Chapter 1: 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 (\( m/s^2 \)), 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 1-1: Standard prefixes in SI units.

<table>
<thead>
<tr>
<th>MULTIPLE</th>
<th>( 10^0 )</th>
<th>( 10^1 )</th>
<th>( 10^2 )</th>
<th>( 10^3 )</th>
<th>( 10^4 )</th>
<th>( 10^5 )</th>
<th>( 10^6 )</th>
<th>( 10^7 )</th>
<th>( 10^8 )</th>
<th>( 10^9 )</th>
<th>( 10^{10} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREFIX</td>
<td>tetra, T</td>
<td>giga, G</td>
<td>mega, M</td>
<td>kilo, k</td>
<td>centi, c</td>
<td>mili, m</td>
<td>micro, ( \mu )</td>
<td>nano, n</td>
<td>pico, p</td>
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</table>

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Majid Bahrami
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 mW/mm² by the manufacturer. Convert this to W/m².

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

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.

**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.

![Diagram of closed system](image)

Fig. 1-2: Closed system, mass cannot cross the boundaries, but energy can.

![Diagram of control volume](image)

Fig. 1-3: 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 posses 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.
Energy as a whole WRT some outside reference, and changes with velocity and elevation to a reference.

**Macroscopic**

- **Kinetic**
  - $KE = \frac{1}{2}mv^2$

- **Potential**
  - $PE = mgh$

**Microscopic**

- **Sensible**
  - Sum of translational, vibrational, rotational. Higher at higher temperatures.

- **Latent**
  - Inter-molecular (phase change), interatomic bonds

- **Chemical**
  - Bonds within nucleolus of atoms

- **Atomic**
  - Related to molecular structure and degree of molecular activity

The summation of all microscopic energies is called internal energy, $U$. The total energy is:

$$E = U + KE + PE$$

(kJ)
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 ($v=V/m$).

![Extensive and intensive properties](image)

**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**.

![Process path](image)

**Fig. 1-6:** 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.

\[
\text{Pressure} = \frac{\text{Force}}{\text{Area}} = \frac{N}{m^2} \equiv Pa
\]

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.

\[
P = \frac{\text{Weight of liquid}}{\text{Area}}
\]

\[
P = \frac{mg}{A} = \frac{\rho Ahg}{A}
\]

\[
P = \rho gh
\]

Fig. 1-8: 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. 

\[ P_{\text{gauge}} = P_{\text{abs}} - P_{\text{atm}} \quad P > P_{\text{atm}} \]

\[ P_{\text{vac}} = P_{\text{atm}} - P_{\text{abs}} \quad P < P_{\text{atm}} \]

In thermodynamics calculations, always use *absolute pressure*. Most pressure measuring devices are calibrated to read zero in the atmosphere (they measure \( P_{\text{gauge}} \) or \( P_{\text{vac}} \)). 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. 1-9**: Absolute, gauge, and vacuum pressures.

**Fig. 1-10**: Basic manometer, \( P_2 = P_1 \).
\[ P_1 = P_{\text{atm}} + \rho gh \quad (\text{kPa}) \]

*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.

**Example 2: Pressure**

The piston of a cylinder-piston device has a mass of 60 kg and a cross-sectional area of 0.04 m², as shown in Fig. 1-12. The depth of the liquid in the cylinder is 1.8 m and has a density of 1558 kg/m³. The local atmospheric pressure is 0.97 bar, and the gravitational acceleration is 9.8 m/s². 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.

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

\[ P_{\text{bottom}} = P_{\text{atm}} + \frac{mg}{A} + \rho gh \]
\[ P_{\text{bottom}} = 0.97\text{(bar)} + \left( \frac{60\text{kg}\times 9.8\text{ m/s}^2}{0.04\text{ m}^2} + \left( 1558\text{ kg/m}^3 \times 9.8\text{ m/s}^2 \times 1.8\text{ m} \right) \right) \]

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

**Fig. 1-12: Sketch for example 2.**

**Temperature**

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

\[ T_A > T_B \]

\[ T_A < T_B \]

**Fig. 1-13: Heat transfer occurs in the direction of higher-to-lower-temperature.**

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

\textit{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.