Lecture 1 is devoted to establishing building blocks for discussing thermodynamics. In addition, the equation of state will be established.

I. Building blocks for thermodynamics
   A. Dimensions, units, etc.

<table>
<thead>
<tr>
<th>Dimension</th>
<th>Units (MKS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mass M</td>
<td>kg</td>
</tr>
<tr>
<td>length L</td>
<td>m</td>
</tr>
<tr>
<td>time T</td>
<td>s</td>
</tr>
<tr>
<td>acceleration L T^-2</td>
<td>m s^-2</td>
</tr>
<tr>
<td>density M L^-3</td>
<td>kg m^-3</td>
</tr>
<tr>
<td>force M L T^-2</td>
<td>kg m s^-2 (N)</td>
</tr>
<tr>
<td>pressure N M^-2</td>
<td>kg m^-1 s^-2</td>
</tr>
<tr>
<td>energy M L^2 T^-2</td>
<td>kg m^2 s^-2 (J)</td>
</tr>
<tr>
<td>specific energy L^2 T^-2</td>
<td>m^2 s^-2 (J kg^-1)</td>
</tr>
<tr>
<td>power M L^2 T^-3 (W)</td>
<td>kg m^2 s^-3 (W)</td>
</tr>
</tbody>
</table>

   a. 1 calorie = 4.1868 J

   b. Avogadro's Number: N = 6.023 x 10^23 molecules/mole
   c. One atomic weight of a substance (atomic, ionic, molecular) has N particles.

   B. Sign convention in thermodynamics.

   1. When a system experiences a gain in some property the sign of that change is positive.
   2. When a system experiences a loss in some property the sign of that change is negative.

   Examples

   a. If a system gains work (W), heat (Q), or a quantity of matter (n; number of moles) a sign is assigned to change, e.g., dW, dQ, dn

   C. Systems

   1. A system is a part of the physical universe confined to a definite space by the boundary that separates it from the rest of the universe.

   a. The surroundings include all matter in the environment (the rest of the universe) that may eventually interact with the system.

   2. Boundaries of a system can be open or closed.

      a. Open system

         i. An open system allows for an exchange of matter and energy with the surroundings or environment (the rest of the universe)

         ii. Most systems are open. Open systems usually are very difficult to study

      b. Closed system

         i. A close system does not exchange matter with the
surroundings or environment
ii. A system is said to be isolated if no matter or energy is
exchanged with the surroundings or environment

D. State parameters and properties
1. A complete description of a system is given by its properties or physical
variables that describe the properties. When a system changes the
magnitude of its properties change. A stage in the change is described by
states of constituents including \( V, \rho, p, T, n, \mu, \) magnetic, electrostatic,
gravitational fields.
a. For example, consider a closed system:
   i. Mass and chemical composition define the system
   ii. \( V, \rho, p, T, n, \mu, \) magnetic, electrostatic,
gravitational fields, etc. define the state of the system
2. A phase of a system is defined as a restricted portion of a system that is
homogeneous with respect to all of its properties.
3. Extensive properties:
a. By definition, extensive properties are dependent on the amount
   of mass in a substance (including the bulk or phase of a system).
i. Examples of an extensive properties are the quantity of
   matter (number of moles), volume, energy, heat, entropy,
   position and molar specific heat
   ii. Extensive properties are additive
4. Intensive properties:
a. By definition, intensive properties are independent of the amount
   of mass in a substance (including the bulk or phase of a system).
i. Examples of an intensive properties are temperature \( (T) \),
   pressure \( (p) \), viscosity \( (\nu) \), force, and concentration
   ii. Intensive properties are independent of the extent of bulk or
   phase of a system and therefore are not additive
5. Combinations of Intensive and Extensive properties
i. The work done by compression can be written as
   \[ dW = P \, dV \] where \( P \) is pressure (intensive) and \( V \) is volume
   (extensive)
ii. Similarly, work can be describe by
   \[ dW = f \, dl \] where \( f \) is force (intensive) and \( l \) is position
   (extensive)
iii. And finally, the change in heat content corresponding to
   a change in temperature (intensive) experienced by a mole of
   a system if molar heat capacity \( C \) (extensive) is
   \[ dQ = C \, dT \]

E. Equilibrium of a system
1. Equilibrium and stable equilibrium
a. A system that is isolated from its surroundings is in stable
   thermodynamic equilibrium when its intensive properties are
   constant in time and not sensitive to small perturbations. When
   small changes are made to the intensive properties they return to
   their original values.
i. There are three important forms of equilibrium; thermal,
   mechanical, and chemical.
ii. Note that independence of time is a necessary but it is not
   sufficient for equilibrium.
iii. "The constancy of properties with time should hold for every portion of the system even if we isolate it from the rest of the system and from its surroundings"

2. Unstable equilibrium
   a. A small change in the state of a given system results in large changes in the system from equilibrium.
      i. The simplest analogy is a rock sitting on top of a hill peak, which is then given a small push. A rolls off the hill and will not return spontaneously to the top of the hill.

3. Metastable equilibrium
   a. A system in metastable equilibrium is stable to small changes, and unstable to large changes.
   b. Another example is a room field with H and O in atomic states. A small catalyst will spark a violent, spontaneous reaction.

4. More on Equilibrium...
   a. Departures from 'true' equilibrium may occur in three ways:
      i. mechanical equilibrium
      ii. chemical equilibrium
      iii. thermal equilibrium

5. Thermal contact
   a. Two substances are said to be in thermal contact when they can exchange heat in the absence of macroscopic (as opposed to molecular scale) work.

6. Zero'th Law of Thermodynamics
   a. The Zero'th Law of Thermodynamics states that if two separate substances A and B are not in contact and each is in thermal equilibrium with a third substance C, then A and B are in thermal equilibrium with each other.
      i. If $T_A = T_C$ and $T_B = T_C$ then $T_A = T_B$

F. Reversible transformation
1. A reversible transformation is one in which each state (point) in a system is in equilibrium so that a reversal in the direction of a small change returns the system to its original equilibrium state. (A reversible transformation is one in which each intermediate state in a system is in equilibrium so that a reversal in the direction of a small change returns a system to its original state.)
   a. An example of a reversible transformation is isothermal expansion / compression. There are no dissipative effects (turbulence, friction, electrical resistance) in a reversible transformation.
   b. There are no dissipative effects in a reversible transformation.
      i. e.g., turbulence, friction, electrical resistance.

2. An irreversible transformation is always a transformation accompanied by a dissipative effect.
   a. An example is free expansion of a gas into a vacuum.

3. In an ideal reversible transformation (e.g., isothermal expansion) a continuous graph can be drawn and unique values of $p$ and $V$ can be assigned.

4. In an irreversible system, no graph can be drawn; no unique values can be assigned to values describing the system.
   a. For example, in a piston system, the pressure immediately behind the piston is less than the average in the medium as a whole because of the time lag in stress. Thus, as was said above, no unique value can be assigned as the pressure of the system.
II. Macroscopic description of an ideal gas
A. The Gas Laws are concerned with the mass $m$ of a gas confined to a volume $V$ at pressure $P$ and temperature $T$.
   1. Pressure is defined as the net force of the molecules exerted per unit area.
   2. Temperature is a measure of the mean kinetic energy of the molecules in the gas $\frac{1}{2} m v^2$ where $m$ is mass and $v$ is velocity. If two gasses have equal temperatures, the one with more massive molecules will have, on average, slower moving molecules. At a temperature of absolute zero, $v = 0$.

B. In general the gas laws are quite complicated. However, if the gas is maintained at very low density (in addition, temperature is sufficiently high and pressure is sufficiently low) then the gas laws can be simplified greatly. An ideal gas assumes that intermolecular attractive forces are negligible. Most gasses at room temperature essentially are ideal gasses.

C. Boyle's Law: Given an ideal gas system with a constant temperature and fixed mass, a change in pressure or volume in the system will result in a changes of pressure and volume such that $PV = f(T)$.

D. Charles' Law: Given an ideal gas system with a constant pressure and fixed mass, the temperature increase and the relative volume increase occur in approximately the same proportion (the approximation owes to the coefficient of expansion of the gas).
   1. Charles' also deduced that given an ideal gas system with a constant volume and fixed mass, the temperature increase and the relative pressure increase occur in approximately the same proportion (the approximation owes to the coefficient of expansion of the gas).

E. Gas Law (Equation of State)
   1. Start with a homogeneous mix of constant composition
      a. $\text{H}_2$ gas.
         i. Mass of 1 kg of $\text{H}_2$ used to define system
      b. The state of the gas may be specified by 2 of 3 variables
         i. $p$, $T$, $V$ are the state variables
         ii. Only two of $p$, $T$, $V$, the state variables, are independent
         iii. $U$, $S$, $H$ (IE, Entropy, Enthalpy) are state functions:
              i.e.; functions of state variables.
         iv. State functions are perfect differentials.
      c. Laboratory experiments suggested that $p$, $T$, $V$ could be related by 'equation of state'.
   2. The equation of state for ideal behavior of gasses (gasses for which molecules are independent of each other; i.e., no attractive forces exist between each other).
      a. $pV = nR^* T = mR^* T/M = mRT$
         i. $n =$ number of moles $= m / M$
         ii. $R^* =$ universal gas constant (8.3143 J mol$^{-1}$ K$^{-1}$)
         iii. $M =$ molecular weight (kg kmol$^{-1}$)
         iv. $R = R^*/M =$ specific gas constant
         v. $m =$ mass of gas
3. Define density as $\rho = \frac{m}{V}$
   a. Equation of state becomes...
      $$pV = mRT$$
      $$p = \frac{(m/V)}{RT} = \rho RT$$
   b. for 1 kg of an ideal gas, specific volume (a) is defined as
      i. $\rho = 1/\alpha$

4. Define the number of moles in a gas as $n = \frac{m}{M} = \text{mass} / (\text{mass/mole})$

5. The universal gas constant $R^*$ is from Avogadro's hypothesis.
   a. Gases containing the same number of molecules occupy the same $V$
      at the same $p$ and $T$
   b. This results in
      $$pV = nR^*T$$

6. Van der waals equation describes behavior of real gases from semi-empirical relations
   $$(p+a V^{-2}) (V-b) = R^*T$$  (for 1 mol)
   a. $a$ and $b$ are constants for each of the gases

7. Gas Law in terms of individual molecules.
   a. Boltzmann's Constant - universal gas constant for molecules
      $$k = \frac{R^*}{N_A} = \frac{8314 \text{ J K}^{-1} \text{ kmol}^{-1}}{6.022 \times 10^{23} \text{ kmol}^{-1}} = 1.381 \times 10^{-23} \text{ J K}^{-1}$$
   b. The equation of state is,
      i. $p = n_0 k T$
      ii. $n_0$ = number molecules / unit volume
      iii. Gas Law applied to molecules.

F. Mixtures of gases
1. Partial pressure
   a. The pressure $p_i$ of the $i$th gas is the pressure it would have if it
      alone occupied the volume at the same temperature $T$.

2. Total pressure. (Dalton's Law)
   For an ideal gas, the total pressure is equal to the sum of the pressures
   exerted by each of its constituents considered separately.
   $$p = \sum p_i$$

3. The Gas Law for each gas in a mixture is
   $$p_i V = n_i R^* T = m_i R_i T, \text{ where } M_i = \frac{m_i}{n_i} = \frac{R^*}{R_i}$$

4. The Gas Law for the gas as a whole is
   $$pV = \left( \sum n_i \right) R^* T = \left( \sum m_i R_i \right) T$$
   a. The total moles number of moles
      $$n = \sum n_i$$

5. The mean 'specific gas constant' and mean molecular weight are
   $$\bar{R} = \frac{\sum m_i R_i}{\sum m_i} \text{ and } \bar{M} = \frac{\sum n_i M_i}{\sum n_i}$$

6. The mole fraction of each constituent of a gas mixture is
   $$N_i = \frac{n_i}{\sum n_i}$$
G. Atmospheric composition
1. Major constituents

<table>
<thead>
<tr>
<th></th>
<th>M</th>
<th>% V</th>
<th>%M</th>
<th>R (J/Kg/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2</td>
<td>28.013</td>
<td>0.7809</td>
<td>0.7552</td>
<td>296.80</td>
</tr>
<tr>
<td>O2</td>
<td>31.999</td>
<td>0.2095</td>
<td>0.2315</td>
<td>259.83</td>
</tr>
<tr>
<td>Ar</td>
<td>39.948</td>
<td>0.0093</td>
<td>0.0128</td>
<td>208.13</td>
</tr>
<tr>
<td>CO2</td>
<td>44.010</td>
<td>0.0030</td>
<td>0.0005</td>
<td>188.92</td>
</tr>
<tr>
<td>H2O</td>
<td>18.016</td>
<td>0.0-4.0</td>
<td>0.0-4.0</td>
<td>461.42</td>
</tr>
</tbody>
</table>

a. Mean gas constant for dry air: R_d = 287.05 J/kg/K
b. Mean M for dry air: M_d = 28.964 g/mol