

5.5.5 Gas Constant and the Heat Capacities

Heat capacity is related to the energy required to heat a gas. Heat capacity of a gas is defined as the energy required to increase the temperature of unit mass of the gas by one degree.

Molar heat capacity is defined as the energy needed to increase the temperature of one mole of the gas by one degree. In SI system its unit is J/(kmol K).

The kinetic energy of molecules in one mole of an ideal gas is

$$E_{k,m} = \frac{3}{2} RT$$

If we increase the temperature of the gas by 1K, we would increase the kinetic of the molecules by an amount equal to the molar heat capacity.

$$E_{k,m} \text{ at } (T+1) \text{ temp.} = (3/2) R(T+1)$$

The increase in kinetic energy with 1K increase in temperature is

$$\Delta E_{k,m} = \frac{3}{2} R(T+1) - \frac{3}{2} RT = \frac{3}{2} R$$

Therefore the molar specific heat of an ideal gas, assuming that all of the energy goes toward increasing the kinetic energy of molecules, is (3/2)R.

The assumption that all of the energy goes toward increasing the kinetic energy is not always satisfied. There are a variety of ways of heating a gas. Two cases of special interest are:

At constant volume: The gas is not allowed to expand or contract, i.e. it is kept in a vessel of constant volume. Heat capacity for a constant volume heating is

$$C_v = \left(\frac{\partial Q}{\partial T} \right)_v \text{ i.e. the amount of heat needed per unit increase in temperature.}$$

Since the volume of the gas does not change, there is no mechanical work done in the process. Hence in this case all of the energy goes toward increasing the kinetic energy of the molecules. Therefore,

$$C_v = (3/2) R$$

At constant pressure: The gas is heated in a container that expands or contracts to keep the pressure constant. The container could be a cylinder equipped with a piston with constant force acting on the other side or a perfectly elastic balloon.

For constant pressure heating, the heat capacity is

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p$$

When a gas is heated at constant pressure, its volume increases with increase in temperature. It means some mechanical work is being done during the process. A part of the energy is used for the mechanical work while the rest goes toward increasing the kinetic energy of the molecules. Hence for estimating the specific heat at constant pressure, we have to use two terms: one for the increase in kinetic energy and the other for the amount of work done. We have already seen what is needed for increasing the kinetic energy. Let us now calculate the energy requirements for the accompanying work that is done in the expansion.

$$\text{Work} = \text{Force} \times \text{Distance} = (P \times A) \times \text{Distance} = P \times (A \times \text{Distance}) = P \times \Delta V$$

$$P \times \Delta V = P(V_{\text{new}} - V_{\text{old}}) = PV_{\text{new}} - PV_{\text{old}} = R(T+1) - RT = R$$

Therefore the mechanical work in increasing the temperature of one mole of an ideal gas at constant pressure by 1 K is equal to R. We still need 3/2R of energy to increase the kinetic energy.

Hence $C_p = C_v + R = (3/2) R + R = (5/2) R$. Also,

$$C_p - C_v = R \text{ and}$$

$$C_p/C_v = (2.5 R)/(1.5 R) = 1.667$$

5.5.6 Mean Free Path and Collision of Molecules

In deriving the ideal gas law from simple kinetic theory, we did not mention anything about the collisions between the molecules. However, in reality a molecule of gas collides with other molecules quite frequently. There are two justifications for neglecting the collisions.

- (1) The simple kinetic theory considers molecules to have zero volume, therefore collisions are not very likely.*
- (2) The kinetic energy and momentum are conserved in collisions, therefore, the collisions do not affect the average velocity of molecules.*

The average distance a molecule travels between collisions is a useful parameter. Its value can be estimated from the simple kinetic theory. Let us first define a few new terms.

Mean Free Path (denoted by λ) is defined as "the average distance a molecule travels between two successive collisions with other molecules"

Collision Diameter (denoted by σ) is defines as "the distance between the centres of two colliding molecules at which the repulsive force between the two becomes large enough to cause a reversal of their momentum."

For hard sphere model of molecules, σ is equal to the molecular diameter.

An expression for Mean Free Path can be derived using a simple model involving spherical molecules.

Assume that all but one molecule in a gas are stationary. That is only one molecule is moving while all others are frozen in space.

If this molecule moves in a straight line, then for it to collide with another molecule, the centre of other molecule must lie inside a cylinder of diameter 2σ around the line of its movement. The volume of this cylinder corresponding to a given length of travel 'L' is $\pi\sigma^2 L$.

Now if there are ρ_N number of stationary molecules per unit volume, then the number of collisions for the moving molecule

$$= \pi\sigma^2 L \cdot \rho_N$$

$$\text{Mean Free Path} = \frac{\text{Dist. Travelled by the moving molecule}}{\text{no. of collisions}}$$

$$\lambda = \frac{L}{\pi\sigma^2 L \cdot \rho_N} = \frac{1}{\pi\sigma^2 \cdot \rho_N}$$

Of course this is a highly simplified scenario! In reality the other molecules are moving and when that is taken into account, the correct value of λ becomes

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \rho_N}$$

A gas molecule, on the average, travels this distance after a collision before it collides with another molecule. It is not the average distance between the molecules at any given time. Now we will what that distance is like. For an ideal gas

$$PV_m = N_A kT$$

or

$$\frac{N_A}{V_m} = \frac{P}{kT}$$

N_A/V_m gives the number of molecules per unit volume, i.e. ρ_N . Therefore, by substituting for ρ_N in the expression for mean free path.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2\rho_N} = \frac{kT}{\sqrt{2}\pi\sigma^2 P}$$

Which shows that the mean free path increases with T and decreases with P.

The inverse of the number density is the effective volume occupied by each molecule in a gas (volume per molecule). It is given by

$$\delta^3 = \frac{1}{\rho_N} = \frac{kT}{P}$$

or

$$\delta = \left[\frac{kT}{P} \right]^{1/3}$$

This gives the mean distance between molecules.

Let us compare the magnitude of these quantities. For air (N_2 or O_2) at 1 atm and 20 °C,

$$\sigma \approx 3 \text{ \AA}$$

$$\delta \approx 30 \text{ \AA}$$

$$\lambda \approx 1000 \text{ \AA}$$

Rate of Molecular Collisions with the Container Walls

Let us say we have a cubical container (a = side of the cube) containing a gas with a number density of ρ_N (i.e. ρ_N molecules per unit volume).

Then the total number of molecules in the cube is $a^3\rho_N$.

Assume that all molecules move in one direction only with an average speed of \bar{c}

Then the number of collisions with the walls for one molecule per unit time is \bar{c}/a collisions per second.

For all molecules the number of collisions per unit time is

$$a^3 \rho_N \bar{c} / a$$

The total surface area of the cube is $6a^2$.

Collision rate per unit area is given by

$$\frac{a^3 \rho_N \bar{c} / a}{6a^2} = \frac{\rho_N \bar{c}}{6}$$

Note that it is independent of a . We had assumed that molecules travel in one direction (perpendicular to the sides) only. But actually they travel randomly in all directions and this produces somewhat more collisions. The actual number of collisions per unit area is

$$\rho_N \frac{\bar{c}}{4}$$

Example Problem 5-4

Methane molecules have a collision diameter of 4.01 \AA . Determine the mean free path for methane molecules at 25°C and 1 atm .

Solution

The Boltzmann's constant k (i.e. R/N_A) = $1.3805 \times 10^{-23} \text{ J/K}$. $T = 298.15 \text{ K}$. $P = 1 \text{ atm}$ or 101325 Pa . When these numbers are substituted into Equation 5.63, the mean free path is given by

$$\lambda = \frac{1.3805 \times 10^{-23} \times 298.15}{\sqrt{2} \times \pi \times (4.01)^2 \times (10^{-10})^2 \times 101 \times 10^3} \text{ m}$$

or $\lambda = 5.7 \times 10^{-8} \text{ m}$ or approximately 570 \AA .