times. Quasi-equilibrium process is an idealized process and is not a true representation of the actual process. We model actual processes with quasi-equilibrium ones. Moreover, they serve as standards to which actual processes can be compared.

Process diagrams are used to visualize processes. Note that the process path indicates a series of equilibrium states, and we are not able to specify the states for a non-quasi-equilibrium process.

Prefix *iso-* is used to designate a process for which a particular property is constant.

- ◆ Isothermal: is a process during which the temperature remains constant
- ◆ Isobaric: is a process during which the pressure remains constant
- ◆ Isometric: is process during which the specific volume remains constant.

A system is said to have undergone a *cycle* if it returns to its initial state at the end of the process.

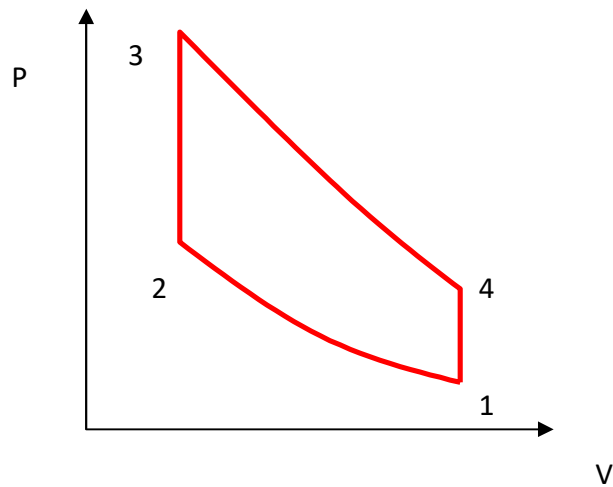


Fig. 1-7: A four-process cycle in a P-V diagram.

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

A system is called simple compressible system in the absence of electrical, magnetic, gravitational, motion, and surface tension effects (external force fields).

Independent properties: two properties are independent if one property can be varied while the other one is held constant.

## Pressure

Pressure is the force exerted by a fluid per unit area.

$$\text{Pressure} = \frac{\text{Force}}{\text{Area}} \quad \frac{N}{m^2} \equiv Pa$$

In fluids, gases and liquids, we speak of *pressure*; in solids this is *stress*. For a fluid at rest, the pressure at a given point is the same in all directions.

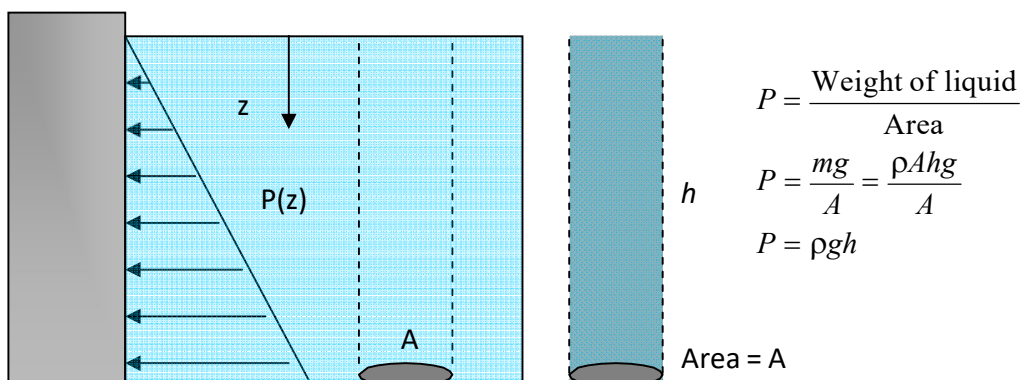


Fig. 8: Pressure of a fluid at rest increases with depth (due to added weight), but constant in horizontal planes.



The actual pressure at a given position is called the *absolute pressure*, and it is measured relative to absolute vacuum.

gauge pressure = absolute pressure - atmospheric pressure

$$P_{gauge} = P_{abs} - P_{atm} \quad P > P_{atm}$$

$$P_{vac} = P_{atm} - P_{abs} \quad P < P_{atm}$$

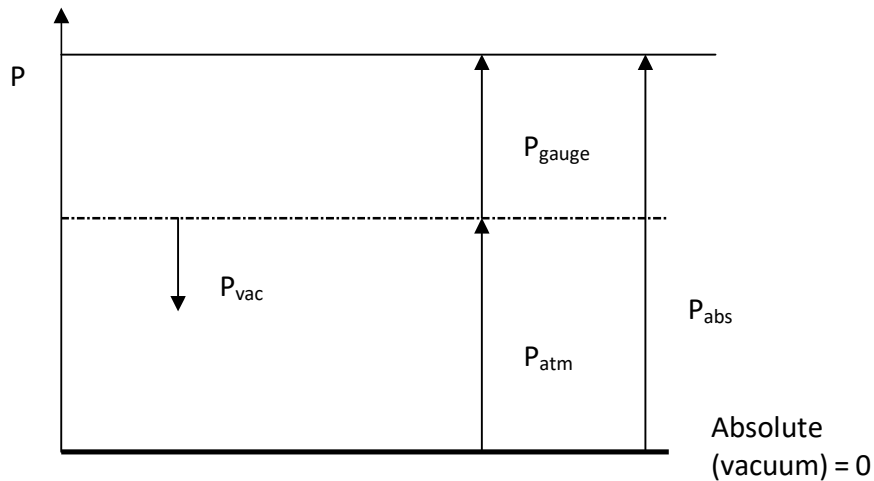


Fig. 9: Absolute, gauge, and vacuum pressures.

In thermodynamics calculations, always use absolute pressure. Most pressure measuring devices are calibrated to read zero in the atmosphere (they measure  $P_{gauge}$  or  $P_{vac}$ ). Be aware of what you are reading!

A device that measures pressure using a column of liquid is called a *Manometer*. The cross sectional area of the tube is not important. The manometer measures the gauge pressure.

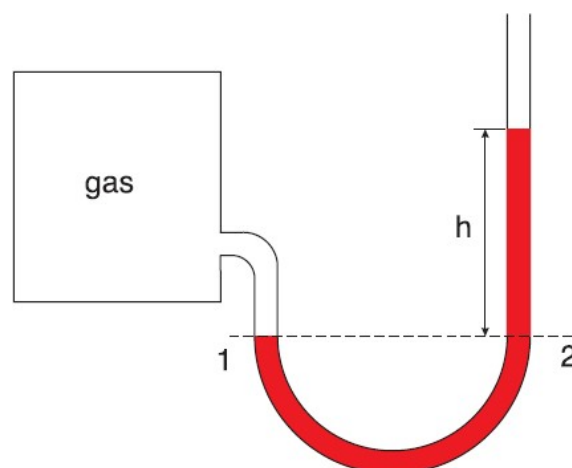


Fig. 10: Basic manometer,  $P_2 = P_1$ .

$$P_1 = P_{atm} + \rho gh \quad (kPa)$$

*Bourdon Tube* is a device that measures pressure using mechanical deformation. *Pressure Transducers* are devices that use piezoelectrics to measure pressure.

- ◆ very accurate and robust
- ◆ can measure from  $10^{-6}$  to  $10^5$  atm
- ◆ can measure  $P_{\text{gauge}}$  or  $P_{\text{abs}}$

*Barometer* is a device that measures atmospheric pressure. It is a manometer with a near vacuum on one end

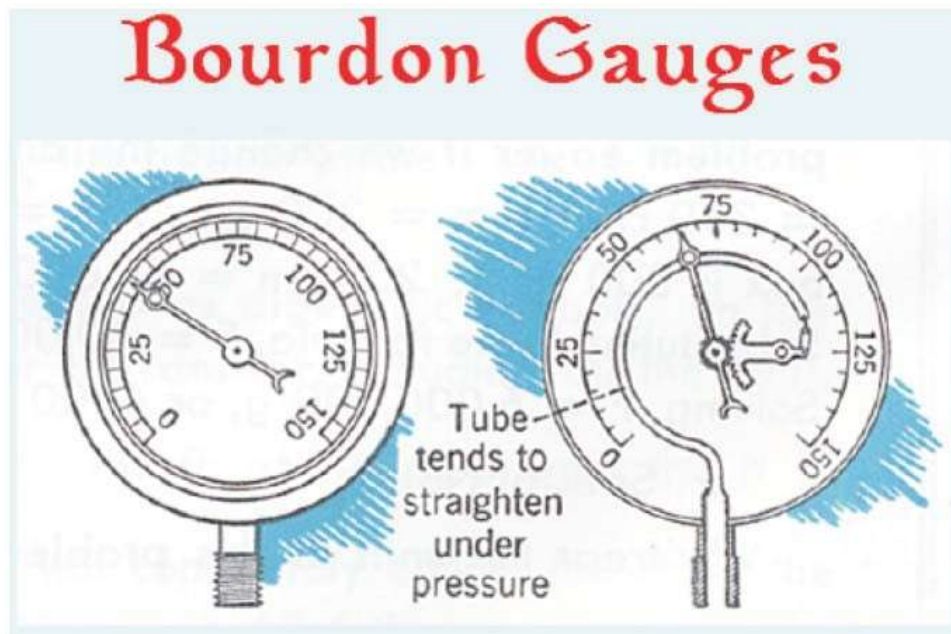


Fig. 11: Bourdon gauge.

### Example 2: Pressure

The piston of a cylinder-piston device has a mass of 60 kg and a cross-sectional area of  $0.04 \text{ m}^2$ , as shown in Fig. 12. The depth of the liquid in the cylinder is 1.8 m and has a density of  $1558 \text{ kg/m}^3$ . The local atmospheric pressure is 0.97 bar, and the gravitational acceleration is  $9.8 \text{ m/s}^2$ . Determine the pressure at the bottom of the cylinder.

Solution: the pressure at the bottom of the cylinder can be found from the summation of the forces due to atmospheric pressure, piston weight, and the weight of the liquid in the cylinder.

$$W_{\text{bottom}} = P_{\text{atm}} A + W_{\text{liquid}} + W_{\text{Piston}}$$

$$P_{\text{bottom}} = P_{\text{atm}} + \frac{mg}{A} + \rho gh$$

$$P_{bottom} = 0.97(\text{bar}) + \left\{ \frac{(60\text{kg})(9.8\text{ m/s}^2)}{0.04\text{ m}^2} + \left( 1558\text{ kg/m}^3 \right) \left( 9.8\text{ m/s}^2 \right) \left( 1.8\text{ m} \right) \right\}$$

$$\left[ \left( \frac{1\text{N/m}^2}{1\text{kg/m}\cdot\text{s}^2} \right) \left( \frac{1\text{bar}}{10^5\text{ N/m}^2} \right) \right] = 1.3918\text{ bars}$$

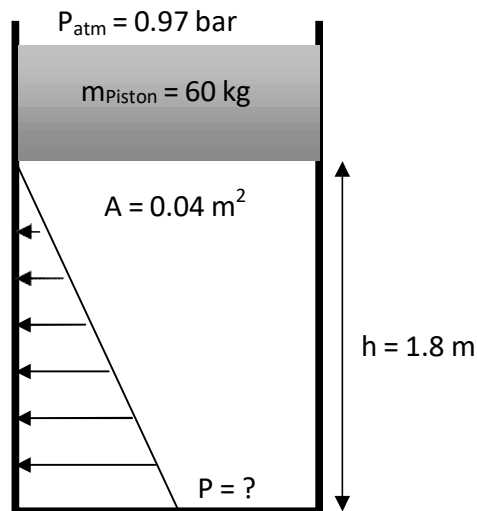


Fig. 12: Sketch for example 2.

## Temperature

Temperature is a pointer for the direction of energy transfer as heat.

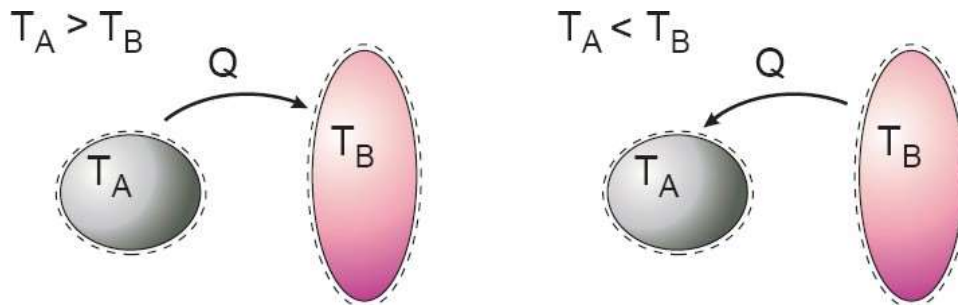


Fig. 13: Heat transfer occurs in the direction of higher-to-lower-temperature.

When the temperatures of two bodies are the same, *thermal equilibrium* is reached. The equality of temperature is the only requirement for thermal equilibrium.

The 0th law of thermodynamics: states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.

The 0th law makes a thermometer possible.

In accordance with the 0th law, any system that possesses an equation of state that relates temperature  $T$  to other accurately measurable properties can be used as a thermometer e.g. an ideal gas obeys the equation of state:

$$T = \frac{PV}{mR}$$

Experimentally obtained Temperature Scales: the *Celsius* and *Fahrenheit* scales, are based on the melting and boiling points of water. They are also called two-point scales.

Conventional thermometry depends on material properties e.g. mercury expands with temperature in a repeatable and predictable way

Thermodynamic Temperature Scales (independent of the material), the Kelvin and Rankine scales, are determined using a constant volume gas thermometer.

# Laws of Thermodynamics



# Thermodynamics

- Thermodynamics is the study of the effects of work, heat, and energy on a system
- Thermodynamics is only concerned with macroscopic (large-scale) changes and observations



# Getting Started

- All of thermodynamics can be expressed in terms of four quantities
  - Temperature ( $T$ )
  - Internal Energy ( $U$ )
  - Entropy ( $S$ )
  - Heat ( $Q$ )
- These quantities will be defined as we progress through the lesson



# Classical vs Statistical

- Classical thermodynamics concerns the relationships between bulk properties of matter. Nothing is examined at the atomic or molecular level.
- Statistical thermodynamics seeks to explain those bulk properties in terms of constituent atoms. The statistical part treats the aggregation of atoms, not the behavior of any individual atom





# Introduction

According to British scientist C. P. Snow, the three laws of thermodynamics can be (*humorously*) summarized as

1. You can't win
2. You can't even break even
3. You can't get out of the game



# 1.0 You can't win (1<sup>st</sup> law)

- The first law of thermodynamics is an extension of the law of conservation of energy
- The change in internal energy of a system is equal to the heat added to the system minus the work done by the system

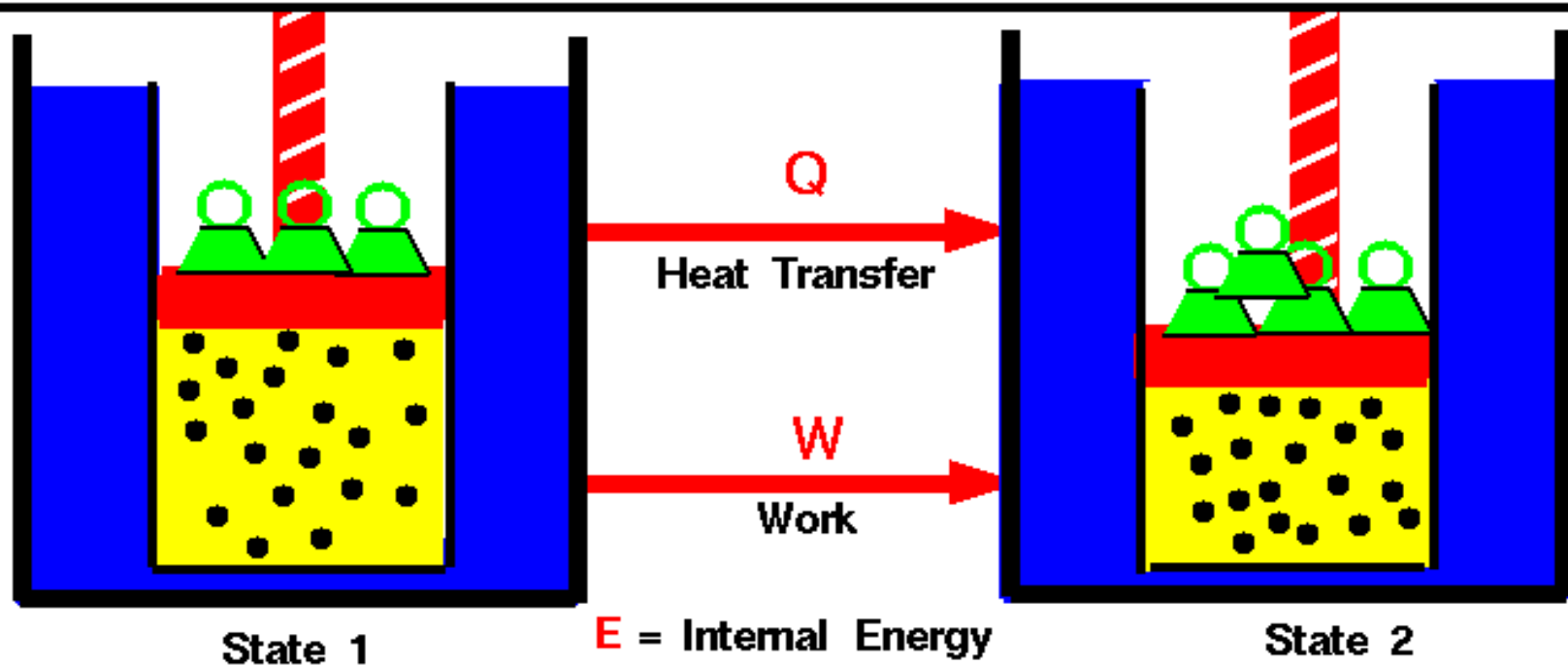
$$\Delta U = Q - W$$





# First Law of Thermodynamics

Glenn  
Research  
Center



Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy ( $E$ ). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.

# 1.1 Process Terminology

- Adiabatic – no heat transferred
- Isothermal – constant temperature
- Isobaric – constant pressure
- Isochoric – constant volume



# 1.1.1 Adiabatic Process

- An adiabatic process transfers no heat
  - therefore  $Q = 0$
- $\Delta U = Q - W$
- When a system expands adiabatically,  $W$  is positive (the system does work) so  $\Delta U$  is negative.
- When a system compresses adiabatically,  $W$  is negative (work is done on the system) so  $\Delta U$  is positive.



# 1.1.2 Isothermal Process

- An isothermal process is a constant temperature process. Any heat flow into or out of the system must be slow enough to maintain thermal equilibrium
- For ideal gases, if  $\Delta T$  is zero,  $\Delta U = 0$
- Therefore,  $Q = W$ 
  - Any energy entering the system ( $Q$ ) must leave as work ( $W$ )



# 1.1.3 Isobaric Process

- An isobaric process is a constant pressure process.  $\Delta U$ ,  $W$ , and  $Q$  are generally non-zero, but calculating the work done by an ideal gas is straightforward

$$W = P \cdot \Delta V$$

- Water boiling in a saucepan is an example of an isobar process



# 1.1.4 Isochoric Process

- An isochoric process is a constant volume process. When the volume of a system doesn't change, it will do no work on its surroundings.  $W = 0$

$$\Delta U = Q$$

- Heating gas in a closed container is an isochoric process





# 1.2 Heat Capacity

- The amount of heat required to raise a certain mass of a material by a certain temperature is called heat capacity

$$Q = mc_x\Delta T$$

- The constant  $c_x$  is called the specific heat of substance  $x$ , (SI units of J/kg·K)



# 1.2.1 Heat Capacity of Ideal Gas

- $C_V$  = heat capacity at constant volume

$$C_V = 3/2 R$$

- $C_P$  = heat capacity at constant pressure

$$C_P = 5/2 R$$

- For constant volume

$$Q = nC_V\Delta T = \Delta U$$

- The universal gas constant  $R = 8.314 \text{ J/mol}\cdot\text{K}$



## 2.0 You can't break even (2<sup>nd</sup> Law)

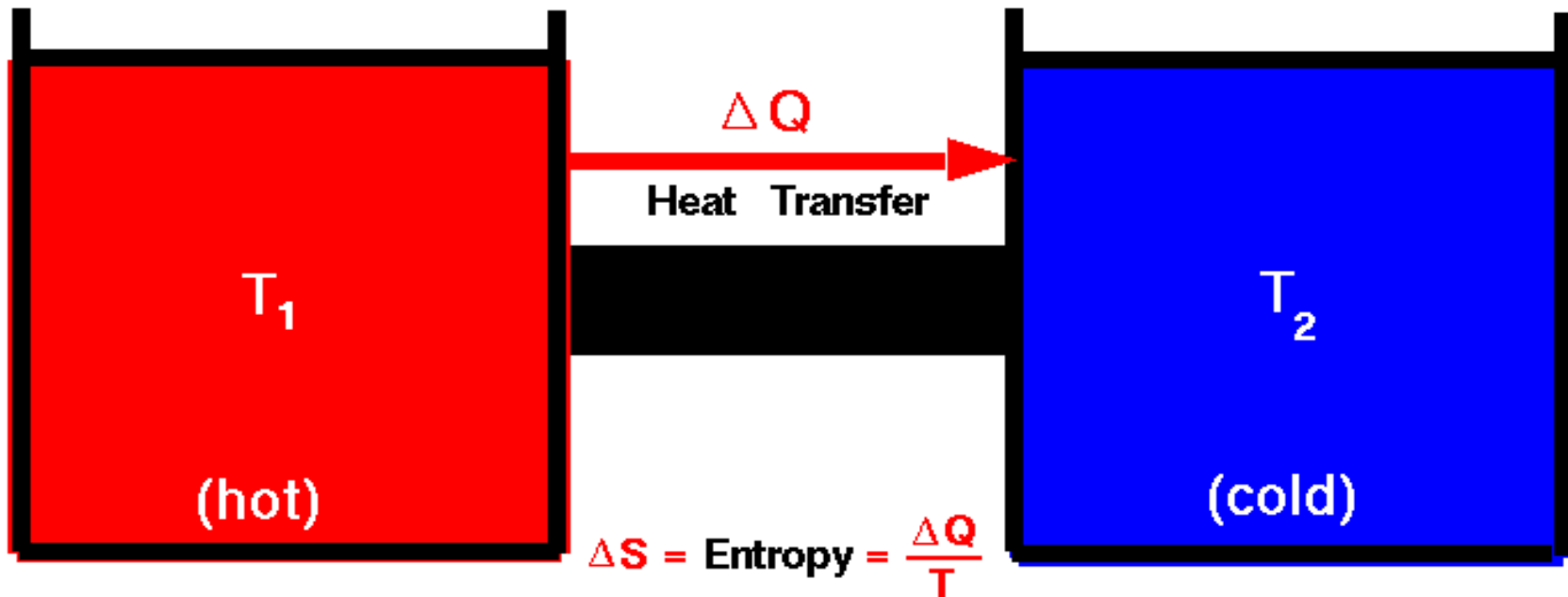
- Think about what it means to not “break even”. Every effort you put forth, no matter how efficient you are, will have a tiny bit of waste.
- The 2<sup>nd</sup> Law can also be stated that heat flows spontaneously from a hot object to a cold object (spontaneously means without the assistance of external work)





# Second Law of Thermodynamics

Glenn  
Research  
Center



There exists a useful thermodynamic variable called entropy (S). A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus the environment to increase for an irreversible process and to remain constant for a reversible process.

$$S_f = S_i \text{ (reversible)}$$

$$S_f > S_i \text{ (irreversible)}$$

## 2.1 Concerning the 2<sup>nd</sup> Law

- The second law of thermodynamics introduces the notion of entropy ( $S$ ), a measure of system disorder (messiness)
- $U$  is the quantity of a system's energy,  $S$  is the quality of a system's energy.
- Another C.P. Snow expression:
  - not knowing the 2<sup>nd</sup> law of thermodynamics is the cultural equivalent to never having read Shakespeare



## 2.2 Implications of the 2<sup>nd</sup> Law

- Time marches on
  - If you watch a movie, how do you know that you are seeing events in the order they occurred?
  - If I drop a raw egg on the floor, it becomes extremely “disordered” (greater Entropy) – playing the movie in reverse would show pieces coming together to form a whole egg (decreasing Entropy) – highly unlikely!



## 2.3 Direction of a Process

- The 2<sup>nd</sup> Law helps determine the preferred direction of a process
- A reversible process is one which can change state and then return to the original state
- This is an idealized condition – all real processes are irreversible



## 2.4 Heat Engine

- A device which transforms heat into work is called a heat engine
- This happens in a cyclic process
- Heat engines require a hot reservoir to supply energy ( $Q_H$ ) and a cold reservoir to take in the excess energy ( $Q_C$ )
  - $Q_H$  is defined as positive,  $Q_C$  is negative



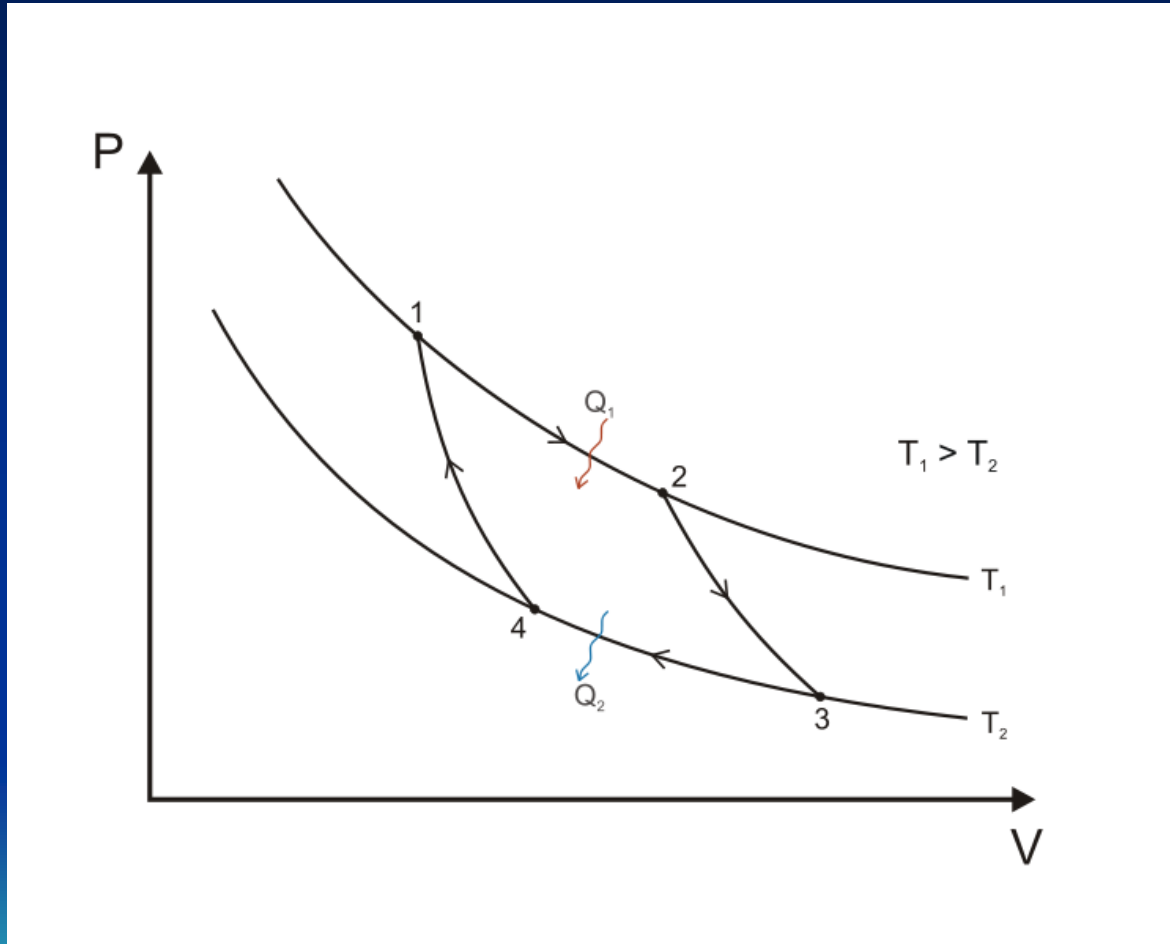


## 2.4.1 Cycles

- It is beyond the scope of this presentation, but here would be a good place to elaborate on:
  - Otto Cycle
  - Diesel Cycle
  - Carnot Cycle
    - Avoid all irreversible processes while adhering to the 2<sup>nd</sup> Law (isothermal and adiabatic only)



# 2.4.2 The Carnot Cycle



## 2.4.2.1 Carnot explained

- Curve A (1  $\rightarrow$  2): Isothermal expansion at  $T_H$ 
  - Work done *by* the gas
- Curve B (2  $\rightarrow$  3): Adiabatic expansion
  - Work done *by* the gas
- Curve C (3  $\rightarrow$  4): Isothermal compression at  $T_C$ 
  - Work done *on* the gas
- Curve D (4  $\rightarrow$  1): Adiabatic compression
  - Work done *on* the gas



## 2.4.2.2 Area under PV curve

- The area under the PV curve represents the quantity of work done in a cycle
- When the curve goes right to left, the work is negative
- The area enclosed by the four curves represents the net work done by the engine in one cycle



## 2.5 Engine Efficiency

- The thermal efficiency of a heat engine is
$$e = 1 - Q_C/Q_H$$
- The “engine” statement of the 2<sup>nd</sup> Law:
  - it is impossible for any system to have an efficiency of 100% ( $e = 1$ ) [Kelvin’s statement]
- Another statement of the 2<sup>nd</sup> Law:
  - It is impossible for any process to have as its sole result the transfer of heat from a cooler object to a warmer object [Clausius’s statement]



## 2.6 Practical Uses

- Automobile engines, refrigerators, and air conditioners all work on the principles laid out by the 2<sup>nd</sup> Law of Thermodynamics
- Ever wonder why you can't cool your kitchen in the hot summer by leaving the refrigerator door open?
  - Feel the air coming off the back - you heat the air outside to cool the air inside
  - See, you can't break even!



## 3.0 You can't get out (3<sup>rd</sup> Law)

- No system can reach absolute zero
- This is one reason we use the Kelvin temperature scale. Not only is the internal energy proportional to temperature, but you never have to worry about dividing by zero in an equation!
- There is no formula associated with the 3<sup>rd</sup> Law of Thermodynamics



# 3.1 Implications of 3<sup>rd</sup> Law

- MIT researchers achieved 450 picokelvin in 2003 (less than  $\frac{1}{2}$  of one billionth!)
- Molecules near these temperatures have been called the fifth state of matter:  
*Bose-Einstein Condensates*
  - Awesome things like super-fluidity and super-conductivity happen at these temperatures
  - Exciting frontier of research





# 4.0 The Zeroth Law

- The First and Second Laws were well entrenched when an additional Law was recognized (couldn't renumber the 1<sup>st</sup> and 2<sup>nd</sup> Laws)
- If objects A and B are each in thermal equilibrium with object C, then A and B are in thermal equilibrium with each other
- Allows us to define temperature relative to an established standard

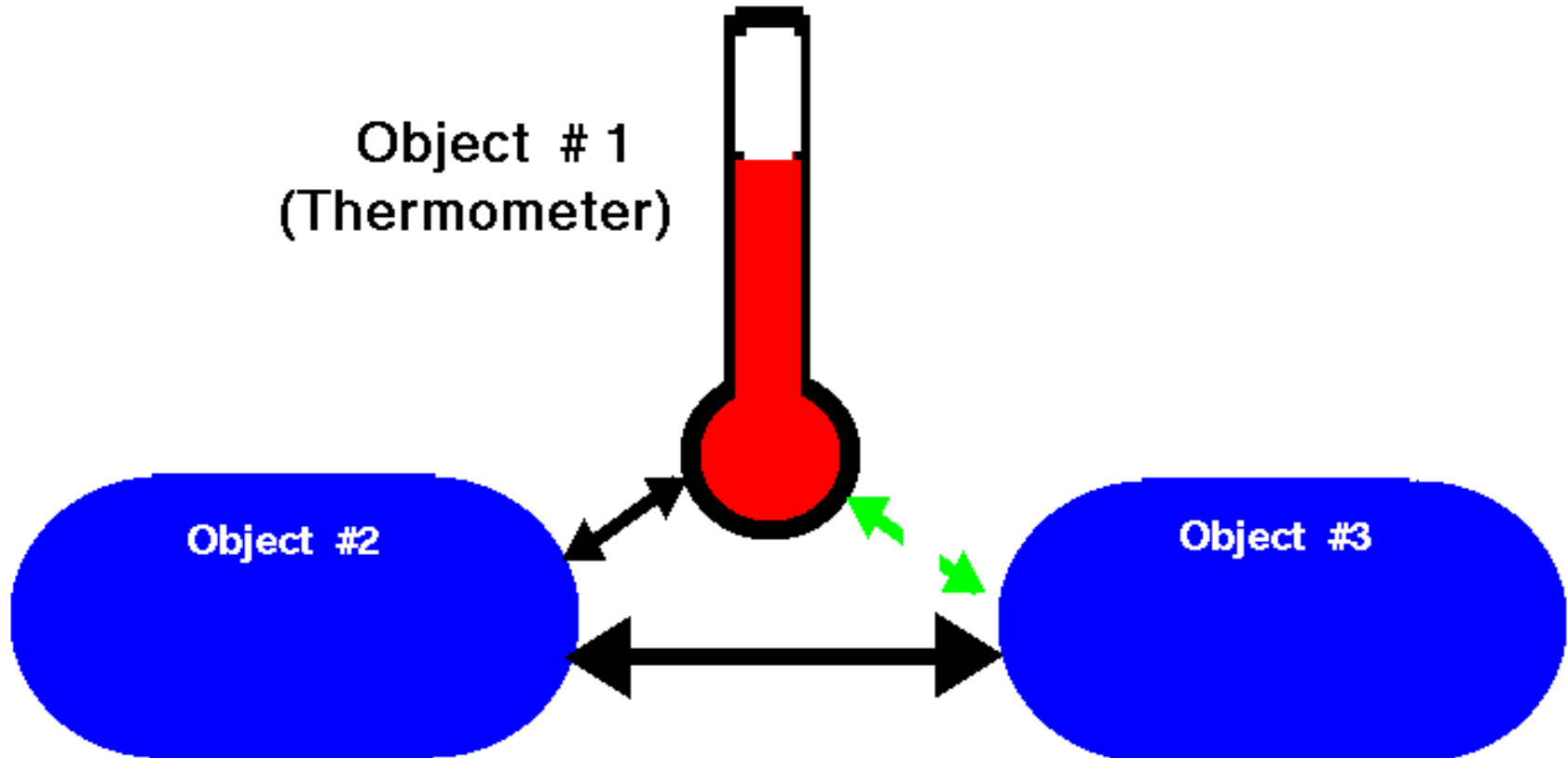




# Thermodynamic Equilibrium

(Zeroth Law)

Glenn  
Research  
Center



When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

**Objects in thermodynamic equilibrium have the same temperature.**

# 4.1 Temperature Standards

- See Heat versus Temperature slides for a discussion of these two concepts, and the misconceptions surrounding them
  - Heat is energy transfer
  - Temperature is proportional to internal energy
  - Fahrenheit, Celsius, and Kelvin temp scales

