Kinetic Theory

- The ideal gas equation connecting pressure (P), volume (V) and absolute temperature (T) is

  $PV = \mu RT = k_B NT$

  where μ is the number of moles and N is the number of molecules. R and k_B are universal constants.

  $R = 8.314\ J\ mol^{-1}\ K^{-1}$.

  $k_B = R/N_A$

  Real gases satisfy the ideal gas equation only approximately, more so at low pressures and high temperatures.

- In equilibrium, the total energy is equally distributed in all possible energy modes, with each mode having an average energy equal to ½ kBT. This is known as the **law of equipartition of energy**. Accordingly, each translational and rotational degree of freedom of a molecule contributes ½ $k_B T$ to the energy while each vibrational frequency contributes 2 × ½ kBT = kBT , since a vibrational mode has both kinetic and potential energy modes.

- Kinetic theory of an ideal gas gives the relation $P = (1/3)nmv^2$

  where n is number density of molecules, m the mass of the molecule and v^2 is themean of squared speed. Combined with the ideal gas equation it yields a kineticinterpretation of temperature.

  $E = (3/2)\ k_B\ NT$

  $E/N = ½\ m\ v^2 = (3/2)\ k_BT$

- For each atom averageenergy is $3k_BT$. Water molecule has three atoms,two hydrogen and one oxygen. So it has $U = 3 \times 3\ k_BT \times NA = 9\ RT$ and $C = ΔQ/ΔT = ΔU/ΔT = 9R$.

  This is the value observed and the agreementis very good. In the calorie, gram, degree units,water is defined to have unit specific heat. As 1calorie = 4.179 joules and one mole of wateris 18 grams, the heat capacity per mole is ~ 75 J mol^{-1} K^{-1} ~ 9R.

- This tells us that the temperature of a gas is a measure of the average kinetic energyof a molecule, independent of the nature of the gas or molecule. In a mixture of gases ata fixed temperature the heavier molecule has the lower average speed.

  The translational kinetic energy$E = (3/2)\ k_B\ NT$.

  This leads to a relation$PV = (2/3)\ E$.

- The law of equipartition of energy states that if a system is in equilibrium at absolutetemperature T, the total energy is distributed equally in different energy modes of absorption, the energy in each mode being equal to $½\ k_B\ T$. Each translational and rotational degree of freedom corresponds to one energy mode of absorption and has energy $½\ k_B\ T$. Each vibrational frequency has two modes of energy (kinetic and potential) with corresponding energy equal to $2 \times ½\ k_B\ T = k_B\ T$.

- Using the law of equipartition of energy, the molar specific heats of gases can be determined and the values are in agreement with the experimental values of specific heats of several gases. The agreement can be improved by including vibrational modes of motion.

- The mean free path l is the average distance covered by a molecule between two successive collisions:

  $l = 1/(\sqrt{2}\ nd^2)$

Sample Examples

- A vessel contains two nonreactivegases : neon (monatomic) andoxygen (diatomic). The ratio of their partialpressures is 3:2. Estimate the ratio of (i)number of molecules and (ii) mass densityof neon and oxygen in the vessel. Atomicmass of Ne = 20.2 u, molecular mass of O_2= 32.0 u.

  Answer

  Partial pressure of a gas in a mixture isthe pressure it would have for the same volumeand temperature if it alone occupied the vessel.(The total pressure of a mixture of non-reactivegases is the sum of partial pressures due to itsconstituent gases.) Each gas (assumed ideal)obeys the gas law. Since V and T are common tothe two gases, we have P1V = μ 1 RT and P2V =μ2 RT, i.e. (P1/P2) = (μ1 / μ2). Here 1 and 2 referto neon and oxygen respectively. Since (P1/P2) =(3/2) (given), (μ1/ μ2) = 3/2.

  By definition μ1 = (N1/NA) and μ2 = (N2/NA) where N1 and N2 are the number of molecules of 1 and 2, and NA is the Avogadro’s number. Therefore, (N1/N2) = (μ1 / μ2) = 3/2.

(ii) We can also write μ1 = (m1/M1) and μ2 = (m2/M2) where m1 and m2 are the masses of 1 and 2; and M1 and M2 are their molecular masses. (Both m1 and M1; as well as m2 and M2 should be expressed in the same units).
If ρ1 and ρ2 are the mass densities of 1 and 2 respectively, we have
(1/2)[(m1/V)/(m2/v)] = 0.947.

- Uranium has two isotopesof masses 235 and 238 units. If both arepresent in Uranium hexafluoride gas which would have the larger average speed ? Ifatomic mass of fluorine is 19 units,estimate the percentage difference in speeds at any temperature.

Solution

At a fixed temperature the averageenergy = ½ m $\langle v^2 \rangle$ is constant. So smaller the mass of the molecule, faster will be the speed.

The ratio of speeds is inversely proportional to the square root of the ratio of the masses. The masses are 349 and 352 units. So,

v_{349} / v_{352} = (352/ 349)1/2 = 1.0044 .

Hence difference

ΔV/V

= 0.44 %.