

Thermodynamic system

A thermodynamic system is a macroscopic region of the universe under study, with a quantity of matter of fixed identity. It is defined by boundaries, which control the transfers between the system and the surroundings (everything which is outside the boundary). The types of transfers that can occur in a thermodynamic process are mass and energy (work and heat).

Classification: A thermodynamic system can be classified as open, closed or isolated, according to the exchanges that can occur with the surroundings.

Closed system- exchanges of energy but not of matter. Example of closed system: Water heated in a closed vessel – Here only heat energy can pass in and out of the vessel.

Open system- exchanges of energy and matter. Example of open system: Water heated in an open container – Here, heat is the energy transferred, water is the mass transferred and container is the thermodynamic system. Both heat and water can pass in and out of the container.

Isolated system- does not exchange energy or matter. In reality, complete isolated systems do not exist. However, some systems behave like an isolated system for a finite period of time, such as: vacuum flask.

State of system: condition of system which is described by measurable properties: state variables.

State variables: macroscopic parameters that describe the properties of the system, when it is in equilibrium: temperature (T), pressure (P), volume (V). The state variables have the same value in every part of the system.

Zeroth Law of Thermodynamics, Thermal Equilibrium & Temperature

Consider the two systems *A* and *C* illustrated in Fig. 1 are separately in thermal equilibrium with system *B*, then system *A* and system *C* are also in thermal equilibrium with each other. This phenomenon are known as zeroth law of thermodynamics. The way to

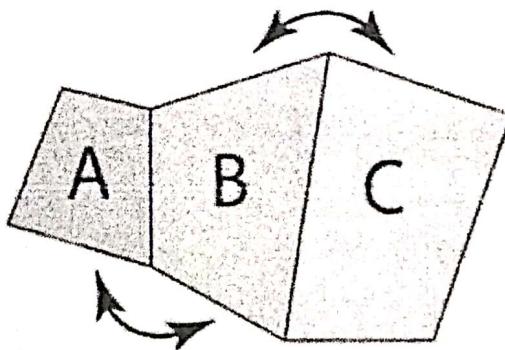


Figure 1: System *A* and system *C* separately in thermal equilibrium with system *B*.

test whether separated systems, *A* and *C*, are in thermal equilibrium is to use a third system, namely *B*. By placing *B* into contact with *A* and then with *C*, we could consider whether *A* and *C* are in thermal equilibrium without ever bringing *A* and *C* into direct contact.

When two systems are in thermal equilibrium, we say that they have the same temperature. Conversely, temperature is that property of a system which equals that of another system when the two systems are in thermal equilibrium. For example, suppose the systems are two gases that initially have different temperatures, pressures and volumes.

After we place them into contact and wait a sufficient long time for them to reach thermal equilibrium, their pressures will be in general no to be equal, nor their volumes; their temperatures, however, will always be equal in thermal equilibrium. *It is only through this argument based on thermal equilibrium that the notion of temperature can be introduced into thermodynamics.*

We wish to identify system B as a thermometer. If the thermometer comes separately into thermal equilibrium with systems A and C and indicates the same temperature, then we may conclude that A and C are in thermal equilibrium and thus do indeed have the same temperature.

Another statement of the zeroth law of thermodynamics, more formal and fundamental, is the following:

There exists a scalar quantity called temperature which is a property of all thermodynamic systems in equilibrium. two systems are in thermal equilibrium if and only if their temperatures are equal.

The zeroth law defines the concept of temperature and specifies it as one macroscopic property of a system that will be equal to that another system when they are in thermal equilibrium. The zeroth law permits us to build and use thermometers to measure the temperature of a system.

A CLOSER LOOK AT HEAT & WORK

In the macroscopic approach to thermodynamics, we describe the *state* of a system using such variables as

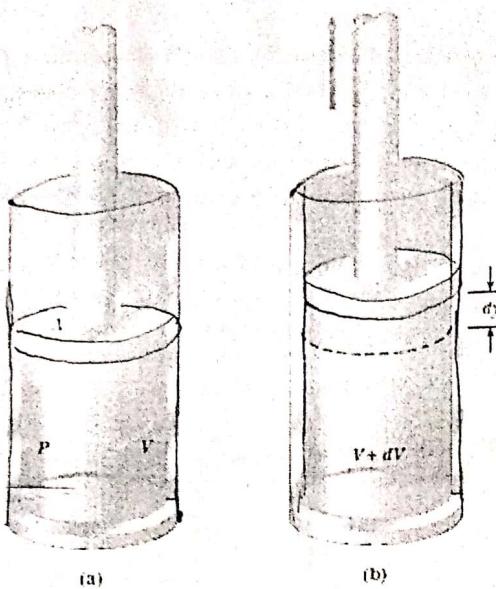


Figure 1: Gas contained in a cylinder at a pressure P does work on a moving piston as the system expands from a volume V to a volume $V + dV$.

pressure, volume, temperature, and internal energy. The number of macroscopic variables needed to characterize a system depends on the nature of the system. For a homogeneous system, such as a gas containing only one type of molecule, usually only two variables are needed. However, it is important to note that a *macroscopic state* of an isolated system can be specified only if the system is in thermal equilibrium internally. In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature.

Consider a gas contained in a cylinder fitted with a movable piston (Fig. 1). At equilibrium, the gas occupies a volume V and exerts a uniform pressure P on the cylinder's walls and on the piston. If the piston has a cross-sectional area A , the force exerted by the gas on the piston is $F = PA$. Now let us assume that the gas expands quasi-statically, that is, slowly enough to allow the system to remain essentially in thermal equilibrium at all times. As the piston moves up a distance dy , the work done by the gas on the piston is

$$dW = Fdy = PAdy$$

Because Ady is the increase in volume of the gas dV , we can express the work done by the gas as

$$dW = PdV \quad (1)$$

Because the gas expands, dV is positive, and so the work done by the gas positive. If the gas were compressed,

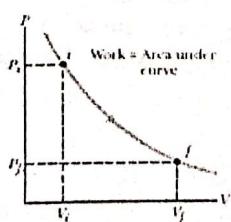


Figure 2: A gas expand quasi-statically(slowly) from state i to state f . The work done by gas equals the area under the PV curve.

dV would be negative, including that the work done by the gas (or work done on the gas) was negative. Thus, in thermodynamics, positive work represents a transfer of energy out of the system.

The total work done by the gas as its volume changes from V_i to V_f is given by the integral of Equation 1:

$$W = \int_{V_i}^{V_f} P dV \quad (2)$$

To evaluate this integral, we must know the values of the thermodynamic variables at every state through which the system passes between initial and final states. In the expansion we are considering here, we can plot the pressure and volume at each instant to create a PV diagram as shown in Figure 2.

The value of the integral in Equation 2 is the area bounded by such a curve. Thus, we can say that *the work done by a gas in the free expansion from an initial state to a final state is the area under the curve connecting the states in the PV diagram.*

As Figure 2 shows, the work done in the expansion from the initial state i to the final state f depends on the path taken between these two states, where the path on a PV diagram is a description of the thermodynamic process through which the system is taken. To illustrate this important point, consider several paths connecting

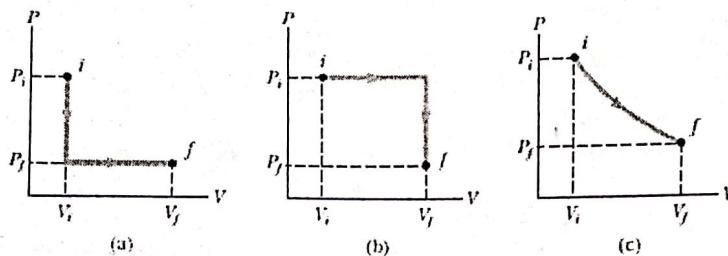


Figure 3: The work done by a gas as it is taken from an initial state to a final state depends on the path between these two states.

i and f (Fig. 3). The work done in each case is different because the paths are different connecting the same two states. Therefore, we see that **the work done by a system depends on the initial and final states and on the path followed by the system between these states.**

The energy transfer by heat Q into or out of a system also depends on the process i.e., depends on the initial, final and intermediate states of the system. In other words, because heat and work depend on the path, neither quantity is determined solely by the end points of a thermodynamics process.

THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is a generalization of the law of conservation of energy that encompasses

changes in internal energy. It is a universally valid law that can be applied to many processes and provides a connection between the microscopic and macroscopic worlds.

Suppose that a system undergoes a change from an initial state to a final state. During this change, energy transfer by heat Q to the system occurs, and work W is done by the system. As an example, suppose that the system is a gas in which the pressure and volume change from P_i and V_i to P_f and V_f . If the quantity $Q - W$ is measured for various paths connecting the initial and final equilibrium states, we find that it is the same for all paths connecting the two states. We conclude that the quantity $Q - W$ is determined completely by the initial and final states of the system, and we call this quantity the **change in the internal energy** of the system. Although Q and W both depend on the path, the quantity $Q - W$ is independent of the path. If we use the symbol E_{int} to represent the internal energy, then the change in internal energy ΔE_{int} can be expressed as

$$\Delta E_{int} = Q - W \quad (3)$$

where all quantities must have the same units of measure for energy. Equation 3 is known as the **first-law equation** and is a key concept in many applications.

When a system undergoes an infinitesimal change in state in which a small amount of energy dQ is transferred by heat and a small amount of work dW is done, the internal energy changes by a small amount dE_{int} . Thus, for infinitesimal processes we can express the first-law equation as

$$dE_{int} = dQ - dW \quad (4)$$

The first-law equation is an energy conservation equation specifying that the only type of energy that changes in the system is the internal energy E_{int} . Let us look at some special cases in which this condition exists.

First, let us consider an *isolated system*--that is, one that does not interact with its surroundings. In this case, no energy transfer by heat takes place and the value of the work done by the system is zero; hence, the internal energy remains constant. That is, because $Q = W = 0$ it follows that $\Delta E_{int} = 0$, and thus $E_{int,i} = E_{int,f}$. We conclude that the **internal energy E_{int} of an isolate system remains constant**.

Next, we consider the case of a system (one not isolated from its surroundings) that is taken through a cyclic process--that is, a process that starts and ends at the same state. In this case, the change in the internal energy must again be zero, and therefore the energy Q added to the system must equal the work W done by the system during the cycle. That is, in a cyclic process, $\Delta E_{int} = 0$ and $Q = W$.

On a PV diagram, a cyclic process appears as a closed curve (The processes described in Figure 3 are represented by open curves because the initial and final states differ.) It can be shown that in a **cyclic process, the net work done by the system per cycle equals the area enclosed by the path representing the process on a PV diagram**.

If the value of the work done by the system during some process is zero, then the change in internal energy ΔE_{int} equals the energy transfer Q into or out of the system:

$$\Delta E_{int} = Q$$

If energy enters the system, then Q is positive and the internal energy increases. For a gas, we can associate this increase in internal energy with an increase in the kinetic energy of the molecules. Conversely, if no energy transfer occurs during some process but work is done by the system, then the change in internal energy equals the negative value of the work done by the system:

$$\Delta E_{int} = -W$$

For example, if a gas is compressed by a moving piston in an insulated cylinder, no energy is transferred by heat and the work done by the gas is negative: thus, the internal energy increases because kinetic energy is transferred from the moving piston to the gas molecules.

One of the important consequences of the first law of thermodynamics is that there exists a quantity known as internal energy whose value is determined by the state of the system. The internal energy function is therefore called a *state function*.

SOME APPLICATIONS OF THE FIRST LAW OF THERMODYNAMICS

An **adiabatic process** is one during which no energy enters or leaves the system by heat--that is, $Q = 0$.

An adiabatic process can be achieved either by thermally insulating the system from its surroundings or by performing the process rapidly, so that there is little time for energy to transfer by heat. Applying the first law of thermodynamics to an adiabatic process, we see that

$$\Delta E_{int} = -W \tag{5}$$

From this result, we see that if a gas expands adiabatically such that W is positive, then ΔE_{int} is negative and the temperature of the gas decreases. Conversely, the temperature of a gas increases when the gas is compressed adiabatically.

The process described in Figure 4, called an **adiabatic free expansion**, is unique. The process is adiabatic because it takes place in an insulated container. Because the gas expands into a vacuum, it does not apply a force on a piston so no work is done on or by the gas. Thus, in this adiabatic process, both $Q = 0$ and $W = 0$. As a result, $\Delta E_{int} = 0$ for this process, as we can see from the first law. That is, the **initial and final internal energies of a gas are equal in an adiabatic free expansion**.

A process that occurs at constant pressure is called an **isobaric process**. In such a process, the values of the heat and the work are both usually nonzero. The work done by the gas is simply

$$W = P(V_f - V_i) \tag{6}$$

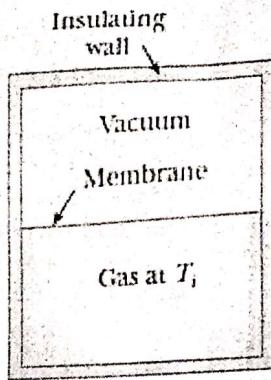


Figure 4: A gas expands rapidly into an evacuated region after membrane is broken

where P is the constant pressure.

A process that takes place at constant volume is called an **isovolumetric process**. In such a process, the value of the work done is clearly zero because the volume does not change. Hence, from the first law we see that in an isovolumetric process, because $W = 0$

$$\Delta E_{int} = 0 \quad (7)$$

This expression specifies that if energy is added by heat to a system kept at constant volume, then all of the transferred energy remains in the system as an increase of the internal energy of the system. For example, when a can of spray paint is thrown into a fire, energy enters the system (the gas in the can) by heat through the metal walls of the can. Consequently, the temperature, and thus the pressure, in the can increases until the can possibly explodes.

A process that occurs at constant temperature is called an **isothermal process**. A plot of P versus V at constant temperature for an ideal gas yields a hyperbolic curve called an *isotherm*. The internal energy of an ideal gas is a function of temperature only. Hence, in an isothermal process involving an ideal gas, $\Delta E_{int} = 0$. For an isothermal process, then, we conclude from the first law that the energy transfer Q must be equal to the work done by the gas—that is, $Q = W$. Any energy that enters the system by heat is transferred out of the system by work; as a result, no change of the internal energy of the system occurs.

Isothermal Expansion osf an Ideal Gas

Suppose that an ideal gas is allowed to expand quasi statically at constant temperature, as described by the

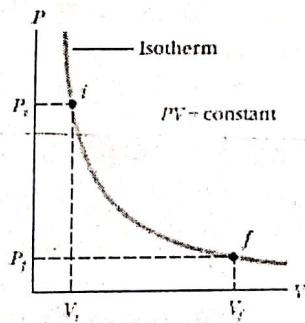


Figure 5: The PV diagram for an isothermal expansion of an ideal gas from an initial state to a final state. The curve is a hyperbola.

PV diagram shown in Figure 5. The curve is a hyperbola, and the equation of state of an ideal gas with T constant indicates that the equation of this curve is $PV = \text{constant}$. Let us calculate the work done by the gas in the expansion from state i to state f . The work done by the gas is given by $W = \int_{V_i}^{V_f} PdV$. Because the gas is ideal and the process is quasi-static, we can use the expression $PV = nRT$ for each point on the

path. Therefore, we have

$$W = \int_{V_i}^{V_f} P dV = \int_{V_i}^{V_f} \frac{nRT}{V} dV$$

Because T is constant in this case, it can be removed from the integral along with n and R :

$$W = nRT \int_{V_i}^{V_f} \frac{dV}{V} = nRT \ln V \Big|_{V_i}^{V_f}$$

To evaluate the integral, we used $\int (ds/x) = \ln x$. Evaluating this at the initial and final volumes, we have

$$W = nRT \ln \left(\frac{V_f}{V_i} \right) \quad (8)$$

Numerically, this work W equals the shaded area under the PV curve shown in Figure 5. Because the gas expands, $V_f > V_i$ and the value for the work done by the gas is positive, as we expect. If the gas is compressed, then $V_f < V_i$ and the work done by the gas is negative.

MOLECULAR MODEL OF AN IDEAL GAS

We are going to develop a microscopic model of an ideal gas. The model shows that the pressure that a gas exerts on the walls of its container is a consequence of the collisions of the gas molecules with the walls. In developing this model, we make the following assumptions:

1. The number of molecules is large, and the average separation between molecules is great compared with their dimensions. This means that the volume of the molecules is negligible when compared with the volume of the container.
2. The molecules obey Newton's laws of motion, but as a whole they move randomly. By "randomly" we mean that any molecule can move in any direction with equal probability. We also assume that the distribution of speeds does not change in time, despite the collisions between molecules. That is, at any given moment, a certain percentage of molecules move at high speeds, a certain percentage move at low speeds, and a certain percentage move at speeds intermediate between high and low.
3. The molecules undergo elastic collisions with each other and with the walls of the container. Thus, in the collisions, both kinetic energy and momentum are constant.
4. The forces between molecules are negligible except during a collision. The forces between molecules are short-range, so the molecules interact with each other only during collisions.
5. The gas under consideration is a pure substance. That is, all of its molecules are identical.

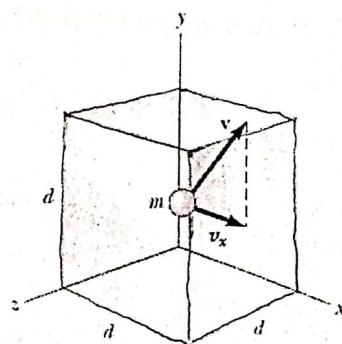


Figure 6: A cubical box with sides of length d containing an ideal gas. The molecule shown moves with velocity v .

Kinetic Interpretation of Pressure Now let us derive an expression for the pressure of an ideal gas consisting of N molecules in a container of volume V . The container is a cube with edges of length d (Fig. 6). Consider the collision of one molecule moving with a velocity v toward the right-hand face of the box. The molecule has

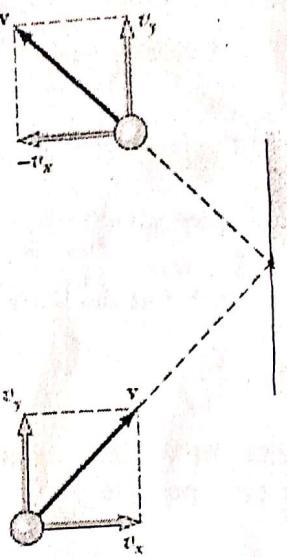


Figure 7: A molecule makes an elastic collision with the wall of the container. Its x component of momentum is reversed, while its y component remains unchanged. In this construction, we assume that the molecule moves in the xy plane.

velocity components v_x , v_y , and v_z . Assume m to represent the mass of one molecule. As the molecule collides with the wall elastically, its x component of velocity is reversed, while its y and z components of velocity remain unaltered (Fig. 7). Because the x component of the momentum of the molecule is mv_x before the collision and $-mv_x$ after the collision, the change in momentum of the molecule is

$$\Delta p_x = -mv_x - (mv_x)$$

Applying the impulse-momentum theorem to the molecule gives

$$F_1 \Delta t = \Delta p_x = -2mv_x$$

where F_1 is the magnitude of the average force exerted by the wall on the molecule in the time Δt . The subscript 1 indicates that we are currently considering only one molecule. For the molecule to collide twice with the same wall, it must travel a distance $2d$ in the x direction. Therefore, the time interval between two collisions with the same wall is $\Delta t = 2d/v_x$. Over a time interval that is long compared with Δt , the average force exerted on the molecule for each collision is

$$F_1 = \frac{-2mv_x}{\Delta t} = \frac{-2mv_x}{2d/v_x} = \frac{-mv_x^2}{d} \quad (9)$$

According to Newton's third law, the average force exerted by the molecule on the wall is equal in magnitude and opposite in direction to the force in Equation 9:

$$F_{1,\text{onwall}} = -F_1 = -\frac{-mv_x^2}{d} = \frac{mv_x^2}{d}$$

Each molecule of the gas exerts a force F_1 on the wall. We find the total force F exerted by all the molecules on the wall by adding the forces exerted by the individual molecules:

$$F = \frac{m}{d} (v_{x1}^2 + v_{x2}^2 + \dots)$$

In this equation, v_{x1} is the x component of velocity of molecule 1, v_{x2} is the x component of velocity of molecule 2, and so on. The summation terminates when we reach N molecules because there are N molecules in the container.

To proceed further, we must note that the average value of the square of the velocity in the x direction for N molecules is

$$\overline{v_x^2} = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

Thus, the total force exerted on the wall can be written

$$F = \frac{Nm}{d} v_x^2$$

Now let us focus on one molecule in the container whose velocity components are v_x , v_y , and v_z . The Pythagorean theorem relates the square of the speed of this molecule to the squares of these components:

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

Hence, the average value of v^2 for all the molecules in the container is related to the average values of v_x^2 , v_y^2 , and v_z^2 according to the expression

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}$$

Because the motion is completely random, the average values $\overline{v_x^2}$, $\overline{v_y^2}$, and $\overline{v_z^2}$ are equal to each other. Using this fact and the previous equation, we find that

$$\overline{v^2} = 3\overline{v_x^2}$$

Thus, the total force exerted on the wall is

$$F = \frac{N}{3} \left(\frac{mv^2}{d} \right)$$

Using this expression, we can find the total pressure exerted on the wall:

$$P = \frac{F}{A} = \frac{F}{d^2} = \frac{1}{3} \left(\frac{N}{d^3} mv^2 \right) = \frac{1}{3} \left(\frac{N}{V} \right) mv^2 = \frac{2}{3} \left(\frac{N}{V} \right) \left(\frac{1}{2} mv^2 \right) \quad (10)$$

This result indicates that the pressure is proportional to the number of molecules per unit volume and to the average translational kinetic energy of the molecules, $\frac{1}{2}mv^2$. In deriving this simplified model of an ideal gas, we obtain an important result that relates the large-scale quantity of pressure to an atomic quantity—the average value of the square of the molecular speed.

One way to increase the pressure inside a container is to increase the number of molecules per unit volume in the container. This is what you do when you add air to a tire. The pressure in the tire can also be increased by increasing the average translational kinetic energy of the air molecules in the tire. As we shall soon see, this can be accomplished by increasing the temperature of that air. It is for this reason that the pressure inside a tire increases as the tire warms up during long trips. The continuous flexing of the tire as it moves along the surface of a road results in work done as parts of the tire distort and in an increase in internal energy of the rubber. The increased temperature of the rubber results in the transfer of energy by heat into the air inside the tire. This transfer increases the air's temperature, and this increase in temperature in turn produces an increase in pressure.

Molecular Kinetic interpretation of Temperature

We can gain some insight into the meaning of temperature by first writing Equation 10 in the more familiar

form

$$PV = \frac{2}{3}N \left(\frac{1}{2}mv^2 \right)$$

Let us now compare this with the equation of state (molecular) for an ideal gas

$$PV = Nk_B T$$

The equation of state is based on experimental facts concerning the macroscopic behavior of gases. Equating the right sides of these expressions, we find that

$$T = \frac{2}{3k_B} \left(\frac{1}{2}mv^2 \right) \quad (11)$$

That is, temperature is a direct measure of average molecular kinetic energy. By rearranging Equation 11, we can relate the translational molecular kinetic energy to the temperature:

$$\frac{1}{2}mv^2 = \frac{3}{2}k_B T \quad (12)$$

That is, the average translational kinetic energy per molecule is $\frac{3}{2}k_B T$. Because $\overline{v^2} = \frac{1}{3}v^2$ it follows that

$$\frac{1}{2}mv_x^2 = \frac{1}{2}k_B T \quad (13)$$

In a similar manner, it follows that the motions in the y and z directions give us $\frac{1}{2}mv_y^2 = \frac{1}{2}k_B T$ and $\frac{1}{2}mv_z^2 = \frac{1}{2}k_B T$ respectively. Thus, each translational degree of freedom contributes an equal amount of energy to the gas, namely, $\frac{1}{2}k_B T$ (In general, "degrees of freedom" refers to the number of independent means by which a molecule can possess energy.) A generalization of this result, known as the **theorem of equipartition of energy**, states that *each degree of freedom contributes $\frac{1}{2}k_B T$ to the energy of a system*.

The total translational kinetic energy of N molecules of gas is simply N times the average energy per molecule, which is given by Equation 12:

$$E_{trans} = N \left(\frac{1}{2}mv^2 \right) = \frac{3}{2}Nk_B T = \frac{3}{2}nRT \quad (14)$$

where we have used $k_B = R/N_A$ for Boltzmann's constant and $n = N/N_A$ for the number of moles of gas. If we consider a gas for which the only type of energy for the molecules is translational kinetic energy, we can use Equation 14 to express the internal energy of the gas. This result implies that the internal energy of an ideal gas depends only on the temperature.

The square root of V is called the **rms speed** of the molecules. From Equation 12 we obtain, for the rms speed,

$$v_{rms} = \sqrt{\overline{v^2}} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \quad (15)$$

where M is the molar mass in kilograms per mole. This expression shows that, at a given temperature, lighter molecules move faster, on the average, than do heavier molecules.

MOLAR SPECIFIC HEAT OF AN IDEAL GAS

Let n moles of an ideal gas at pressure P and temperature T , confined to a cylinder of fixed volume V . This initial state of the gas is denoted by i . Suppose you add a small amount of energy to the gas as heat Q . The gas temperature rises a small amount to $T + \Delta T$, and its pressure rises to $P + \Delta P$, bringing the gas to final state f . In such experiments, we would find that the heat Q is related to the temperature change ΔT by

$$Q = nC_V \Delta T \quad (16)$$

where C_V is a constant called the **molar specific heat at constant volume**. Substituting this expression for Q into the first law of thermodynamics as given by ($\Delta E_{int} = Q - W$) yields

$$\Delta E_{int} = nC_V \Delta T - W \quad (17)$$

With the volume held constant, the gas cannot expand and thus cannot do any work. Therefore, $W = 0$, and Eq. 17 gives us

$$C_V = \frac{\Delta E_{int}}{n\Delta T} \quad (18)$$

But we know, the change in internal energy must be

$$\Delta E_{int} = \frac{3}{2}nR\Delta T \quad (19)$$

Substituting this result into Eq. 18 yields

$$C_V = \frac{3}{2}R = 12.5 J/mol.K \quad (20)$$

Eq. 20 is applicable for monatomic gases.

We now assume that the temperature of our ideal gas is increased by the same small amount ΔT as previously but now the necessary energy (heat Q) is added with the gas under constant pressure. we find that the heat Q is related to the temperature change ΔT by

$$Q = nC_P\Delta T \quad (21)$$

where C_P is a constant called the molar specific heat at constant pressure. This C_P is greater than the molar specific heat at constant volume C_V , because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work.

To relate molar specific heats C_P and C_V , we start with the first law of thermodynamics:

$$\Delta E_{int} = Q - W = nC_P\Delta T - W \quad (22)$$

For $\Delta E_{int} = nC_V\Delta T$ and $W = P\Delta V$, Eq. 22 reduces to

$$nC_V\Delta T = nC_P\Delta T - P\Delta V \quad (23)$$

For the ideal gas ($PV = nRT$), the work can be written as $W = P\Delta V = nR\Delta T$. Eq. 23 is giving us with dividing by $n\Delta T$

$$C_V = C_P - R \quad (24)$$

and then

$$C_P = C_V + R \quad (25)$$

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

ADIABATIC PROCESSES FOR AN IDEAL GAS

An adiabatic process is one in which no energy is transferred by heat between a system and its surroundings.

For example, if a gas is compressed (or expanded) very rapidly, very little energy is transferred out of (or into) the system by heat, and so the process is nearly adiabatic. Another example of an adiabatic process is the very slow expansion of a gas that is thermally insulated from its surroundings.

Proof That $PV^\gamma = \text{constant}$ for an Adiabatic Process

When a gas expands adiabatically in a thermally insulated cylinder, no energy is transferred by heat between the gas and its surroundings; thus, $Q = 0$. Let us take the infinitesimal change in volume to be dV and the infinitesimal change in temperature to be dT . The work done by the gas is PdV . Because the internal energy of an ideal gas depends only on temperature, the change in the internal energy in an adiabatic expansion is the same as that for an isovolumetric process between the same temperatures, $dE_{int} = nC_VdT$. Hence, the first law of thermodynamics, $\Delta E_{int} = Q - W$, with $Q = 0$, becomes

$$dE_{int} = nC_VdT = -PdV \quad (26)$$

Taking the total differential of the equation of state of an ideal gas, $PV = nRT$, we see that

$$PdV + VdP = nRdT$$

Eliminating dT from these two equations, we find that

$$PdV + VdP = -\frac{R}{C_V}PdV$$

Substituting $R = C_P - C_V$ and dividing by PV , we obtain

$$\frac{dV}{V} + \frac{dP}{P} = -\left(\frac{C_P - C_V}{C_V}\right)\frac{dV}{V} = (1 - \gamma)\frac{dV}{V}$$

$$\frac{dP}{P} + \gamma \frac{dv}{V} = 0$$

Integrating this expression, we have

$$\ln P + \gamma \ln V = \text{constant}$$

which is equivalent to

$$PV^\gamma = \text{constant} \quad (27)$$

The PV diagram for an adiabatic expansion is shown in Figure 8. Because $\gamma > 1$, the PV curve is steeper than it would be for an isothermal expansion.

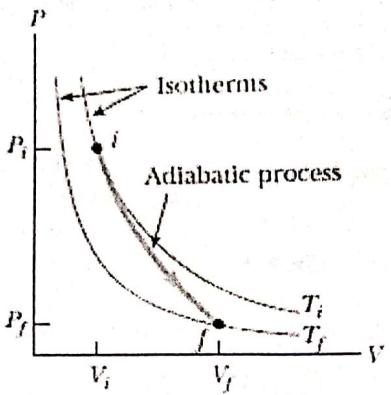


Figure 8: The PV diagram for an adiabatic expansion. Note that $T_f < T_i$ in this process.

than it would be for an isothermal expansion. Applying Equation 27 to the initial and final states, we see that

$$P_i V_i^\gamma = P_f V_f^\gamma \quad (28)$$

Using the ideal gas law, we can express Equation 28 as

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \quad (29)$$

MEAN FREE PATH

Most of us are familiar with the fact that the strong odor associated with a gas such as ammonia may take

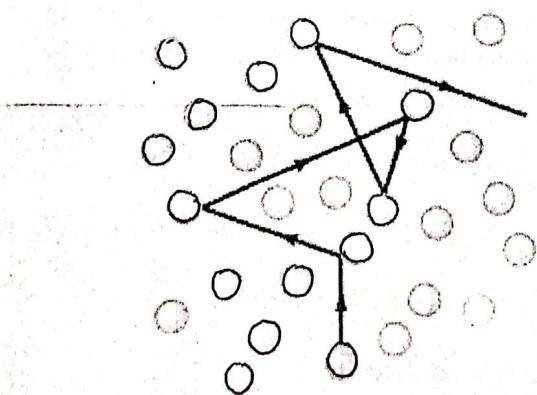


Figure 9: A molecule moving through a gas collides with other molecules in a random fashion. This behavior is sometimes referred to as a *random-walk process*.

a fraction of a minute to diffuse throughout a room. Molecules collide with one other because they are not geometrical points. Therefore, they do not travel from one side of a room to the other in a straight line. Between collisions, the molecules move with constant speed along straight lines. The average distance between

collisions is called the mean free path λ . The path of an individual molecule is random and resembles that shown in Figure 9. We now describe how to estimate the mean free path for a gas molecule. For this calculation, we assume that the molecules are spheres of diameter d . We see from Figure 10a that no two molecules collide unless their centers are less than a distance d apart as they approach each other. An equivalent way to describe the collisions is to imagine that one of the molecules has a diameter $2d$ and that the rest are geometrical points (Fig. 10b). Let us choose the large molecule to be one moving with the average speed \bar{v} . In a time t , this molecule

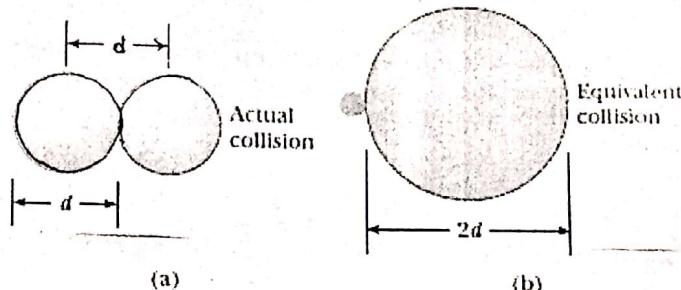


Figure 10: (a) Two spherical molecules, each of diameter d , collide if their centers are within a distance d of each other. (b) The collision between the two molecules is equivalent to a point molecule's colliding with a molecule having an effective diameter of $2d$.

travels a distance $\bar{v}t$. In this time interval, the molecule sweeps out a cylinder having a cross-sectional area πd^2 and a length $\bar{v}t$ (Fig. 11). Hence, the volume of the cylinder is $\pi d^2 \bar{v}t$. If n_V is the number of molecules per

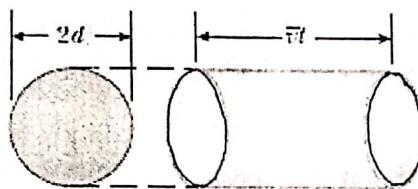


Figure 11: In a time t , a molecule of effective diameter $2d$ sweeps out a cylinder of length $\bar{v}t$, where \bar{v} is its average speed. In this time, it collides with every point molecule within this cylinder.

unit volume, then the number of point-size molecules in the cylinder is $(\pi d^2 \bar{v}t)n_V$. The molecule of equivalent diameter $2d$ collides with every molecule in this cylinder in the time t . Hence, the number of collisions in the time t is equal to the number of molecules in the cylinder, $(\pi d^2 \bar{v}t)n_V$.

The mean free path λ equals the average distance $\bar{v}t$ traveled in a time t divided by the number of collisions that occur in that time:

$$\lambda = \frac{\bar{v}t}{(\pi d^2 \bar{v}t)n_V} = \frac{1}{\pi d^2 n_V} \quad (30)$$

Because the number of collisions in a time t is the number of collisions $(\pi d^2 \bar{v}t)n_V$ per unit time, or collision frequency f , is

$$f = \pi d^2 \bar{v}n_V \quad (31)$$

The inverse of the collision frequency is the average time between collisions, known as the mean free time. Our analysis of the mean free path has assumed that molecules in the cylinder are stationary is known as Clausius expression. When the motion of these molecules is included in the calculation, the correct result for mean free path (Maxwell's expression):

$$\lambda = \frac{1}{\sqrt{2\pi d^2 n_V}} \quad (32)$$

Equation of ideal gas

Suppose we have a cylinder filled with gas. Now, if we change the pressure on the gas keeping temperature

and amount of gas unchanged, we will have a relation between pressure P and volume V as

$$P \propto \frac{1}{V} \quad (33)$$

Eq. 33 is known as the Boyle's law.

Again if we now keep pressure and amount of gas as unchanged and change the temperature T (where T is in Kelvin scale), we will have a relation between pressure T and volume V as

$$V \propto T \quad (34)$$

Eq. 34 is known as the Charles' law. Finally, if we do not change the pressure and temperature, we will see that different amount of gas (or the different number of molecules of gas) N occupy different volume as a following relation

$$V \propto N \quad (35)$$

Eq. 35 is known as the Avogadro's law. Combining Eqs. 33, 34, and 35, we have an equation known as equation of ideal gas

$$V \propto N \frac{1}{V} T \Rightarrow PV = Nk_B T \quad (36)$$

where k_B is the Boltzmann's constant for each molecule. The eq. 36 is called the molecular form of ideal gas. For the gases, the amount is expressed by no. of moles n which is related to the N as $n = N/N_A$, where N_A is the Avogadro's number equal to 6.023×10^{23} . Substituting n in Eq. 36 gives

$$PV = nRT \quad (37)$$

where R is called the universal gas constant for n mole related with k_B as $R = kN_A$. The value of R is $8.314 \text{ J}/(\text{mol.K})$. The eq. 37 is called the molecular form of ideal gas.