Chapter 1

Introduction
The word *thermodynamics* means *heat power* or *power developed from heat*.

In its broader sense, thermodynamics is the science which deals with *transformations of energy of all kinds from one form to another*.

The chemical engineer must be able to cope with a particularly wide variety of problems. Among the most important of these problems are the determination of heat and work requirements for many physical and chemical processes, and the determination of equilibrium conditions for chemical reactions.
Some basic definitions 1/4

✓ **System** - that portion of the universe set aside for study
✓ **Surroundings** - the environment - the rest of the universe
✓ **Boundaries** - walls - separate system from surroundings
✓ **Closed system** - constant mass but energy can cross boundaries
✓ **Open system** - mass and energy can cross boundaries
✓ **Isolated system** - constant mass and energy - rigid, adiabatic boundaries
✓ **Adiabatic walls** - prevent thermal equilibrium - no heat transfer
✓ **Units** - scales used to quantify dimensions (g,, ft, s, K, etc.)
Some basic definitions 2/4

✓ **Measurable properties** - concepts suggested by sense perceptions relating to internal aspects of a system (e.g., $T^o$, $V$, etc.)

✓ **Derived properties** - concepts which arise in analysis through convenience of definition (e.g., enthalpy, chemical potential, etc.)

✓ **Extensive properties** - depend on the extent of the system (volume, mass, internal energy, etc.)

✓ **Intensive properties** - do not depend on extent of the system (e.g., density, specific internal energy, temperature, etc.)

✓ **State (of a system)** - specified by a unique set of intensive properties
Some basic definitions 3/4

✓ **Process** - change in the state of a system –
   ✓ **Isothermal** (const. T),
   ✓ **Isobaric** (const. P),
   ✓ **Isometric** or **isochoric** (const. V),

✓ **Cycle** - series of processes leading back to the initial state of the system

✓ **Temperature** - the property which tells us whether systems are in thermal equilibrium

✓ **Heat** - energy in transition across the boundaries of a system due to a temperature difference
Some basic definitions 4/4

✓ **Work** - energy in transition across the boundaries of a system due to a driving force other than T, and not associated with mass flow

✓ **State functions** - depend only on the state of a system and not its past history (e.g., U, H, S, etc.)

✓ **Path functions** - related to changes in state of a system - depend on how these processes take place (e.g., Q, W)

✓ **Equilibrium** - a state of absolute rest - no tendency to change state - no fluxes of heat, mass, or momentum
Main systems of basic units

- There are three main systems of basic units employed at present in engineering and science:

<table>
<thead>
<tr>
<th>System</th>
<th>Length</th>
<th>Mass</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>SI system</td>
<td>m</td>
<td>kg</td>
<td>s</td>
</tr>
<tr>
<td>English system</td>
<td>ft</td>
<td>lb(_m)</td>
<td>s</td>
</tr>
<tr>
<td>cgs system</td>
<td>cm</td>
<td>g</td>
<td>s</td>
</tr>
</tbody>
</table>

- For the SI system of units, the other standard units (N, J, W, Pa) are derived from these basic quantities.

- In the English system, the pound force (lb\(_f\)) is considered as a basic unit → introduction of the proportionality factor g\(_c\).
Measures of amount or size

- Three measures of amount or size are in common use:

<table>
<thead>
<tr>
<th>Mass, m</th>
<th>Number of moles, n</th>
<th>Total volume, V_t</th>
</tr>
</thead>
</table>

- These measures for a specific system are in direct proportion to one another:

  Mass may be divided by the molecular weight to yield number of moles:

  \[ n = \frac{m}{M} \quad (m = M \times n) \]

  The total volume may be divided by the mass or number of moles of the system to yield *specific* or *molar volume*:

  \[ V \equiv \frac{V_t}{m} \quad V \equiv \frac{V_t}{n} \]
**Intensive and extensive properties**

*Intensive properties* are those which are independent of the size of a system such as temperature, pressure and density.

*Extensive properties* are those whose values depend on the size of the system such as mass, volume and the total energy.

When the system is divided into to equal parts, each part will have the same value of intensive properties as the original system, but half the value of the extensive properties.
Force

- The SI unit of force (F) is *newton* \((N = \text{kg m s}^{-2})\) with:

\[ F = m \cdot a \]

- In the English system, force is treated as an additional independent dimension along with length, time and mass. Its unit is called “the pound force” and the Newton’s law must include a dimensional proportionality constant \((g_c)\):

\[ F = \left(\frac{1}{g_c}\right) \cdot m \cdot a \]

\[ gc = 32,1740 \, \text{lb}_m \cdot \text{ft} \cdot \text{lb}^{-1}_f \cdot \text{s}^{-2} \]

The pound force \(\text{lb}_f\) is equivalent to 4.4482216 N

Weight refers to the force of gravity on a body \((m \cdot g)\) and not to its mass \((m)\)
Temperature

- Temperature is commonly measured with liquid-in-glass thermometers, wherein the liquid expands when heated.
- There are four temperature scales in common use in Chemical Engineering: °C, °F, °R and K.

- The following equations can be used to convert from one scale to another:

  °F = 32 + 1.8 (°C)
  °C = 1/1.8 (°F – 32)
  °R = °F + 459.67
  K = °C + 273.15

**Figure 1.1:** Relations among temperature scales.
Pressure

The pressure $P$ exerted by a fluid on a surface is defined as the normal force exerted by the fluid per unit area of the surface.

$$P = \frac{F}{A}$$

- The primary standard for pressure measurement is the dead weight gauge in which a known force ($F = m*g$) is balanced by fluid pressure acting on a known area ($A$).

- The pressure is also expressed as the equivalent height of a fluid column (by application of the Newton’s law):

$$P = \frac{m*g}{A} = h*\rho*g$$
Work

Work $W$ is performed whenever a force acts through a distance:

\[ dW = F \times dl \]

By convention, work is regarded as positive when the displacement is in the same direction as the applied force and negative when they are in the opposite direction.

Example: compression or expansion of a fluid in a cylinder.

\[ dW = F \times dl = - P \times A \times d(V_t / A) \]