Honors Classical Physics I

PHY141
Lecture 36
Volume & Temperature
Heat (Flow)
The Ideal Gas Law
H6B Up and down-stream
H6B Beam Line – setting up
Substances exist in three phases:
- solid,
- liquid,
- gas/vapor

Changing volume $V$, pressure $p$, and or temperature $T$ allows us to “scan” the whole phase space, which is a surface in 3-DIMENSIONAL space!
Kinetic Gas Theory

Derivation of $pV=\rho RT$: Assume a gas of $nN_A$ molecules, all of mass $m$. Assume these to be point-like, and colliding elastically with the walls of a box with $V=L^3$, and with each other...

- the molecules bounce off the wall (wall’s mass $\gg m$) and thereby exert a minute force...

- Let’s calculate: consider a molecule $i$ with velocity $v_i$; then the force on the molecule by the wall is:

$$F_{xi} = \frac{\Delta p_{xi}}{\Delta t} = m \frac{\Delta v_{xi}}{\Delta t} = m \frac{(-v_{xi}) - v_{xi}}{\Delta t} = -\frac{2mv_{xi}}{\Delta t}$$

- the reaction force on the wall is thus $2mv_{xi}/\Delta t$.

- We find the TIME-AVERAGED force on the wall when we take $\Delta t$ as the time between successive collisions with the (same) wall:

$$\Delta t = 2L_x/v_{xi} \Rightarrow F_{xi} = \frac{mv_{xi}^2}{L_x}$$

- there are $nN_A$ molecules in the volume; for each molecule: $v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2$, but the averages of the squared velocity components of the molecules are equal:

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \equiv \overline{3v_x^2}$$

- the total force by $nN_A$ molecules is:

$$F_x = nN_A \frac{mv_{ix}^2}{L} = nN_A \frac{mv_{ix}^2}{3L} \Rightarrow p = \frac{F_x}{L^2} = nN_A \frac{mv_{ix}^2}{3L^3} \Rightarrow pV = nN_A \frac{mv_{ix}^2}{3} = n\frac{2}{3} N_A K$$
Kinetic Gas Theory

Using $F = dp/dt$ and $pV = nRT$:

$$pV = \frac{F}{L^2} L^3 = nN_A \frac{2mv^2}{\Delta t} = nN_A \frac{2mv^2}{2L/v_x} = nN_A \frac{mv_x^2}{v_x} = \frac{2}{3} nN_A \overline{K} = nRT \Rightarrow \overline{K} = \frac{3}{2} \frac{R}{N_A} T = \frac{3}{2} kT$$

- i.e. the molecules’ average kinetic energy is proportional to the (Kelvin) temperature, with proportionality constant $k_B \equiv R/N_A = 1.38 \times 10^{-23}$ J/K (Boltzmann constant)

In terms of molecular speed:

$$\overline{K} = \frac{1}{2} mv^2 = \frac{3}{2} kT \Rightarrow \sqrt{3kT/m} = \sqrt{v^2} = v_{\text{root-mean-square}} \equiv v_{rms}$$

- e.g. air at room temperature:

$$m(O_2) = \frac{32 \text{ g/mol}}{6.022 \times 10^{23} \text{ /mol}} = 5.31 \times 10^{-26} \text{ kg} \Rightarrow v_{rms}(O_2) = \sqrt{\frac{3kT}{m}} = 478 \text{ m/s}$$

Molecular speeds cover a RANGE of values, which can be DERIVED from statistical principles:

$$f(v) = \frac{8\pi}{m} \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} Ke^{\frac{k}{kT}}$$

(Maxwell speed distribution). The most probable value:

$$v_{mp} = \sqrt{2kT/m}$$
Molecular Origin of Specific Heat

The heat added to a substance generally raises its temperature (if the phase doesn’t change!):

\[ dQ = m \cdot c \cdot dT = nM \cdot c \cdot dT = nC_V \cdot dT, \quad (M \text{ is the mass per mole, in kg}) \]

- where \( c \) is the “SPECIFIC HEAT CAPACITY”, i.e. heat required per unit mass (kg) and per unit temperature change (Kelvin or °C)
- where \( C_V \) is the “MOLAR HEAT CAPACITY” at CONSTANT VOLUME, i.e. the specific heat on a molar basis:

\[ C_V = \frac{1}{n} \frac{dQ}{dT} = \frac{d}{dT} \left( N_A \cdot \frac{3}{2} kT \right) = \frac{3}{2} kN_A = \frac{3}{2} R = 12.47 \text{ J/K/mol} \]

- Checking with actual data on Gases:
  - monatomic: \( C_V(\text{He}) = 12.47, \ C_V(\text{Ar}) = 12.47, \ldots \)
  - di-atomic: \( C_V(\text{H}_2) = 20.42, \ C_V(\text{N}_2) = 20.76, \ldots \)
  - tri-atomic: \( C_V(\text{CO}_2) = 28.46, \ C_V(\text{H}_2\text{S}) = 25.95, \ldots \)

So, what is this? \( \Rightarrow \) Heat energy also going into rotations and vibrations!

- **EQUIPARTITION THEOREM**: each molecule’s “DEGREE OF FREEDOM” (DoF) absorbs on average \( dQ/dT = \frac{1}{2} k \) of energy/K, e.g.:
  - translations: 3 DoF \( \Rightarrow \frac{3}{2} k \Rightarrow C_V = \frac{3}{2} R = 12.47 \)
  - rotations: di-atomic molecules +2 DoF \( \Rightarrow +\frac{2}{2} k \Rightarrow C_V = \frac{5}{2} R = 20.78; \)
  - vibrations (only at high \( T \)): di-atoms: + 2 DoF (SHM kinetic + potential)
Molecular Origin of the Heat Capacity

Molar Heat capacity $C_V$ for **Solids**: consider only *monatomic* solids

- the translational and rotational DoF don’t contribute, only vibrations
  $\Rightarrow +6$ DoF (3 directions for kinetic and potential energies) $\Rightarrow C_V = 3R$
  $= 25.0 \text{ J/K}$
- explains the empirical rule by Dulong and Petit

For **CALORIMETRIC** calculations involving **liquids** and **solids**, the **SPECIFIC** Heat capacity $c$ (as opposed to the **MOLAR** Heat capacity $C_V$) is used more often:

- defined in: $Q = mc\Delta T$
- no subscript “$V$” because liquids and solids do not expand appreciably when heated ...
- units: $[c] = \text{J/kg/K}$