3.1 Molecular Model of an Ideal Gas
The goal of the molecular model of an ideal gas is to understand the macroscopic properties (such as pressure $p$ and temperature $T$) of gas in terms of its microscopic behavior (such as molecular velocity and kinetic energy). This model represents the gas as a large number of molecules bouncing around in a closed container with following assumptions:

1. A container with volume $V$ contains a very large number $N$ of identical molecules, each with mass $m$.
2. The molecules behave as point particles; their size is small in comparison to the average separation between particles and to the dimension of the container.
3. The molecules obey Newton’s laws of motion; they move randomly and occasionally make elastic collisions with each other and with the walls of the container.
4. The molecules exert no forces on each other except during the collisions; hence no gravitational potential energy of the molecules is considered.
5. The container walls are perfectly rigid and infinitely massive and do not move.

Deriving the relationship between molecular kinetic energy and the pressure

Suppose that one of the walls of the container is perpendicular to the $x$-axis, and let $v_{1x}$ be the $x$ component of the velocity of a molecule $m_i$. The $x$ component of the momentum of a molecule is $m_i v_{1x}$ before it hits the wall. Since wall is perfectly rigid and massive, its momentum is reversed $m_i (-v_{1x})$ after the hit.

Since the molecules obey Newton’s laws, we can apply the impulse-momentum theorem to find the average force on the wall by the molecule.

$$ F_{1x} = \frac{\Delta p_{1x}}{\Delta t} = \frac{2m_i v_{1x}}{\Delta t} $$

$\Delta t$ is the collision time. In order for the molecule to make another collision with the same wall, it needs to travel a distance of $2d$ across the container. Hence, the collision time can also be written as

$$ \Delta t = \frac{2d}{v_{1x}} $$

For $N$ molecules, the total average force on the wall is

$$ F_x = \sum_{i} F_{ix} = \sum_{i} \frac{2m_i v_{ix}^2}{\Delta t} = \sum_{i} \frac{m_i v_{ix}^2}{d} = \frac{d}{d} \sum_{i} \frac{N}{v_{ix}^2} $$

$m_i$ equals $m$ since all of the molecules are identical.
For small number of molecules, the actual force on the wall would vary with time. However, for a very large number of molecules, these variations are smoothed out, and hence the average force can be considered constant.

\[ F_x = \frac{m}{d} \sum_i N v_{ix}^2 = \frac{m}{d} N \overline{v_x^2}, \]

where \( \overline{v_x^2} = \frac{1}{N} \sum_{i} v_{ix}^2 \) is the average value of \( v_x^2 \).

Since the motion of the molecules is completely random, \( \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} \).

Knowing the square of the speed \( v^2 = v_x^2 + v_y^2 + v_z^2 \), we can write \( \overline{v_x^2} = \frac{1}{3} v^2 \).

The total force on wall is rewritten as \( F_x = \frac{1}{3} \frac{N}{d} m \overline{v^2} \).

With this expression, we can find the pressure exerted on the wall.

\[ p = \frac{F_x}{A} = \frac{1}{3} \left( \frac{N}{V} \right) m \overline{v^2} \]

\[ = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m \overline{v^2} \right) \]

\[ = \frac{2}{3} \left( \frac{N}{V} \right) \left( \frac{1}{2} m v_{\text{rms}}^2 \right) \]

The square root of \( \overline{v^2} \) is called the root-mean-square (\textit{rms}) speed of the molecules.

**Interpretation:**

This result indicates that the pressure of a gas is proportional to
- the number of molecules per unit volume
- the average translational kinetic energy of the molecules

Using the ideal-gas equation \( pV = nRT = Nk_B T \), the average translational kinetic energy of a single molecule is

\[ \frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_B T \]

The total translational kinetic energy of \( N \) molecules of gas is

\[ K_{\text{total\,trans}} = N \frac{3}{2} k_B T = \frac{3}{2} nRT \]

where \( k_B = R / N_A \) and \( n = N / N_A \).

\[ v_{\text{rms}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \]

where \( M (= N_A m) \) is molar mass in SI units.
Example 1: An oxygen tank contains 1.00 mol of oxygen gas at 27.0 °C.
(a) What is the total translational kinetic energy of the gas molecules?

$$ K_{\text{total trans}} = \frac{3}{2} nRT $$

$$ = \frac{3}{2} (1.00 \text{ mol})(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K}) $$

$$ = 3740 \text{ J} $$

(b) What is the average translational kinetic energy of a molecule?

$$ \frac{1}{2} m v_{rms}^2 = \frac{3}{2} k_B T $$

$$ = \frac{3}{2} (1.38 \times 10^{-23} \text{ JK}^{-1})(300 \text{ K}) $$

$$ = 6.21 \times 10^{-21} \text{ J} $$

(c) What is the root-mean-square speed of an oxygen molecule at this temperature?

Molar mass of oxygen gas $ M $ is $(2 \times 16.0) \text{ g } \text{ mol}^{-1}$

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

$$ = \sqrt{\frac{3(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(300 \text{ K})}{32.0 \times 10^{-3} \text{ kg mol}^{-1}}} $$

$$ = 484 \text{ ms}^{-1} $$

Note: The SI units of $ M $ are kilograms per mole, not grams per mole.

Exercise: A 5.00-liter vessel contains nitrogen gas at 27.0°C and 3.00 atm. Find (a) the number of molecules in the vessel, (b) the total translational kinetic energy of the gas molecules and (c) the average translational kinetic energy per molecule.

Answer: $3.67 \times 10^{23}$ molecules, 2.28 kJ, $6.22 \times 10^{-21} \text{ J}$

### 3.2 Molar Specific Heat of an Ideal Gas

When heat $ Q $ is added to (or released from) a substance of mass $ m $, the change of temperature $ \Delta T $ of the substance is governed by

$$ Q = mc \Delta T $$

where $ c = $ specific heat of the substance [i.e. amount of heat required to raise 1 kg of that substance by 1 K]

If the quantity of the substance is expressed in number of moles $ n $, $ Q $ is more conveniently to be written as

$$ Q = nC \Delta T $$

where $ C $ is molar specific heat. [i.e. amount of heat required to raise 1 mole of that substance by 1 K] SI unit: J mol$^{-1}$ K$^{-1}$.

1. Suppose we heat up $ n $ moles of gas while keeping its volume constant. The result of adding heat to the system is an increase of its temperature

$$ Q = nC_v \Delta T $$

$ C_v $ is the molar heat capacity at constant volume.
Since the volume is kept constant, the work done by the gas is $W = 0$. The first law of thermodynamics shows that
\[ \Delta E_{\text{int}} = Q - W = Q - 0 \]
\[ \Delta E_{\text{int}} = n C_v \Delta T \quad \text{(also true for any process)} \]

The internal energy of a gas is related to the kinetic energy of its molecules. Let us consider the simplest case of a monatomic ideal gas, that is, a gas containing one atom per molecule, such as helium or argon. The internal energy of the gas consists only of the translational kinetic energy:
\[ E_{\text{int}} = K_{\text{trans}} = \frac{3}{2} nRT \]

This energy is a function of $T$ only. When heat is added to a monatomic gas in a container of fixed volume, all of the added energy goes into increasing the translational kinetic energy of the atoms.

\[ Q = \Delta E_{\text{int}} \]
\[ n C_v \Delta T = \frac{3}{2} nR \Delta T \]
\[ C_v = \frac{3}{2} R \quad \text{(only for monatomic gas)} \]

2. Suppose that, while heat is added to the system, the volume is allowed to change such that the gas pressure does not change. Again, the first law of thermodynamics shows that
\[ Q = \Delta E_{\text{int}} + W = n C_p \Delta T \]

where $C_p$ is the molar heat capacity at constant pressure.

The work done by the gas in this constant-pressure process is $W = p \Delta V$. Using the ideal-gas equation of state $pV = nRT$, we can relate $\Delta V$ to $\Delta T$ as
\[ p \Delta V = nR \Delta T. \]

The first law of thermodynamics can be rewritten as
\[ \Delta E_{\text{int}} + nR \Delta T = n C_p \Delta T \]

However, the internal energy $E_{\text{int}}$ depends only on the temperature and not on how the volume and/or pressure is changing. Thus, the change in internal energy during any process is only determined by the temperature change: $\Delta E_{\text{int}} = n C_v \Delta T$.

The previous equation can therefore be rewritten as
\[ n C_v \Delta T + nR \Delta T = n C_p \Delta T \]
\[ C_p = C_v + R \]

Example 2: A cylinder contains 3.00 mol of helium gas at a temperature of 300 K. How much heat must be added to the gas to increase its temperature to 500 K, if it is heated at (a) constant volume (b) constant pressure?

Helium is monatomic, so $C_v = \frac{3}{2} R$ and $C_p = C_v + R$.
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(a) At constant volume, the heat added is
\[ Q = nC_v \Delta T \]
\[ = (3.00 \text{ mol})(\frac{3}{2})(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(500 - 300) \text{ K} \]
\[ = 7.50 \times 10^3 \text{ J} \]

(b) At constant pressure, the heat added is
\[ Q = nC_p \Delta T \]
\[ = (3.00 \text{ mol})(\frac{5}{2})(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(500 - 300) \text{ K} \]
\[ = 12.5 \times 10^3 \text{ J} \]

Exercise: Calculate the change in internal energy of 3.00 mol of helium gas when its temperature is increased by 2.00 K.

Answer: 74.8 J

3.3 The Adiabatic Processes for an Ideal Gas

An adiabatic process is a process in which no heat transfer takes place between the system and its surroundings. Suppose that a gas is expanded adiabatically, thus \( Q = 0 \). Consider an infinitesimal change in volume \( dV \). The work done by the gas during the process is \( dW = pdV \). Since the internal energy only depends temperature, the internal energy change \( dE_{\text{int}} \) for any process, adiabatic or not, is \( dE_{\text{int}} = nC_v dT \). Hence, the first law of thermodynamics, \( \Delta E_{\text{int}} = Q - W, Q = 0 \) becomes

\[ dE_{\text{int}} = nC_v dT = -pdV \]

Taking the total differential of the ideal-gas equation of state, \( pV = nRT \), we see that

\[ pdV + Vdp = nRdT \]

or

\[ ndT = \frac{pdV + Vdp}{R} = \frac{pdV + Vdp}{C_p - C_v} \]

Eliminating \( dT \) from these two equations, we find that

\[ \frac{pdV + Vdp}{C_p - C_v} = -\frac{pdV}{C_v} \]

\[ C_v \left( \frac{pdV + Vdp}{R} \right) = \left( C_p - C_v \right) \frac{pdV}{V} \]

This expression can be rewritten as

\[ \frac{dp}{p} + \gamma \frac{dV}{V} = 0 \]

where \( \gamma = (C_p/C_v) \). After integrating this expression we obtain

\[ \ln p + \gamma \ln V = \text{constant} \]

or

\[ p V^\gamma = \text{constant} \]

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Using the ideal-gas equation in the form \( p = \frac{nRT}{V} \) to eliminate \( p \) from the expression we obtain

\[
\left( \frac{nRT}{V} \right)^{\gamma} = \text{constant}
\]

Thus

\[
TV^{\gamma-1} = \text{constant}
\]

For monatomic ideal gas:

\[
C_v = \frac{3}{2} R
\]

\[
= \frac{3}{2} (8.31 \text{Jmol}^{-1} \text{K}^{-1}) = 12.5 \text{Jmol}^{-1} \text{K}^{-1}
\]

\[
\gamma = \frac{C_p}{C_v} = \frac{\frac{3}{2} R + R}{\frac{3}{2} R} = \frac{5}{3} = 1.67
\]

Example 3: During the compression stroke of a certain gasoline engine, the pressure increases from 1.00 atm to 20.0 atm. Assuming that the process is adiabatic and that the gas is ideal, with \( \gamma = 1.40 \), (a) by what factor does the volume change and (b) by what factor does the temperature change? (c) If the compression starts with 0.0160 mol of gas at 27.0°C, find the values of \( Q, W, \) and \( \Delta E_{\text{int}} \) that characterize the process.

\[
p_1 = 1.00 \text{ atm} \quad p_2 = 20.0 \text{ atm} \quad \gamma = 1.40
\]

(a) \( p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \)

\[
\frac{V_2}{V_1} = \left( \frac{p_1}{p_2} \right)^{\frac{1}{\gamma}} = \left( \frac{1.00 \text{ atm}}{20.0 \text{ atm}} \right)^{\frac{1}{1.40}} = 0.11768
\]

(b) Method 1: \( T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \)

\[
\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1} = \left( \frac{1}{0.11768} \right)^{1.40-1} = 2.3535
\]

Method 2: \( pV = nRT \), so \( \frac{pV}{T} = \text{constant} \)

\[
\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}
\]

\[
\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1} = \left( \frac{20.0 \text{ atm}}{1.00 \text{ atm}} \right)(0.11768) = 2.3535
\]

(c) \( T_1 = 27.0 ^\circ C = 27.0 + 273.15 = 300.15 \text{ K} \)

\[
n = 0.0160 \text{ mol} \quad T_2 = 2.3535 \ T_1
\]

\[
\Delta T = T_2 - T_1 = 2.3535 T_1 - T_1 = 1.3535 T_1
\]

\[
\gamma = \frac{C_p}{C_v} = 1.40 = \frac{7}{5}
\]
\[
\frac{C_v + R}{C_v} = \frac{7}{5}, \text{ so } C_v = \frac{5}{2} R
\]

\[
\Delta E_{\text{int}} = nC_v \Delta T = (0.0160 \text{ mol})(\frac{5}{2})(8.315 \text{ J mol}^{-1} \text{ K}^{-1})(1.351)(300 \text{ K})
\]

= 135 J

Adiabatic process: \( Q = 0 \). So, \( \Delta E_{\text{int}} = -W \).

\( W = -135 \text{ J} \)

Exercise: One mole of Helium gas expands adiabatically from 2 atm pressure to 1 atm pressure. If the original temperature of the gas is 20°C, what is the final temperature of the gas? \( (\gamma = 1.67) \)

Answer: 222 K

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Things to know (Chapter 1 to 3)

\[
T_F = \frac{9}{5} T_C + 32 \quad \text{(Substitute 100°C to check)}
\]

\[
T_K = T_C + 273.15
\]

\[
\Delta L = \alpha d\theta \Delta T; \quad \beta = 3\alpha
\]

\[
pV = nRT = Nk_BT; \quad k_B = \frac{R}{N_A}
\]

\[
n = \frac{\text{# of molecules}, N}{\text{Avogadro's number}, N_A}
\]

\[
W = \int_{V_f}^{V_i} p \, dV \quad \text{(work done by gas)}
\]

\[
\Delta E_{\text{int}} = Q - W
\]

\[
Q = nC_p \Delta T
\]

\[
Q = nC_v \Delta T
\]

\[
H = \int H = \int \sum_i L_i/k_i
\]

\[
H = \alpha A e^T^4
\]

\[
H_{\text{net}} = \alpha A e(T^4 - T_i^4)
\]

\[
\frac{1}{2} m v_{\text{rms}}^2 = \frac{3}{2} k_BT \quad \text{(one molecule)}
\]

\[
K_{\text{trans}} = \frac{3}{2} k_BT = \frac{3}{2} nRT
\]

\[
v_{\text{rms}} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}
\]

\[
\Delta E_{\text{int}} = nC_v \Delta T \quad \text{(for any process)}
\]

\[
C_v = \frac{3}{2} R \quad \text{(monatomic gas)}
\]

\[
C_p = C_v + R; \quad \gamma = \frac{C_p}{C_v}
\]

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<table>
<thead>
<tr>
<th>Constant</th>
<th>Process</th>
<th>( \Delta E_{\text{int}} = Q - W )</th>
<th>etc</th>
</tr>
</thead>
<tbody>
<tr>
<td>( p )</td>
<td>Isobaric</td>
<td>( W = p \Delta V )</td>
<td>( Q = n , C_p \Delta T )</td>
</tr>
<tr>
<td>( V )</td>
<td>Isochoric</td>
<td>( W = 0 ) ( \Rightarrow \Delta E_{\text{int}} = Q )</td>
<td>( Q = n , C_v \Delta T )</td>
</tr>
<tr>
<td>( T )</td>
<td>Isothermal</td>
<td>( \Delta E_{\text{int}} = 0 ) ( \Rightarrow Q = W )</td>
<td>( W = nRT \ln (V_2/V_1) )</td>
</tr>
<tr>
<td>All ( (p, V, T) ) not constant</td>
<td>Adiabatic</td>
<td>( Q = 0 ) ( \Rightarrow \Delta E_{\text{int}} = -W )</td>
<td>( p_1 V_1 \gamma = p_2 V_2 \gamma ); ( T_1 V_1 \gamma = T_2 V_2 \gamma )</td>
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