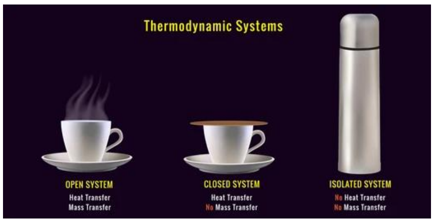
Fundamentals of Thermodynamics

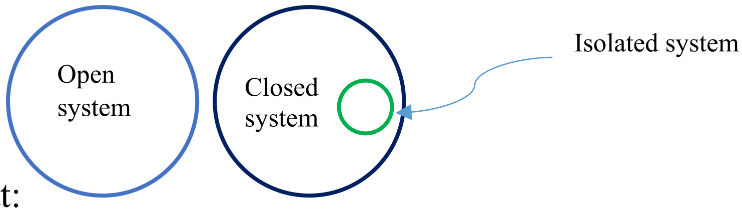
Lecture 3. Thermodynamic Systems and Types of Energy

3.1 Thermodynamic Systems

- A system is some identifiable collection of matter and or energy. Examples of systems are: (A parcel of air, a glass of water, an ice cube, the entire atmosphere, the entire Earth and atmosphere, the Universe.
- An *open system* is a system that exchanges matter with its surroundings. Examples of open systems are:
- A glass of water with no lid, allowing evaporation into the air above it,
- An internal combustion engine, since it gains matter through the intake valves and loses matter through the exhaust manifold.

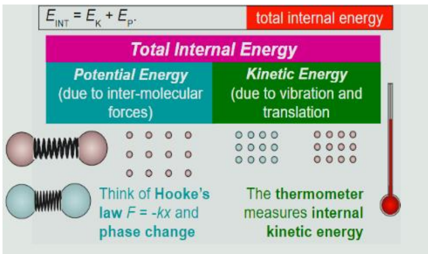


- A *closed system* is a system that does not exchange matter with its surroundings. Examples would be:
- A glass of water with a lid,
- A sealed soda can,
- the inside of a Thermos bottle with the top screwed on,
- An *isolated* system is a system that does not exchange any kind of matter or energy with its surroundings. Examples would be:
- The inside of a ThermosTM bottle with the top screwed on (assuming it was perfectly insulated).
- The relationship between open, closed, and isolated systems can be illustrated using a Venn diagram.



- From this diagram we see that:
- The set of all open systems does not intersect the set of all closed systems. Every system is either open or closed.
- The set of all isolated systems is a subset of the set of all closed systems.
- In plain language, we can infer the following:
- Any isolated system is also a closed system, but a closed system is not necessarily an isolated system.
- An open system cannot be an isolated system.
- Any matter or energy that is not part of the system is considered to be part of the *surroundings* or *environment.*

3.2 Types of Energy



- Potential energy (energy stored in object due to its position, shape, or condition), which can be due to:
  - Gravitational field (PE = mgh),
  - Spring or elastic band, molecular bonds.
- Kinetic energy (energy of motion) which include:
  - Motion of bodies (KE = ½ mv^2),
  - Motion of individual molecules in a body
- Thermal energy- Sum of the kinetic energy of all the molecules in a substance.
- Internal energy- The sum of the thermal energy and any potential energy due to the forces between the molecules of a substance.
- The thermometer measures internal kinetic energy (not internal potential energy)
- Einstein's theory of special relativity established the equivalence of energy and mass, via $E = mc^2$, so that mass is also a form of energy.

3.3 State Variables and the Fundamental Equation

- The state of a system is defined by the position and momentum of every piece of matter in the system.
- For a cubic meter of air at sea level this requires the knowledge of the position and momentum of every 2.56×10^{25} molecules in the volume!
- It is impossible to measure or know the state of the system as defined above. Therefore, we content ourselves with knowing something about the "average" or macroscopic properties of the system as a whole. This is what the subject of thermodynamics attempts to do.
- The thermodynamic state of a simple system in thermodynamic equilibrium is completely characterized by specifying the internal energy (U), volume (V), and the number of moles, n_i, of each of its components.
- Example: If the system consists of a closed container of liquid water and water vapor, then there are four state variables: U, V, n_{liquid}, and n_{vapor}.
- The *fundamental equation* relates the entropy (another state variable denoted as *S*) to *U, V* and n_i, as

$$S = f(U, V, n_i) \qquad (1)$$

Equation (1) says that if U, V, and n_i, are known, then the entropy, S, can be found. Knowledge of the fundamental equation implies complete knowledge about the thermodynamic state of the system.

- S, U, V, and n_i are referred to as <u>state variables</u>, because they describe the thermodynamic state of the system.
- If the system is not in thermodynamic equilibrium, then additional variables are needed to describe the thermodynamic state of the system. We will confine ourselves mostly to systems in equilibrium.

- The fundamental equation, (1), can also be written as

$$U = f(S, V, n_i) \qquad (2)$$

where the only difference between Eqs. (1) and (2) is whether U or S are independent or dependent variables.
- *U, V*, and n_i are not the only possible state variables. Other state variables can be derived from U, S, V, n_i, and their derivatives, via equations called equations of state.
  - Other state variables we will use will include pressure (p), mass (m), density (ρ), temperature (T), enthalpy (H), etc.

3.4 Intensive Versus Extensive Variables

- An ***intensive property*** is one that does not depend on how much substance is present.
- Temperature is an example of an intensive property. If two identical masses are at the same temperature and are added together, the temperature remains the same even though the mass is doubled.
- An ***extensive property*** depends on how much substance is present.
- Internal energy is an example of an extensive property. If the two identical masses are added together there is twice as much internal energy.

Intensive property	Pressure	Temperature	Density	Concentration	Melting point	Boiling point	Surface tension	Viscosity, etc.
Extensive property	Mass	enthalpy	Volume	Heat capacity	Internal energy	entropy	Helmholtz energy	Gibbs energy, etc.

- There are two ways to convert an extensive property into an intensive property.
- Divide by the mass. The result is a property that is normalized by the mass. We add the term specific to indicate that we've divided by the mass. For example, the specific internal energy u is defined as U/m.
- Divide by the number of moles. The result is a property that is normalized by the number of moles present. We add the term molar specific to indicate we've divided by the number of moles. For example, the molar specific internal energy, u_m, is defined as U/n.
- In general, extensive properties are denoted using upper-case letters, while intensive properties are denoted using lower-case letters. However, there are exceptions, including *one notable exception*: Temperature is denoted using upper-case T, even though it is an intensive property.

3.5 Transformations

- A system that moves from one equilibrium state to another will experience a change in state variables.
- Initial and final equilibrium states can be represented on a thermodynamic diagram.
  - Note that only equilibrium states of a closed system can be represented on a 2-dimensional thermodynamic diagram. Why is this?
  - There are an infinite number of paths on the diagram by which the system can be transformed from one equilibrium state to another. However, regardless of which path is taken, the change in the state variables will be the same between the two points.
- We can express this property of state variables mathematically in two ways:
  - The change in any of the state variables (say U) doesn't depend on the path of the system on a thermodynamic diagram. It only depends on the endpoints.

$$\int_a^b dU = U(b) - U(a)$$

  - The integral of a state variable around a closed path is zero.

$$\oint dU = 0$$

- Mathematically, this means that differentials of state variables are *exact differentials.*
  - In order to be a state variable, the differential of the variable must be exact.

3.6 Reversible and Irreversible Processes

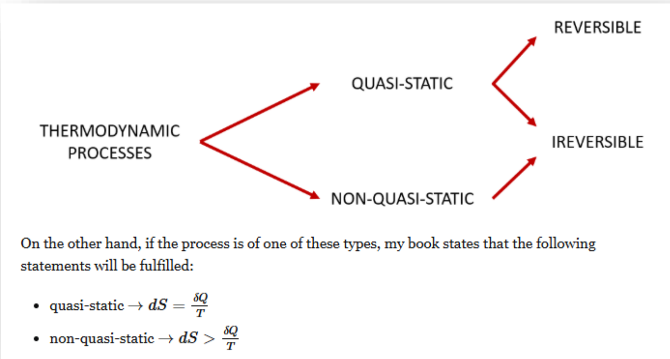
- A quasi-static process is a process that proceeds through a sequence of equilibrium states that are spaced infinitesimally close together.
- A quasi-static process is almost always nearly in equilibrium. It is not in equilibrium between successive equilibrium states, but since the equilibrium states are infinitesimally close, the time spent out of equilibrium is very small.
- A quasi-static process must proceed infinitesimally slow, so that the system is always nearly in equilibrium.
- Each equilibrium state can be represented on a thermodynamic diagram, and since they are infinitesimally close, a quasi-static process would appear as a path or curve on the thermodynamic diagram.
- However, if the curve is magnified, it would be apparent that it is not continuous, but consists of a series of infinitesimally spaced dots.
- A *reversible* process is a quasi-static in which the system is always in equilibrium, so the curve on the thermodynamic diagram is continuous, even when magnified.
- For a reversible process, at any point the transformation can be stopped and then made to proceed in the exact opposite direction.

- An irreversible process is a process (quasi-static or not) that cannot be reversed. Examples of irreversible processes are:
  (1) Free expansion of a gas.
  (2) Mixing of two gasses.
- Note the following rules:
  - All reversible processes are also quasi-static processes.
  - Not all quasi-static processes are reversible processes.
  - An irreversible process may also be quasi-static.
- No real processes are truly quasi-static or truly reversible.
  - We often assume, however, that some real processes are quasi-static or reversible because it makes doing thermodynamics so much easier, and the errors are often not significant.

A reversible process is a theoretical, ideal process that can be perfectly reversed without leaving any trace on the universe, meaning no entropy is generated.

A **quasi-static process** is a hypothetical, infinitely slow process where all intermediate states are in equilibrium, but it is not necessarily reversible because energy-dissipating effects like friction can still occur.

Irreversible processes are real-world processes that cannot be reversed to their exact initial state without changing the surroundings, due to energy loss and entropy generation



Homework:

1. Is thermodynamic concerned with macroscopic or microscopic features?
2. What is mole?
3. Why state variables have exact differentials?