

Molecular model of an ideal gas

- An ideal gas consists of a very large number of atoms moving around. Although each atom obeys (roughly) Newton's laws of motion, it is impossible to determine the trajectories of each atom individually.
- However, by making several assumptions, we can determine the *average* properties of this very large number of atoms.
 - Large number of molecules with large separation
 - Molecules obey Newton's laws of motion, but move randomly on average.
 - Molecules interact only by short range forces during collisions.
 - Molecules make elastic collisions with the walls.
 - Gas is a pure substance, consisting of identical molecules.

Pressure and the speed of molecules

- We can use what we know about the conservation of momentum to discuss the relationship between the pressure of an ideal gas, and the average speed of the gas molecules.
- It can be shown (section 20-1 in the textbook), that the pressure of an ideal gas is related to the root mean square (RMS) average speed (square root of the mean of the squares of the velocity) of the gas molecules by

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

$$P = \frac{2N}{3V} \frac{mv_{rms}^2}{2}$$

- Comparing this to the ideal gas law we find that:

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}}$$

Translational kinetic energy

• The average kinetic energy of a single molecule is simply $K_{\text{avg}} = \frac{1}{2} m v_{\text{rms}}^2$, assuming that averaging the speed of a single molecule over time is the same as averaging the speed over all molecules at a single time.

• Then, using our expression for v_{rms} we find that:
$$K_{\text{avg}} = \left(\frac{1}{2} m\right) \frac{3RT}{M}$$

• Since M/m is simply N_A and R/N_A is k_B this is equivalent to:

$$K_{\text{avg}} = \frac{3}{2} k_B T$$

• This equation states that at a given temperature *all ideal gas molecules have the same average translational kinetic energy.*

• This means that measuring the temperature of an ideal gas is equivalent to measuring the average translational kinetic energy of the molecules of the gas.

Internal Energy of an Ideal Gas

- The *internal energy* of an ideal gas depends only on the *temperature* T of the gas.
- Consider a *monatomic* ideal gas consisting only of single atoms.
- In the case the only contribution to the internal energy comes from the *translational motion* of the atoms.
- We know that the *average* energy of each atom is $K_{\text{avg}} = 3/2 k_B T$, so that $E_{\text{int}} = 3/2 nRT$.
- For *diatomic* and *polyatomic* ideal gases (made of molecules with more than one atom), the internal energy will not simply be $3/2 nRT$ (it will be larger), but it will still depend only on temperature (T).

Specific Heat of an Ideal Gas

- Recall that the *First Law of Thermodynamics* states that $\Delta E_{\text{int}} = Q + W$.
- Recall also that the *specific heat* (C) is defined by $Q = C\Delta T$.
- Consider the *molar specific heat* at constant volume (C_V) of an ideal gas (the heat capacity per mole, measured keeping the gas at a *fixed volume*).
- Since the volume is constant $W=0$ so $\Delta E_{\text{int}} = Q$.
- For an ideal monatomic gas with N atoms, $\Delta E_{\text{int}} = N(3/2 k_B \Delta T) = 3/2 nR\Delta T$.
- Then $3/2 nR\Delta T = nC_V\Delta T$ so that $C_V = 3/2 R$.
- Remember, R is a constant, so we know that $C_V = 12.5 \text{ J/mol}\cdot\text{K}$ for an *ideal monatomic* gas regardless of what kind of atoms make up the gas.
- In general $\Delta E_{\text{int}} = nC_V\Delta T$, for all ideal gases (monatomic or otherwise).

Specific Heat at Constant Pressure

- When heat is added to an ideal gas at *constant pressure*, there will be some change in volume ΔV , so the gas does *work*, and the change in internal energy is not simply Q .
- The gas does *work* $p\Delta V = nR\Delta T$, using the *ideal gas law*
- Define C_p as the *molar specific heat at constant pressure* so that $Q = nC_p\Delta T$ for constant pressure thermodynamic processes.
- Then, the First Law of Thermodynamics is $\Delta E_{int} = Q + W$ so $nC_V\Delta T = nC_p\Delta T - nR\Delta T$ (substituting for ΔE_{int} , Q , and W as appropriate for a constant pressure thermodynamic process), resulting in $C_p = C_V + R$

Adiabatic Expansion

- Recall that adiabatic expansion means that the ideal gas undergoes a volume change with no heat flowing into or out of the system ($Q=0$), at least on time scales of the expansion.
- It can be shown (20-4 in textbook) that for adiabatic expansion $pV^\gamma = \text{constant}$, where γ is the ratio of C_p and C_v , $\gamma = C_p/C_v$.
- Using the ideal gas law ($pV = nRT$) to replace p with nRT/V , we find $TV^{\gamma-1} = \text{constant}$ for adiabatic expansion.

Specific Heat and Degrees of Freedom

- We stated that the molar specific heat at constant volume was different for *polyatomic* gases compared to *monatomic* gases.
- This is because the energy that can be stored in each molecule depends on the *number of different* ways a molecule can move, the number of *degrees of freedom* of that molecule.
- Each degree of freedom for molecular motion contributes $1/2 k_B$ to C_V .
- *Monatomic* gases have 3 degrees of freedom (*translation* along x, y , and z) so $C_V = 3/2 k_B$.
- *Diatomic* gases have 5 degrees of freedom (*translation* along x, y , and z plus *rotation* around the the 2 axes perpendicular to the line connecting the two atoms), so $C_V = 5/2 k_B$.
- In general, for ideal gases $C_V = (f/2)k_B$ where f is the *number of degrees of freedom*.
- In practice only certain degrees of freedom can occur at different temperatures (because of *Quantum Mechanics*) so in the above equation, strictly speaking, f should be replaced by “allowed degrees of freedom”.

Distribution of Molecular Speeds

• We have discussed the RMS speed of ideal gas molecules at a certain temperature T , but *not all the molecules will have this exact value of speed.*

• There is a distribution of molecular speeds in an ideal gas at temperature T , given by:

$$N_v = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

• Using this equation, we can calculate the *average* speed (not RMS speed) is:

$$v_{avg} = \sqrt{8k_B T / \pi m}$$

and the *most probable* speed (the largest number of molecules will have this speed) is:

$$v_{MP} = \sqrt{2k_B T / m}$$