Kinetic Theory of Gases

13

In the simplest model of an ideal gas, which was presented in Chap. 11, we consider each atom/molecule to be a hard sphere that collides elastically with other atoms/molecules or with the walls of the container holding the gas.

In this chapter, our aim is to relate *macroscopic* parameters (such as volume, pressure, temperature, ... etc.) to *microscopic* parameters (such as average kinetic energy per molecule, internal energy of the gas, ... etc.). To keep the mathematics relatively simple, we develop a microscopic model that incorporates further justified assumptions.

13.1 Microscopic Model of an Ideal Gas

In this model, the pressure P that a gas exerts on the walls of its encompassing container, of volume V, is due to the collisions of n moles of the gas (or $N = nN_A$ molecules) with those walls. Moreover, in such a model we *assume* that gases have the following:

1. *A large number of molecules*
2. *Large separations between molecules compared to their average sizes*
3. *Molecules that move randomly and obey Newton's laws of motion*
4. *Negligible molecular collisions and experience only elastic collisions with the walls of the container*
5. *A thermal equilibrium at temperature T with the container's walls.*

Now consider the collision of the i$^{\text{th}}$ molecule of such a gas with the colored yz wall of a cubical container of side L, as shown in Fig. 13.1. In this figure, the gas

H. A. Radi and J. O. Rasmussen, *Principles of Physics*,
Undergraduate Lecture Notes in Physics, DOI: 10.1007/978-3-642-23026-4_13,

molecule of mass m is moving with velocity $\vec{v}_i$ which has the velocity components v_{xi}, v_{yi}, and v_{zi}.

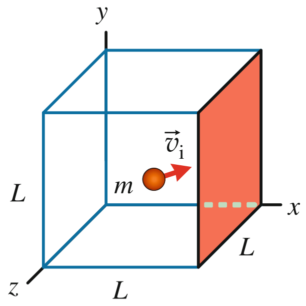


Fig. 13.1 A cubical container of side L, containing n moles or N molecules of an ideal gas. The figure shows an i$^{\text{th}}$ molecule of mass m and velocity $\vec{v}_i$ that is about to collide with the colored right yz wall

Because we assume elastic collisions, only the x component of the above molecule's velocity changes, while its y and z components remain unchanged. This is illustrated in Fig. 13.2, which captures only the motion in the xy plane. Using the definition of momentum (see Sect. 7.1), the only change in the molecule's momentum is along the x-axis. Its momentum before the collision is mv_{xi} and its momentum after the collision is $-mv_{xi}$. The change in momentum in one collision is:

$$\left.\begin{aligned} \Delta p_{xi} &= (p_{xi})_{\text{fin}} - (p_{xi})_{\text{ini}} = -mv_{xi} - mv_{xi} = -2mv_{xi} \\ \Delta p_{yi} &= 0 \\ \Delta p_{zi} &= 0 \end{aligned}\right\} \tag{13.1}$$

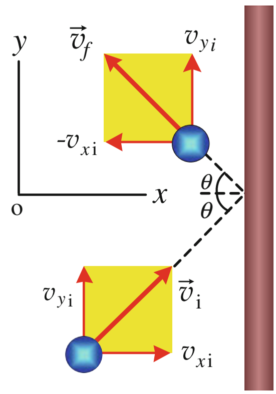


Fig. 13.2 A molecule moving in the xy plane undergoes an elastic collision with a wall perpendicular to that plane. The x component of the velocity is reversed, while the y component remains unchanged

Since the momentum of the system (molecule + wall) is conserved, the momentum delivered by the wall to the molecule for the i$^{\text{th}}$ molecule is $\Delta p_{xi} = -2mv_{xi}$. The molecule in Fig. 13.1 will travel to the opposite wall and back again. It will repeat this journey, hitting the colored wall repeatedly. The time between two successive collisions with this wall is Δt. This means that the molecule travels with a speed v_{xi} a distance $2L$ in time Δt. Thus:

$$\Delta t = \frac{2L}{v_{x\mathrm{i}}} \tag{13.2}$$

This time is very small and the molecule will make many collisions with the wall, each separated by time Δt. Therefore the number of collisions per unit time is large. Consequently, the average force exerted on the i$^{\mathrm{th}}$ molecule over many collisions will be equal to the momentum change during one collision $\Delta p_{x\mathrm{i}}$ divided by the time Δt between collisions (Newton's second law).

If $\overline{F}_{x\mathrm{i}}$ is the average perpendicular force exerted by the wall on the molecule, then from Newton's third law, the average perpendicular force exerted on the wall by the molecule is $\overline{F}_{x\mathrm{i,on\,wall}} = -\overline{F}_{x\mathrm{i}}$. That is:

$$\begin{aligned} \overline{F}_{x\mathrm{i,on\ wall}} &= -\overline{F}_{x\mathrm{i}} = -\frac{\Delta p_{x\mathrm{i}}}{\Delta t} = -\frac{-2mv_{x\mathrm{i}}}{\Delta t} = \frac{2mv_{x\mathrm{i}}}{2L/v_{x\mathrm{i}}} \\ &= \frac{mv_{x\mathrm{i}}^2}{L} \end{aligned} \tag{13.3}$$

To find the total average force $\overline{F}_{x,\mathrm{on\ wall}}$ exerted on the wall we must add up the contributions of all molecules that strike the wall and then divide this total force by the area of the wall. This gives the average pressure P on the wall. Thus:

$$\begin{aligned} P &= \frac{\Sigma \overline{F}_{x\mathrm{i,on\,wall}}}{L^2} = \frac{mv_{x1}^2/L + mv_{x2}^2/L + \cdots + mv_{xN}^2/L}{L^2} \\ &= \frac{m}{L^3}(v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2) \\ &= \frac{m}{L^3}\sum_{\mathrm{i}=1}^{N} v_{x\mathrm{i}}^2 \end{aligned} \tag{13.4}$$

Since the average value of the square of the x component of all the molecular speeds is given by:

$$\begin{aligned} \overline{v_x^2} &= \frac{v_{x1}^2 + v_{x2}^2 + \cdots + v_{xN}^2}{N} \\ &= \frac{\sum_{\mathrm{i}=1}^{N} v_{x\mathrm{i}}^2}{N} \end{aligned} \tag{13.5}$$

and the volume of the container is given by $V = L^3$, then we can express the average pressure in the following form:

$$P = \frac{mN}{V}\,\overline{v_x^2} \tag{13.6}$$

Since $v_{\mathrm{i}}^2 = v_{x\mathrm{i}}^2 + v_{y\mathrm{i}}^2 + v_{z\mathrm{i}}^2$ for the i$^{\text{th}}$ molecule, then this result and Eq. 13.5 lead to $\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$. In addition, because there is a large number of molecules moving randomly in all directions, the average values of the squares of their velocity components are equal, i.e. $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$.

Thus:

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \tfrac{1}{3}\overline{v^2} \tag{13.7}$$

Hence, Eq. 13.6 can be expressed as:

$$P = \tfrac{2}{3}\frac{N}{V}\left(\tfrac{1}{2}m\overline{v^2}\right) \tag{13.8}$$

The square root of $\overline{v^2}$ is called the *root mean square* (rms) *speed* of the molecules and is symbolically written as v_{rms}, i.e. $v_{\mathrm{rms}}^2 = \overline{v^2}$. Thus:

$$\boxed{v_{\mathrm{rms}} = \sqrt{\overline{v^2}}} \tag{13.9}$$

By substitution, Eq. 13.8 will take on the form:

$$\boxed{P = \tfrac{2}{3}\frac{N}{V}\left(\tfrac{1}{2}mv_{\mathrm{rms}}^2\right)} \tag{13.10}$$

where $\frac{1}{2}mv_{\mathrm{rms}}^2$ is the average translational kinetic energy per molecule. Equation 13.10 connects the macroscopic quantities P and V to the microscopic quantity representing the average molecular speed v_{rms}.

We should remember that we ignored inter-molecular collisions as we derived Eq. 13.10. Note that these collisions only affect the momenta of the molecules and have no net effect on the walls, so including such collisions will yield the same equation. This is consistent with the random motion assumption, which implies that the velocity distribution of the molecules does not change with time despite the collision between molecules. In addition, this equation is valid for any shaped container, although it was derived assuming a cubical container.

To get some insight into the meaning of temperature, we first rewrite Eq. 13.10 in the following form:

$$\boxed{PV = \tfrac{2}{3}N\left(\tfrac{1}{2}mv_{\mathrm{rms}}^2\right)} \tag{13.11}$$

Then we compare this with the ideal gas law Eq. 11.10:

$$PV = Nk_B\, T \tag{13.12}$$

where this equation is based on experimental facts concerning the macroscopic behavior of the ideal gas. Equating the right-hand sides of the last two equations, we find that:

$$T = \frac{2}{3\, k_B}\ \left(\tfrac{1}{2} m v_{rms}^2\right) \tag{13.13}$$

Since $K = \frac{1}{2} m v_{rms}^2$ is the average translational kinetic energy per molecule, we see that temperature is a direct measure of it. In addition, we can relate the average translational molecular kinetic energy per molecule to the temperature as follows:

$$K = \tfrac{1}{2} m v_{rms}^2 = \tfrac{3}{2} k_B T \tag{13.14}$$

With $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3}\overline{v^2} = \frac{1}{3} v_{rms}^2$, we can find the average translational kinetic energy per molecule associated with the motion along the x, y, and z axes as follows:

$$\begin{aligned} \tfrac{1}{2} m\overline{v_x^2} &= \tfrac{1}{2} k_B T \\ \tfrac{1}{2} m\overline{v_y^2} &= \tfrac{1}{2} k_B T \\ \tfrac{1}{2} m\overline{v_z^2} &= \tfrac{1}{2} k_B T \end{aligned} \tag{13.15}$$

Thus, each translational degree of freedom[1] contributes an equal amount of energy to the gas, namely $\frac{1}{2} k_B T$. A generalization of that is known as the theory of equipartition of energy.

Theory of equipartition of energy:
The energy of a system experiencing thermal equilibrium is equally divided among all degrees of freedom. Each degree of freedom contributes $\frac{1}{2} k_B T$ to the energy of the system.

The total translational energy K_{tot} (*which is the internal energy in this model*) of N molecules of an ideal gas is the product of N with the average translational energy per molecule $K = \frac{1}{2} m v_{rms}^2$. That is:

[1] The translational degrees of freedom refer to the number of independent ways by which a molecule can possess energy when moving in a three-dimensional space.

$$\boxed{K_{\text{tot}} = N\left(\tfrac{1}{2}mv_{\text{rms}}^2\right) = \tfrac{3}{2}Nk_{\text{B}}T = \tfrac{3}{2}nRT} \tag{13.16}$$

where we have used $N = nN_{\text{A}}$ for the number n of kilomoles of the gas and $k_{\text{B}} = R/N_{\text{A}}$ for Boltzmann's constant.

Using the molar mass $M = mN_{\text{A}}$ in Eq. 13.16, where m here is the molecular mass and not to be confused with the mass of the gas as in Chap. 11, we can relate v_{rms} to the gas temperature T as follows:

$$v_{\text{rms}} = \sqrt{\frac{3k_{\text{B}}T}{m}} = \sqrt{\frac{3RT}{M}} \tag{13.17}$$

Table 13.1 shows some rms speeds calculated from Eq. 13.17.

Table 13.1 Some molecular speeds at room temperature ($T = 300$ K)

Gas	Molar mass (kg/kmol)	v_{rms} (m/s)
Hydrogen (H_2)	2.02	1,925
Helium (He)	4.0	1,368
Water vapor (H_2O)	18	645
Nitrogen (N_2) or Carbon monoxide (CO)	28	517
Nitrogen oxide (NO)	30	499
Oxygen (O_2)	32	484
Carbon dioxide (CO_2)	44	412
Sulfur dioxide (SO_2)	48	394

Example 13.1

Three moles of hydrogen gas are confined to a volume of 0.4 m^3 at a temperature of 24 °C. (a) What is the total translational kinetic energy of the gas molecules? (b) What is the average kinetic energy per molecule? (c) What is the rms speed of the molecules?

Solution: (a) Using Eq. 13.16 with $T = 24 + 273 = 297$ K, we get:

$$K_{\text{tot}} = \tfrac{3}{2}nRT = \tfrac{3}{2}\,(3\times10^{-3}\,\text{kmol})(8.314\times10^{3}\,\text{J/kmol.K})(297\,\text{K}) = 1.1\times10^{4}\,\text{J}$$

(b) Using Eq. 13.14 with $T = 297$ K, we get:

$$K = \tfrac{3}{2}k_{\text{B}}T = \tfrac{3}{2}\,(1.38\times10^{-23}\,\text{J/K})(297\,\text{K}) = 6.15\times10^{-21}\,\text{J}$$

(c) Using Eq. 13.17 with $T = 297$ K and the known hydrogen molar mass $M = 2.02$ kg/kmol, we get

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3(8.314 \times 10^3\ \text{J/kmol.K})(297\ \text{K})}{2.02\ \text{kg/kmol}}} = 1{,}915\,\text{m/s}$$

Internal Energy of a Monatomic Ideal Gas

In the ideal-gas model presented in this section, we assumed each molecule behaved like a hard sphere and had no structure. We were then able to find its average translational kinetic energy in terms of the temperature of the gas. This average kinetic energy is associated with the motion of the center of mass of each molecule. This model does not include the energy associated with the internal motions of the gas, such as the vibrational and rotational motions of the molecules.

In light of this, consider an ideal monatomic gas, such as helium (He), where the gas molecules include only one atom. Essentially, all of the kinetic energy of such monatomic molecules are associated with the motion of each molecule's center of mass. Therefore, when we add energy to a monatomic gas, all the added energy goes into increasing the translational kinetic energy of the atoms. Thus, the total internal energy E_{int} of an ideal monatomic gas of N atoms (or n kmol) at pressure P, volume V, and temperature T will all be translational energy K_{tot}, i.e. $E_{\text{int}} = K_{\text{tot}}$. Using $K_{\text{tot}} = \frac{3}{2}Nk_{\text{B}}T = \frac{3}{2}nRT$ we find:

$$E_{\text{int}} = \begin{cases} \frac{3}{2}Nk_{\text{B}}T \\ \frac{3}{2}nRT \end{cases} \quad \text{or} \quad \Delta E_{\text{int}} = \begin{cases} \frac{3}{2}Nk_{\text{B}}\Delta T \\ \frac{3}{2}nR\Delta T \end{cases} \qquad \text{(Monatomic ideal gas)} \tag{13.18}$$

In general, *the internal energy of an ideal gas is a function of T only*, and the exact relationship depends on the type of gas.

Internal energy of an ideal gas:
The internal energy E_{int} of n kilomoles of an ideal gas is a function of the gas temperature only; it does not depend on any other variable.

With this result, we are going to find two expressions for the molar specific heat of an ideal gas. By convention, the symbol C_V will be used when the gas volume is constant while heat energy is added, whereas the symbol C_P will be used when the gas pressure remains constant while heat energy is added.

13.2 Molar Specific Heat Capacity of an Ideal Gas

Consider an ideal gas undergoing several processes such that the change in temperature is achieved by taking a variety of different paths from one isotherm at temperature T to another isotherm at temperature $T + \Delta T$, as shown in Fig. 13.3. Because ΔT is the same for each path, the change in internal energy ΔE_{int} is the same for all paths. However, from the first law of thermodynamics, $\Delta E_{\text{int}} = Q - W$, we know that the heat Q is different for each path because W is different. Thus, the heat associated with a given change in temperature ΔT does not have a unique value.

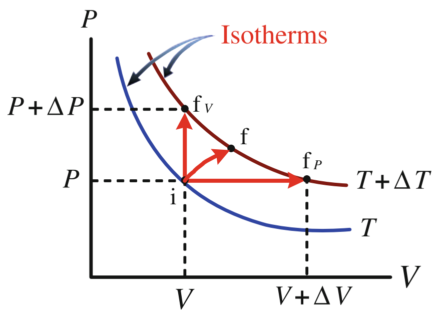


Fig. 13.3 An ideal gas is taken from initial state i of isotherm at temperature T to another at temperature $T + \Delta T$ along three different paths. The change in internal energy is the same for all paths

We can treat this situation by defining specific heats for two processes that frequently occur: changes at constant volume and changes at constant pressure. Because the number of *moles* is a convenient measure of the amount of gas, we define the *molar specific heats* associated with these processes with the following equations:

$$\boxed{Q_V = nC_V\,\Delta T} \quad \text{(Constant volume)} \tag{13.19}$$

$$\boxed{Q_P = nC_P\,\Delta T} \quad \text{(Constant pressure)} \tag{13.20}$$

where n ***now*** is the number of moles, C_V is the **molar specific heat at constant volume**, and C_P is the **molar specific heat at constant pressure**. When we deliver heat to the gas at constant pressure, the heat Q_P must account for both the increase in internal energy ΔE_{int} and the work W. But, when we deliver heat to the gas at constant volume, then the heat Q_V must account for only the same increase in internal energy

ΔE_{int}, since $W = 0$. For this reason, Q_P is greater than Q_V for all given values of n and ΔT. Thus, C_P is greater than C_V.

The molar specific heat capacities C_V and C_P are related to the specific heats c_V and c_P by the following two relations:

$$\boxed{\begin{aligned} C_V &= M\, c_V \\ C_P &= M\, c_P \end{aligned}} \tag{13.21}$$

where M is the molar mass of the gas.

13.2.1 Molar Specific Heat at Constant Volume

We consider n moles of an ideal gas at pressure P and temperature T, confined to a cylinder of fixed volume V, as shown in Fig. 13.4a. The *initial state* i of the gas is identified on the PV graph of Fig. 13.4b. When we add a small amount of heat Q_V to the gas, by slowly turning up the temperature of a heat reservoir, the gas temperature rises to $T + \Delta T$ and its pressure rises to $P + dP$, bringing the gas to the *final state* f that is identified in Fig. 13.4b.

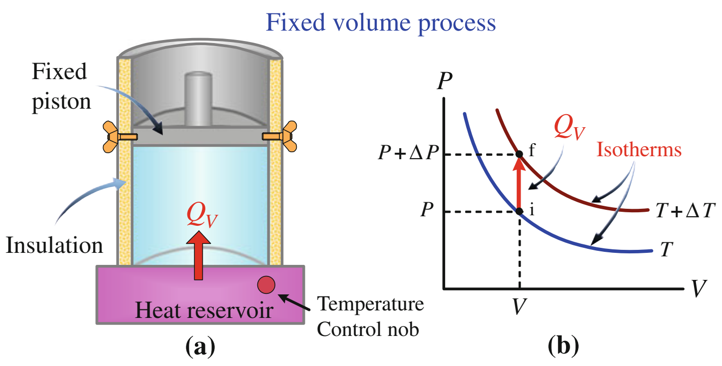


Fig. 13.4 (a) The temperature of an ideal gas is increased from T to $T + \Delta T$ in a constant *volume* process by adding heat Q_V. (b) The constant volume process i $\rightarrow$ f on a PV diagram

Since $W = \int P\, dV = 0$ for a *constant volume process*, then all of the transferred energy will be stored in the gas as an increase in its internal energy, and the change in the internal energy of the gas will be given by the first law of thermodynamics as:

$$\boxed{\Delta E_{\text{int}} = Q_V} \tag{13.22}$$

Substituting this expression into Eq. 13.19, we get:

$$\boxed{Q_V = \Delta E_{\text{int}} = nC_V \Delta T} \quad \text{(Ideal gas)} \tag{13.23}$$

If the molar specific heat C_V is constant, we can express the internal energy of an ideal gas as:

$$\boxed{E_{\text{int}} = nC_V T} \quad \text{(Ideal gas)} \tag{13.24}$$

This equation applies to all ideal gases (to gases having one or more than one atom per molecule). In the limit of infinitesimal changes, we can use Eq. 13.24 to express the molar specific heat at constant volume as follows:

$$\boxed{C_V = \frac{1}{n}\frac{dE_{\text{int}}}{dT}} \tag{13.25}$$

For monatomic gases, if we substitute the internal energy $E_{\text{int}} = \frac{3}{2}nRT$ from Eq. 13.18 into Eq. 13.25, we get:

$$\boxed{C_V = \tfrac{3}{2}R = \begin{cases} 12.5 \text{ J/mol.K} \\ 12.5 \times 10^3 \text{ J/kmol.K} \end{cases}} \quad \text{(Monatomic ideal gas)} \tag{13.26}$$

This result is in agreement with experimentally measured values for monatomic gases at a wide range of temperatures.

13.2.2 Molar Specific Heat at Constant Pressure

We now consider n moles of an ideal gas at pressure P and temperature T, confined to a volume V by a freely moving piston, as shown in Fig. 13.5a. The *initial state* i of the gas is identified on the PV diagram of Fig. 13.5b. Under a constant pressure, a small amount of heat Q_P is added to the gas, by slowly turning up the temperature of a heat reservoir; the gas temperature rises to $T + \Delta T$, bringing the gas to the *final state* f that is identified in Fig. 13.5b.

To relate C_P to C_V, we start with the first law of thermodynamics:

$$\Delta E_{\text{int}} = Q_P - W \tag{13.27}$$

and then replace each term. From Eq. 13.23, we have:

$$\Delta E_{\text{int}} = nC_V \Delta T \tag{13.28}$$

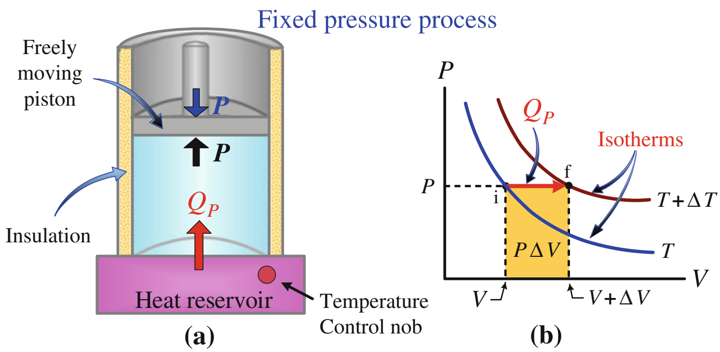


Fig. 13.5 (a) The temperature of an ideal gas is increased from T to $T + \Delta T$ in a constant *pressure* process by adding heat Q_P. (b) The work PdV is given by the colored area for the constant pressure process i → f on the PV diagram

Also, from Eq. 13.20, we have:

$$Q_P = nC_P\Delta T \tag{13.29}$$

The work done by the ideal gas in the *constant pressure process* of Fig. 13.5b is $W = P\Delta V$. Then we use the ideal-gas equation $PV = nRT$ to find W as follows:

$$W = P\Delta V = nR\Delta T \tag{13.30}$$

Substituting with Eq. 13.28, 13.29, and 13.30 into Eq. 13.27, and then dividing by $n\Delta T$, we find

$$\boxed{C_P - C_V = R} \tag{13.31}$$

This prediction of kinetic theory agrees well with experiments, not only for monatomic gases but for gases in general, as long as their density is low enough so that we may treat them as ideal.

For monatomic gases, we substitute with $C_V = 3R/2$ into Eq. 13.31 to find:

$$\boxed{C_P = \tfrac{5}{2}R = \begin{cases} 20.8\ \text{J/mol.K} \\ 20.8 \times 10^3\ \text{J/kmol.K} \end{cases}} \quad \text{(Monatomic ideal gas)} \tag{13.32}$$

The ratio of the molar specific heats C_P and C_V is a dimensionless quantity γ given by:

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67 \quad \text{(Monatomic ideal gas)} \tag{13.33}$$

Theoretical values of C_V, C_P, and γ are in excellent agreement with experimental values obtained for monatomic gases, but they are in serious disagreement with the values for more complex gases (those with multiple atoms per molecule). This is because their internal energy E_{int}, and their molar specific heats C_P and C_V include components from rotational and vibrational motions of the molecules.

Example 13.2

A cylinder contains 2 moles of helium at a temperature of 27 °C. Heat is added to the gas to increase its temperature to 227 °C. (a) Find the quantity of heat Q_V used if the gas was heated at constant volume. (b) Find the quantity of heat Q_P and the work done by the gas W if the gas was heated at constant pressure.

Solution: (a) Treating the helium gas as an ideal monatomic gas, the work done in this case is zero. We use $C_V = 3R/2 = 12.5$ J/mol.K and $\Delta T = 227\,°\text{C} - 27\,°\text{C} = 200\,\text{C}° = 200$ K in Eq. 13.23 to get:

$$Q_V = nC_V \Delta T = (2 \text{ mol})(12.5 \text{ J/mol.K})(200 \text{ K}) = 5{,}000 \text{ J}$$

(b) For a constant pressure process we use $C_P = 5R/2 = 20.8$ J/mol.K in Eq. 13.20 to get:

$$Q_P = nC_P \Delta T = (2 \text{ mol})(20.8 \text{ J/mol.K})(200 \text{ K}) = 8{,}320 \text{ J}$$

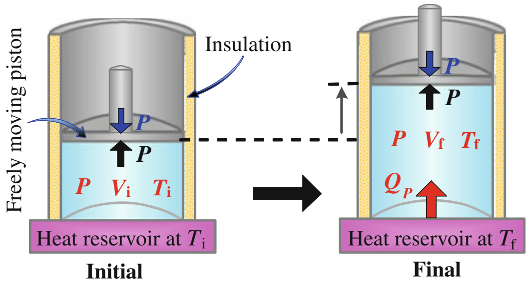
The work done by the gas in this process is:

$$W = Q_P - Q_V = 8{,}320 \text{ J} - 5{,}000 \text{ J} = 3{,}320 \text{ J}$$

Example 13.3

A cylinder contains 5 moles of monatomic helium. At constant pressure, the helium gas undergoes a volume expansion and a temperature increase $\Delta T = T_f - T_i = 20\,\text{C}°$ due to the addition of heat Q_P, as shown in Fig. 13.6. (a) How much heat Q_P is added to the helium? (b) What is the change ΔE_{int} in the internal energy of the helium? (c) How much work W is done by the helium as it expands?

Fig. 13.6



Solution: (a) Treating the helium as an ideal monatomic gas undergoing a constant-pressure process, we use $C_P = 20.8\,\mathrm{J/mol.K}$ and $\Delta T = 20\,\mathrm{C}^\circ = 20\,\mathrm{K}$ in Eq. 13.20 to get:

$$Q_P = nC_P\Delta T = n(5R/2)\Delta T = (5\text{ mol})(20.8\text{ J/mol.K})(20\text{ K}) = 2{,}080\,\mathrm{J}$$

(b) Even though the temperature of the helium increases at a constant pressure (not at constant volume), we use Eq. 13.23 to calculate the change in internal energy when $C_V = 12.5\,\mathrm{J/mol.K}$ as follows:

$$\Delta E_{\mathrm{int}} = nC_V\Delta T = n(3R/2)\Delta T = (5\text{ mol})(12.5\text{ J/mol.K})(20\,\mathrm{K}) = 1{,}250\,\mathrm{J}$$

(c) From the first law of thermodynamics, $\Delta E_{\mathrm{int}} = Q_P - W$, we calculate the work done by the gas in this process as follows:

$$W = Q_P - \Delta E_{\mathrm{int}} = 2{,}080\,\mathrm{J} - 1{,}250\,\mathrm{J} = 830\text{ J}$$

Of all the heat energy $Q_P = 2{,}080\,\mathrm{J}$ that is transferred to the helium during the increase in temperature, only 1,250 J goes to increasing the helium's internal energy and hence its temperature. The remaining 830 J is transferred out of the helium as work done during the expansion.

Internal Energy of a Diatomic Ideal Gas

In a diatomic ideal-gas model, a molecule can rotate about two different axes, while the rotation about the third axis passing through the two atoms gives very little energy because the moment of inertia about this axis is very small, see Fig. 13.7.

Therefore, a diatomic gas is said to have five energy degrees of freedom: three translational and two rotational. According to the principle of equipartition of energy, each active degree of freedom of a molecule has on average an energy equal to $\frac{1}{2}k_BT$. Thus, the average energy for a molecule in a diatomic gas is:

$$\boxed{E = \tfrac{5}{2}k_BT} \quad \text{(Diatomic ideal gas)} \tag{13.34}$$

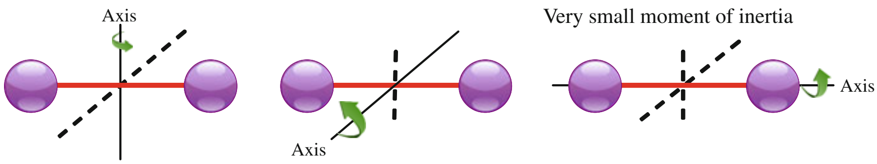


Fig. 13.7 A diatomic molecule can rotate about two perpendicular axes with appreciable rotational energy while the rotation about the third axis gives very little rotational energy (i.e. only two degrees of freedom)

Hence, the internal energy E_{int} of a diatomic ideal gas of N (or n kmol) at pressure P, volume V, and temperature T will be:

$$\boxed{E_{\text{int}} = \begin{cases} \tfrac{5}{2}Nk_BT \\ \tfrac{5}{2}nRT \end{cases}} \quad \text{(Diatomic ideal gas)} \tag{13.35}$$

In general, *the internal energy of an ideal gas is a function of T only*, and the exact relationship depends on the type of gas. The vibrational (kinetic and potential) degrees of freedom have only a tiny effect on Eqs. 13.34 and 13.35 unless the temperature is extremely high. Quantum mechanical study (which is not our aim) predicts discrete vibrational levels with spacing generally much larger than k_BT.

We can use the above results and Eq. 13.25 to find C_V and C_P as follows:

$$\boxed{\begin{aligned} C_V &= \frac{1}{n}\frac{dE_{\text{int}}}{dT} = \frac{1}{n}\frac{d}{dT}\left(\tfrac{5}{2}nRT\right) = \tfrac{5}{2}R \\ C_P &= C_V + R = \tfrac{7}{2}R \end{aligned}} \quad \text{(Diatomic ideal gas)} \tag{13.36}$$

Table 13.2 displays the measured molar specific heats of some gases. These results are in good agreement with the predicted C_V and C_P. The small deviations from the predicted values are due to the fact that real gases are not ideal gases. Real gases experience weak intermolecular interactions, which are not addressed in the presented ideal gas model.

Table 13.2 Some molar specific heats of various gases at 15 °C

Molar specific heat (J/mol C°)				
Gas	C_p	C_V	$C_P - C_V$	$\gamma = C_P/C_V$
Monatomic gases				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
Diatomic gases				
H_2	20.8	20.4	8.33	1.41
N_2	29.1	20.8	8.33	1.40
O_2	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl_2	34.7	25.7	8.96	1.35
Triatomic gases				
CO_2	37.0	28.5	8.50	1.30
SO_2	40.4	31.4	9.00	1.29
H_2O	35.4	27.0	8.37	1.30

13.3 Distribution of Molecular Speeds

Molecules in a gas at thermal equilibrium are assumed to be in random motion, i.e. they have a wide range of molecular speeds. In 1859, James Clerk Maxwell derived an expression that describes the distribution of speeds in a gas containing N molecules in thermal equilibrium at temperature T. The number of molecules dN with speeds in the range v and $v + dv$ is defined by the distribution function $f(v)$ (known as Maxwell-Boltzmann distribution) through the following relation:

$$dN = f(v)\,dv = 4\pi N \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2\, e^{-\frac{1}{2}mv^2/k_B T}\,dv \tag{13.37}$$

where m is the mass of a gas molecule, k_B is Boltzmann's constant, and T is the absolute gas temperature. A sketch of the distribution function $f(v)$ is shown in Fig. 13.8 at a certain temperature T.

The average speed $\bar{v}$ can be obtained by integrating the product of the speed v with dN and dividing by the total number N. In addition, one can find v_{rms} and the most probable speed v_p as follows:

$$\bar{v} = \frac{1}{N} \int_{0}^{\infty} v f(v)\, dv = \sqrt{\frac{8}{\pi} \frac{k_B T}{m}} \tag{13.38}$$

$$v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{1}{N} \int_0^\infty v^2 f(v)\, dv} = \sqrt{\frac{3 k_B T}{m}} \tag{13.39}$$

$$v_p = \sqrt{\frac{2 k_B T}{m}} \tag{13.40}$$

From these results, we see that $v_{\mathrm{rms}} > \bar{v} > v_p$ as displayed in Fig. 13.8.

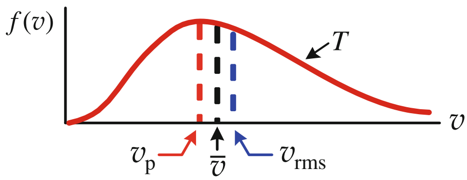


Fig. 13.8 Distribution of speeds of an ideal gas, $f(v)$. The area under the curve gives the total number of gas molecules. The speed at the peak v_p is less that $\bar{v}$ and v_{rms} because $f(v)$ is skewed to the right of the peak

13.4 Non-ideal Gases and Phases of Matter

The isothermal PV-diagram presented in Sect. 12.4 and Sect. 13.2 can help us grasp the overall behavior of a gas described by the gas law $PV = nRT$. The PV-isotherm for a constant amount of an ideal gas is displayed for temperatures $T_4 > T_3 > T_2 > T_1$ in Fig. 13.9a. Notice that the pressure P is inversely proportional to V and that the isotherms are hyperbolic curves.

Fig. 13.9b displays a PV-diagram for a substance that does not obey the ideal gas law for temperatures $T_4 > T_3 > T_c > T_2 > T_1$. The solid curve at T_4 represents the behavior of the non-ideal gas, while the dashed curve represents the behavior predicted by the ideal gas law at the same temperature. The curves at T_3 and T_c deviate more from the dashed curves predicted by the ideal gas law. At successively lower temperatures T_2 and T_1 (both below T_c), the behavior deviates even more from the curves of part a, and the isotherms develop flat regions in which the substance can be compressed without an increase in its pressure. Observation shows that the non-ideal gas is condensing from vapor (gas) to a **liquid state**. The colored region represents isotherms in their **liquid-vapor phase equilibrium**. A transition from one phase to another requires **phase equilibrium** between the two phases. This occurs at only one definite temperature for a given pressure value.

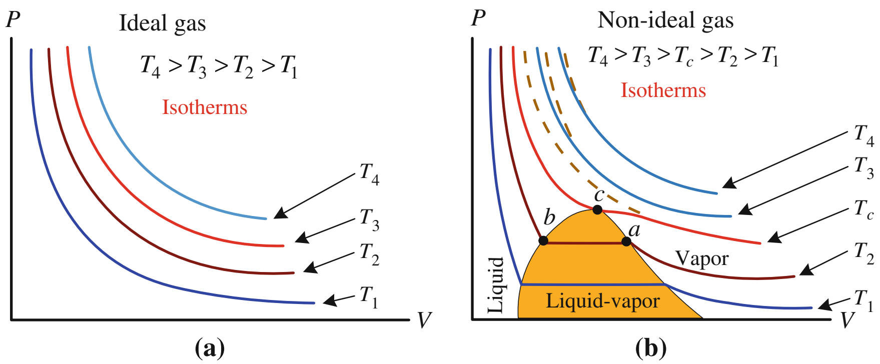


Fig. 13.9 (a) An isothermal P-V diagram of an ideal gas for temperatures $T_4 > T_3 > T_2 > T_1$. (b) An isothermal P-V diagram for a non-ideal gas for temperatures $T_4 > T_3 > T_c > T_2 > T_1$.

Kinetic theory can help us understand this behavior if we note that at higher pressures, and particularly at lower temperatures, the attractive potential energy due to attractive forces between molecules cannot be ignored as in the case of an ideal gas. These attractive forces at lower temperatures tend to pull the molecules and cause liquefaction.

The curve at T_c in Fig. 13.9b represents the substance at its **critical temperature**, and point c on the curve is called the **critical point**. When we compress the gas at constant temperature $T_2 (< T_c)$ it will be in the vapor state until point a is reached. As the volume decreases even more, it begins to liquefy and both the temperature and pressure remain constant. At point b, the substance is in the liquid state. Note that, a substance below T_c in the gaseous state is called a **vapor**, whereas above T_c, it is called a **gas**.

We can represent the condition of phase equilibrium on a PT-diagram such as that in Fig. 13.10. This diagram is referred to as a phase diagram and displays the following:

1. The curve labeled L-V represents points where liquid and vapor phases are in equilibrium (*boiling point* versus *pressure* curve)
2. The curve labeled S-L represents points where solid and liquid phases are in equilibrium (*freezing point* versus *pressure* curve)

3. The curve labeled S-V represents points where solid and vapor phases are in equilibrium (*sublimation point* versus *pressure* curve)

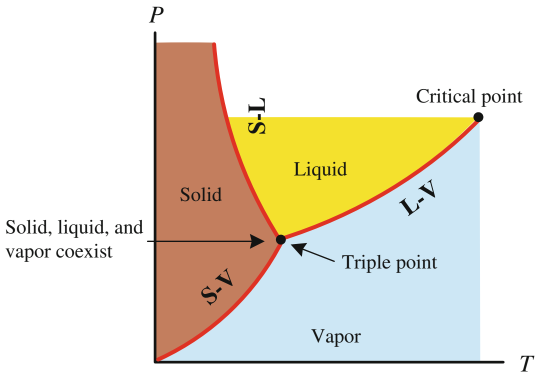


Fig. 13.10 A P-T diagram of a non-ideal substance showing regions of temperature and pressure at which the various phases exist

All three curves meet at the **triple point**, the only condition under which all three phases can coexist. Because the triple point corresponds to a unique value of temperature and pressure, it is precisely reproducible and is frequently used as a reference point. In Sect. 11.1, we used the triple-point temperature of water to define the Kelvin scale. This point occurs at $T = 273.16$ K and $P = 4.58$ mm Hg $= 6.026 \times 10^{-3}$ atm.

13.5 Exercises

Section 13.1 Microscopic Model of an Ideal Gas

(1) In an interval of 1 s, the total number of oxygen molecules that collide perpendicularly with a wall of an area $A = 10^{-3}\ \text{m}^2$ is $N = 5 \times 10^{23}$ molecules. Assume that each molecule has a mass $m = 5.3 \times 10^{-26}$ kg and moves with a perpendicular speed $v = 500$ m/s. What is the pressure exerted on the wall by these oxygen molecules?

(2) A 2-mol sample of oxygen gas is at STP [A *standard temperature and pressure* implies a temperature of 0 °C (273.15 K) and an atmospheric pressure of 1 atm]. (a) What is the average translational kinetic energy of an oxygen molecule under these conditions? (b) What is the total translational kinetic energy of the oxygen molecules?

(3) A gas is at 27 °C. Find the temperature at which the rms (*root mean square*) speed of its molecules is doubled.

(4) Bellatrix (or Amazon) star is one of the hottest stars that we can see with the naked eye and its surface temperature is about 3×10^4 K. (a) Find the rms speed of helium atoms near the surface of this star. (b) Compare the value of part (a) with the rms speed at 27 °C.

(5) A vessel of volume $V = 4 \times 10^{-2}$ m^3 filled with nitrogen gas contains $n = 4$ mol at a pressure $P = 2$ atm. (a) What is the temperature of this gas? (b) What is the average translational kinetic energy of a nitrogen molecule under these conditions?

(6) (a) Use the definition of Avogadro's number to find the mass of a helium atom, given that the molar mass of He is 4.00 kg/kmol. (b) How many atoms of helium are confined in a container of volume $V = 10^{-4}$ m^3 at 27 °C and 1 atm? (c) What is the rms speed of the helium atoms?

(7) A sample of 2-mol of monatomic argon is at 27 °C. The molar mass of argon (Ar) is 39.95 kg/kmol. (a) What is the average translational kinetic energy of an argon atom in this sample? (b) What is the total translational kinetic energy of all the argon atoms?

(8) At a temperature of 100 °C, a mixture of the monatomic helium and argon gases is in thermal equilibrium. (a) What is the average kinetic energy for each type of atom? (b) What is the rms speed for each type of atom? Assume this mixture displays the properties of an ideal gas, and that the molar mass of helium (He) is 4.00 kg/kmol, and the molar mass of argon (Ar) is 39.95 kg/kmol.

(9) (a) Find the change in internal energy of $n = 4$ mol of monatomic neon gas when its temperature is increased by 10 C°. (b) Will your answer change if the gas is diatomic? Explain your reasoning.

(10) Assume that oxygen at STP is an ideal gas, and that each molecule occupies the same cubical volume a^3, where a is the length of one side of the cube. (a) Find the volume of each molecule. (b) Estimate of the average distance between the oxygen molecules.

(11) Find a relation that gives the rms speed $v_{\mathrm{rms}} = \sqrt{3RT/M}$ of gas molecules in terms of the pressure P of the gas and its density ρ.

(12) A sample of nitrogen gas is at 0 °C. (a) What is the rms speed of a nitrogen molecule at this temperature? (b) Assuming that each molecule has no preferred direction and does not collide with any other molecule, find the time that one molecule will cross a cubical container of side $a = 1.5$ m. (c) Estimate the number of times that a molecule would move back and forth on the average.

Section 13.2 Molar Specific Heat Capacity of an Ideal Gas

(13) A cylinder contains 3 kmol of helium at a temperature of 27 °C. Heat is added to the gas to increase its temperature to 127 °C, (a) Find the quantity of heat Q_V if the gas is heated at a constant volume. (b) As the gas is heated at a constant pressure, find the amount of added heat Q_P, the work done by the gas W, and the increase in internal energy.

(14) A cylinder contains 1 kmol of monatomic ideal gas at initial temperatures of 27 °C, see the Fig. 13.4. In a fixed volume process, $Q_V = 2 \times 10^5$ J of heat is transferred to the gas from a heat reservoir. Find (a) the increase in the internal energy of the gas, and (b) its final temperature.

(15) A monatomic ideal gas has a specific heat $c_V = 95.2069$ J/kg.C°, which is nearly constant over a wide range of temperatures. What is the molar mass of the gas? Use the periodic table to find the name of this gas.

(16) A room 4 m × 4.5 m × 2.8 m contains air at 17 °C and 1 atm. Assume that the air in the room is an ideal diatomic gas with a molar specific heat at constant volume $C_V = 20.79 \times 10^3$ J/kmol.K. Also assume that there is no air or heat loss to the outside. If a heater in the room supplies 10^6 J/h, by how much will the temperature of the room rise in one hour?

(17) A two mol of an ideal diatomic gas at 20 °C is heated to 70 °C at constant pressure of 1 atm. (a) What is the change in the internal energy? (b) What is the work done by the gas? (c) Determine the quantity of heat added to the gas?

(18) A four mol of an ideal diatomic gas is at −30 °C. Assume that all the active degrees of freedom are three translational, two rotational, and two vibrational. What is the internal energy of the gas?

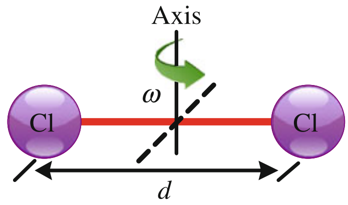
(19) Assume that a molecule in an ideal gas has α active degrees of freedom. Show that for n moles of this gas, the principle of equipartition theory predicts that: (a) the total internal energy is $E_{\text{int}} = \frac{1}{2}\alpha nRT$; (b) the molar specific heat at constant volume is $C_V = \frac{1}{2}\alpha R$; (c) the molar specific heat at constant pressure is $C_P = \frac{1}{2}(\alpha+2)R$; (d) the molar specific heat ratio is $\gamma = C_P/C_V = (\alpha+2)/\alpha$.

(20) The diatomic molecule of chlorine (Cl_2) has a molar mass $M = 70$ kg/kmol. The distance between two chlorine atoms is $d = 2 \times 10^{-10}$ m. These two atoms rotate about their center of mass with an angular speed $\omega = 2 \times 10^{12}$ rad/s, see Fig. 13.11. What is the rotational kinetic energy of such a molecule?

(21) A cylinder contains 2 moles of air (a diatomic ideal gas) of volume $V = 6 \times 10^{-3}\,\text{m}^3$ at 27 °C. At constant pressure, the air undergoes a volume

expansion due to the addition of heat $Q_P = 5\,\text{kJ}$, as shown in Fig. 13.12. (a) Use Table 13.2 to find the values of C_P and C_V for air, if air contains 78.08% N_2, 20.95% O_2, 0.93% Ar, and 0.03% CO_2. (b) Find the change in temperature. (c) What is the change ΔE_{int} of the internal energy of the air? (d) Find the final volume of the air.

Fig. 13.11 See Exercise (20)



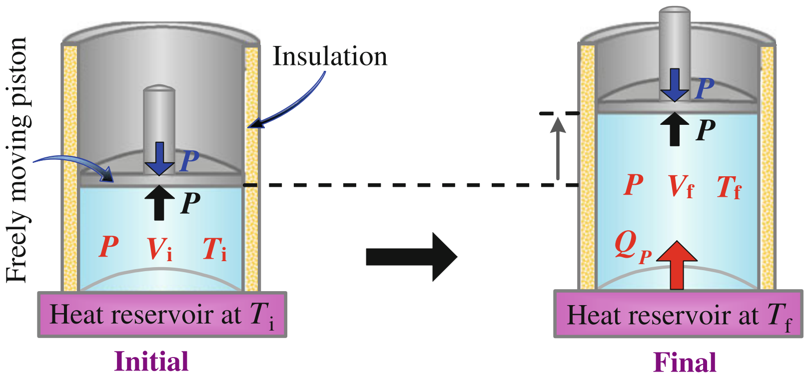


Fig. 13.12 See Exercise (21)

Section 13.3 Distribution of Molecular Speeds

(22) For the Maxwell-Boltzmann speed distribution given by Eq. 13.37 and displayed in Fig. 13.8, the most probable speed v_{p} of a gas molecule corresponds to a point on the curve at which the slope is zero, i.e. when the condition $df(v)/dv|_{v=v_{\text{p}}} = 0$ is fulfilled. Use this condition to show that v_{p} is given by Eq. 13.40.

(23) A container is filled with oxygen gas at $T = 300\,\text{K}$. (a) Find the rms speed v_{rms} of the oxygen molecule. (a) What is the average speed $\bar{v}$ of the oxygen molecule? (c) Find the value of the most probable speed v_{p}?

(24) The rms speed v_{rms} of a gas at temperature T_1 is equal to the most probable speed v_{p} at temperature T_2. Evaluate the ratio T_2/T_1.

(25) A container is composed of $N = 10^6$ oxygen molecules at $T = 300\,\mathrm{K}$. Assume that the gas obeys the Maxwell's speed distribution and the oxygen molecule has a mass $m = 5.31 \times 10^{-26}\,\mathrm{kg}$. Calculate the number of molecules with speeds between: (a) 300 m/s and 301 m/s; (b) 1,000 m/s and 1,001 m/s.