FUNDAMENTALS

OF

CLASSICAL AND STATISTICAL

THERMODYNAMICS

SPRING 2005

1. Basic Concepts of Thermodynamics

The basic concepts of thermodynamics such as system, energy, property, state, process, cycle, pressure, and temperature are explained.

Thermodynamics can be defined as the science of energy. *Energy* can be viewed as the ability to cause changes.

Thermodynamics is concerned with the *transfer of heat* and the appearance or disappearance of work attending various chemical and physical processes.

- The natural phenomena that occur about us;
- Controlled chemical reactions;
- The performance of engines
- Hypothetical processes such as chemical reactions that do not occur but can be imagined.

HISTORY:

Thermodynamics emerged as a science with the construction of the first successful atmospheric steam engines in England by **Thomas Savery** in 1697 and **Thomas Newcomen** in 1712. These engines were very slow and inefficient, but they opened the way for the development of a new science.

The *first and second laws of thermodynamics* emerged simultaneously in the 1850s primarily out of the works of **William Rankine**, **Rudolph Clausius**, and **Lord Kelvin** (formerly William Thomson). The term *thermodynamics* was first used in a publication by Lord Kelvin in 1849. The first thermodynamic textbook was written in 1859 by William Rankine, a professor at the University of Glasgow.

Classical vs. Statistical Thermodynamics

Substances consist of large number of particles called *molecules*. The properties of the substance naturally depend on the behavior of these particles. For example, the pressure of a gas in a container is the result of momentum transfer between the molecules and the walls of the container. But one does not need to know the behavior of the gas particles to determine the pressure in the container. It would be sufficient to attach a pressure gage to the container.

This macroscopic approach to the study of thermodynamics which does not require knowledge of the behavior of individual particles is called ***classical thermodynamics***. It provides a direct and easy way to the solution of engineering problems.

> The only quantities and concepts which enter thermodynamics are the experimental properties of matter such as pressure, volume, temperature and composition. Such properties are the properties of matter in bulk rather than of individual isolated molecules and are, therefore, called *macroscopic properties* as opposed to *microscopic properties*.

A more elaborate approach, based on the average behavior of large groups of individual particles, is called ***statistical thermodynamics***.

The Usefulness of Thermodynamics

Thermodynamics is exceedingly general in its applicability, and this makes it a powerful tool for solving many kinds of important problem.

Every engineering activity involves an interaction between energy and matter; thus it is hard to imagine an area which does not relate to thermodynamics in some respect. Therefore, developing a good understanding of thermodynamic principles has long been an essential part of engineering education.

Examples:

- Can predict if a particular chemical process can take place under any given conditions.
    - The amount of energy that must be put into the process and its maximum yield can also be determined.
    - The effect of changes in these conditions upon the equilibrium state can also be predicted.

- Equations may be written correlating physical and chemical properties of substances.
- The measurement of the heat evolved during the combustion of all kinds of fuel has obvious practical significance for the fuel technologists.

Limitations of Thermodynamics

- Thermodynamics can often tell us, for example, that a process will occur but not how fast it will occur,

- It can often provide a quantitative description of an overall change in state without giving any indication of the character of the process by which the change might take place.

- Thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by microscopic models and theories.

- The **weakness** is that thermodynamics does not provide the deep insight into chemical and physical phenomena that is afforded by microscopic models and theories.

The Laws of Thermodynamics

Thermodynamics is the science of heat and temperature and, in particular, of the laws governing the conversion of heat into mechanical, electrical or other macroscopic forms of energy.

- It permits the derivation of relationships between different laws of nature, even though the laws themselves are not a consequence of thermodynamics.
- The relationships based upon it are completely independent of any microscopic explanation of chemical and physical phenomena.

Classical thermodynamics is based on the four laws of thermodynamics. In thermodynamics we are concerned with the behavior of vast quantities of particles in the substances that we study. The laws of thermodynamics are the laws of the generalized behavior of the particles. These laws are as follows:

1. The **zeroth law** deals with temperature and temperature scale.

2. The **first law** deals with macroscopic properties, work, energy, enthalpy, etc.

One of the most fundamental laws of nature is the conservation of energy principle. It simply states that during an interaction, energy can change from one form to another but the total amount of energy remains constant. That is, energy cannot be created or destroyed. A rock falling off a cliff, for example, picks up speed as a result of its potential energy being converted to kinetic energy.

The first law of thermodynamics is simply an expression of the conservation of energy principle, and it asserts that *energy* is a thermodynamic property.

3. The **second law** mainly deals with entropy, a property most fundamentally responsible for the behavior of matter.

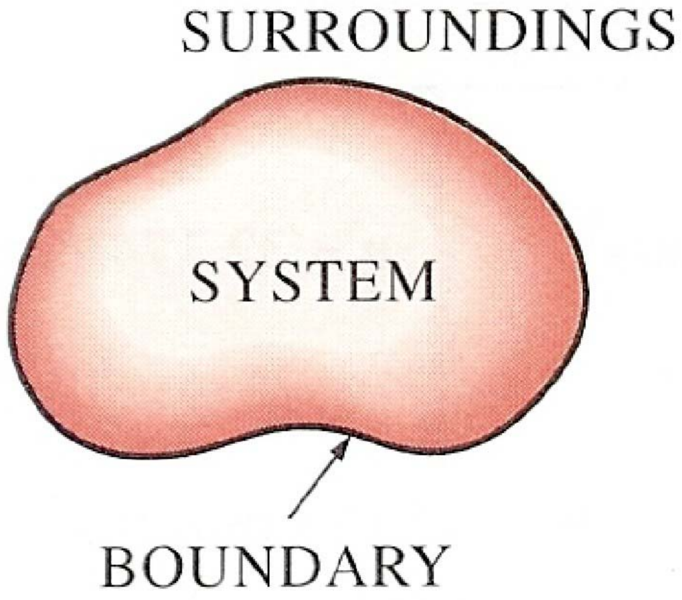
The second law of thermodynamics asserts that energy has *quality* as well as *quantity,* and actual processes occur in the direction of decreasing quality of energy.

Example: cooling of a cup of coffee is irreversible.

4. The **third law** deals with the determination of entropy.

Thermodynamic System

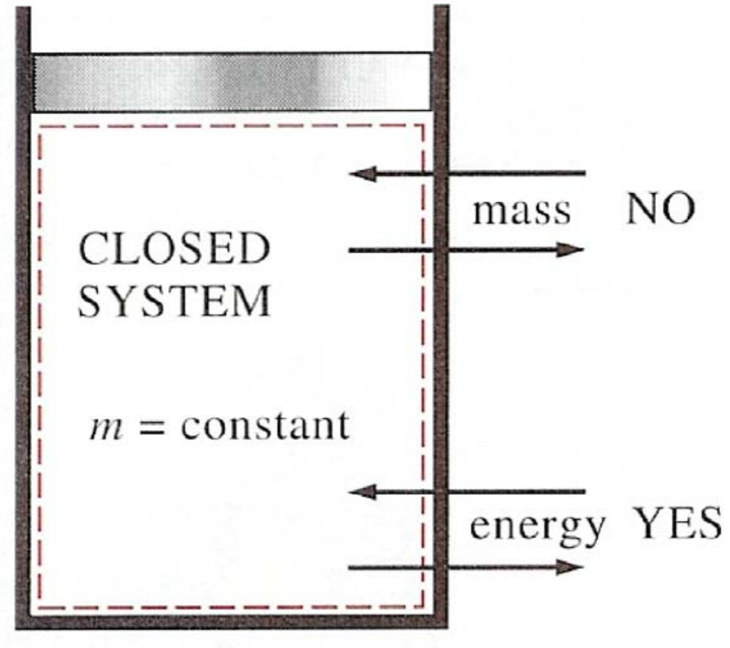
A thermodynamic system, or simply a system, is defined as a *quantity of matter or a region in space chosen for study*. The mass or region outside the system is called the surroundings. The real or imaginary surface that separates the system from its surrounding is called the boundary.



The **boundary** of a system can be *fixed* or *movable*. The boundary is the contact surface shared by both the system and the surroundings, and has zero thickness (does not contain any mass and does not occupy any volume in space).

Systems may be considered to be *closed* or *open*, depending on whether a fixed mass or a fixed volume in space is chosen for study.

- A closed system (also known as a control mass) consists of a fixed amount of mass, and no mass can cross its boundary. That is, no mass can enter or leave a closed system.

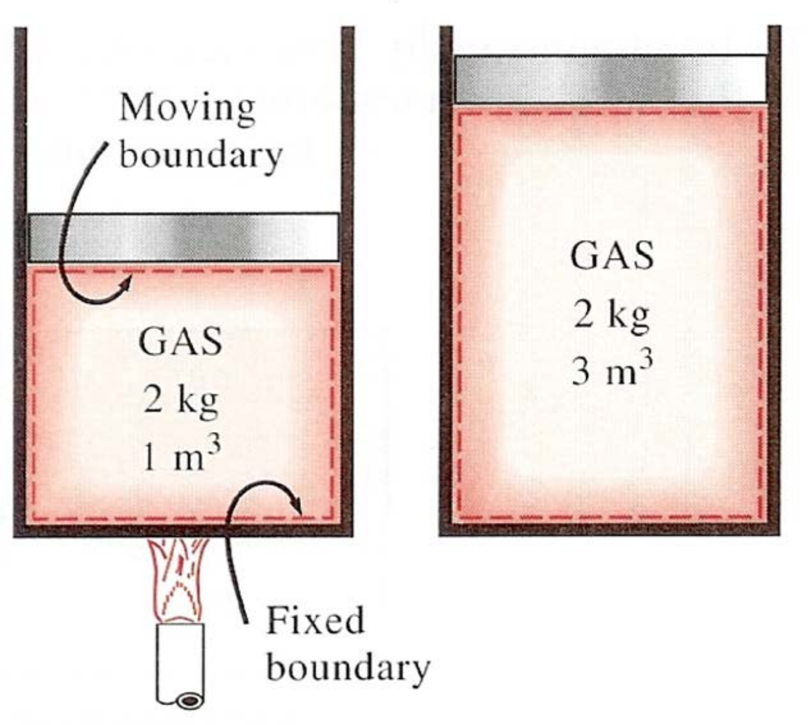


Energy, in the form of heat or work, can cross the boundary. Volume of a closed system does not have to be fixed.

- As a special case, even energy is not allowed to cross the boundary, that system is called an isolated system.

Example:

A piston-cylinder device:

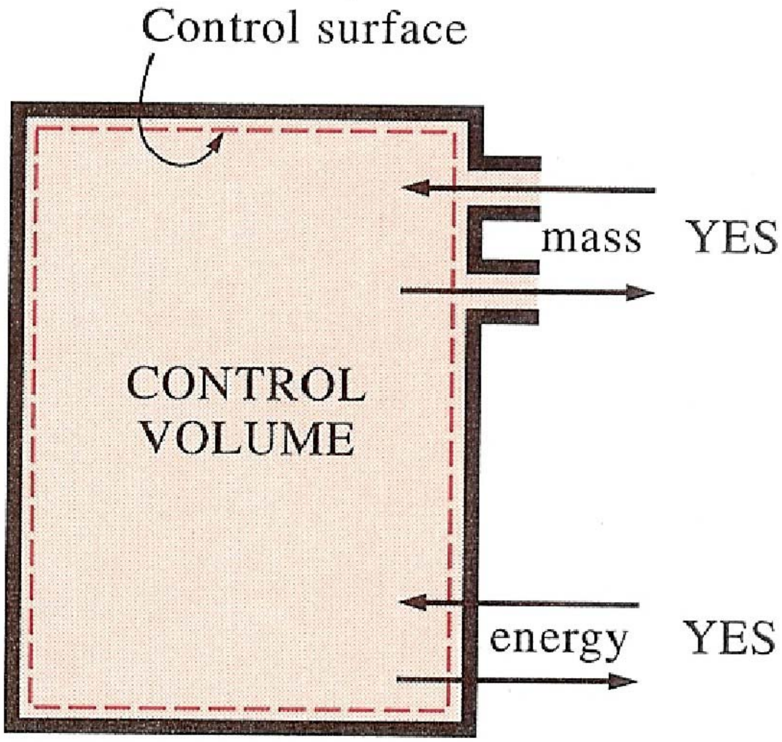


Inside the cylinder is a gas that is heated.

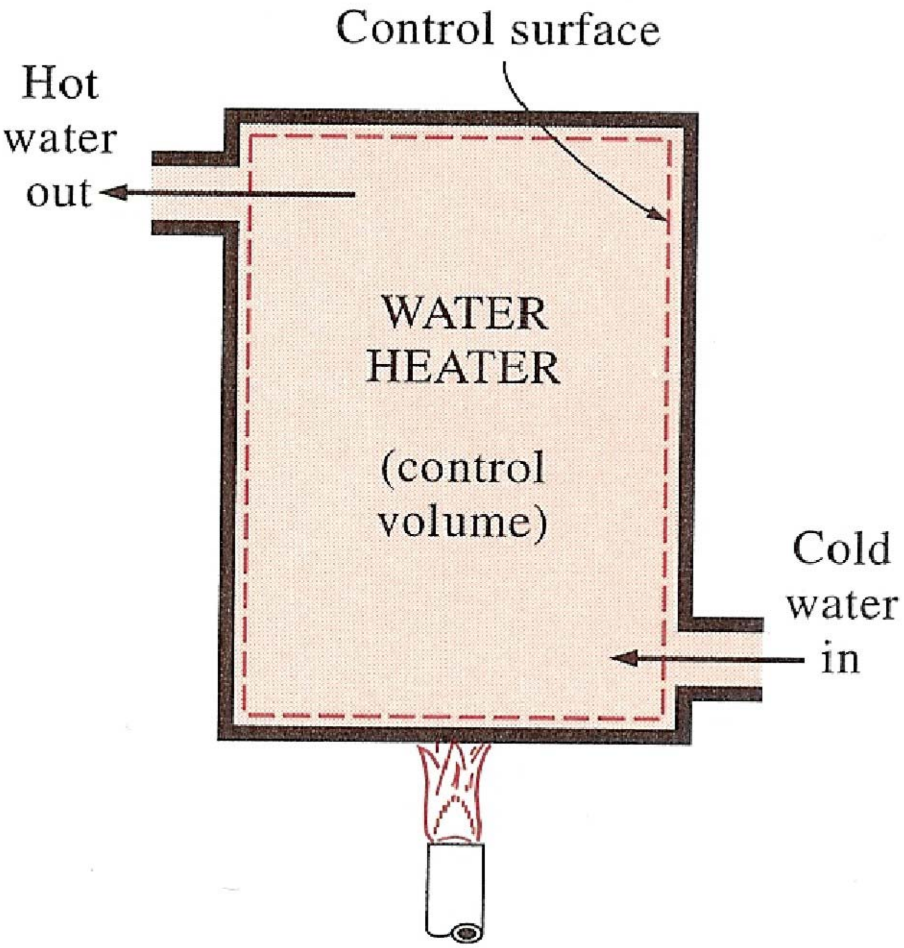
- The gas is the system.
- The inner surfaces of the piston and the cylinder form the boundary.
- Since no mass is crossing this boundary, it is a closed system.
- Energy may cross the boundary,
- Part of the boundary (the inner surface of the piston, in this case) may move.
- Everything outside the gas, including the piston and the cylinder, is the surroundings.
- An open system (or a control volume), is a properly selected

region in space.

- **Example**: It usually encloses a device that involves mass flow such as a compressor, turbine, or nozzle. Flow through these devices is best studied by selecting the region within the device as the control volume.
- Both mass and energy can cross the boundary of a control volume, which is called a control surface.



Example: the water heater shown below. Let us say that we would like to determine how much heat we must transfer to the water in the tank in order to supply a steady stream of hot water.



Since hot water will leave the tank and be replaced by cold water, it is not convenient to choose a fixed mass as our system for the analysis. Instead, we can concentrate our attention on the volume formed by the interior surfaces of the tank and consider the hot and cold water streams as mass leaving and entering the control volume.

The interior surfaces of the tank form the control surface for this case, and mass are crossing the control surface at two locations.

The thermodynamic relations that are applicable to closed and open systems are different. Therefore, it is extremely important that we recognize the type of system we have before we start analyzing it.

In all thermodynamic analyses, the system under study *must* be defined carefully. In most cases, the system investigated is quite simple and obvious, and defining the system may seem like a tedious and unnecessary task. In other cases, however, the system under study may be rather involved, and a proper choice of the system may greatly simplify the analysis.

Forms of Energy

Energy: thermal, mechanical, kinetic, potential, electric, magnetic, chemical, and nuclear, and their sum constitutes the **total energy *E* of a system**. The total energy of a system on a unit mass basis is denoted by e and is defined as:

$$e = \frac{E}{m}$$

The units are kJ/kg.

Thermodynamics only deals with the change of the total energy. Thus the total energy of a system can be assigned a value of zero ($E = 0$) at some convenient reference point.

The change in total energy of a system is independent of the reference point selected.

The decrease in the potential energy of a falling rock, for example, depends on only the elevation difference and not the reference level chosen.

Forms of energy that make up the total energy of a system in two groups: macroscopic and microscopic.

- The macroscopic forms of energy are those a system possesses as a whole with respect to some outside reference frame, such as kinetic and potential energies.
  - The macroscopic energy of a system is related to motion and the influence of some external effects such as gravity, magnetism, electricity, and surface tension.

- The energy that a system possesses as a result of its motion relative to some reference frame is called kinetic energy ***KE***. When all parts of a system move with the same velocity, the kinetic energy is expressed as:

$$KE = \frac{mV^2}{2}$$

where the script V denotes the velocity of the system relative to some fixed reference frame.

- The energy that a system possesses as a result of its elevation in a gravitational field is called potential energy ***PE*** and is expressed as

$$PE = mgz \ \text{(kJ)}$$

where g is the gravitational acceleration and z is the elevation of the center of gravity of a system relative to some arbitrarily selected reference plane.

- The microscopic forms of energy are those related to the molecular structure of a system and the degree of the molecular activity, and they are independent of outside reference frames.
    - The sum of all the microscopic forms of energy is called the internal energy of a system and is denoted by ***U***.

The term *energy* was coined in 1807 by Thomas Young, and its use in thermodynamics was proposed in 1852 by Lord Kelvin. The term *internal energy* and its symbol U first appeared in the works of Rudolph Clausius and William Rankine in the second half of the nineteenth century.

- The magnetic, electric, and surface tension effects are significant in some specialized cases only and are not considered in this course. In the absence of these effects, the total energy of a system consists of the kinetic, potential, and internal energies and is expressed as

$$E = U + KE + PE$$

- Most closed systems remain stationary during a process and thus experience no change in their kinetic and potential energies. Closed systems whose velocity and elevation of center of gravity remain constant during a process are frequently referred to as stationary systems.

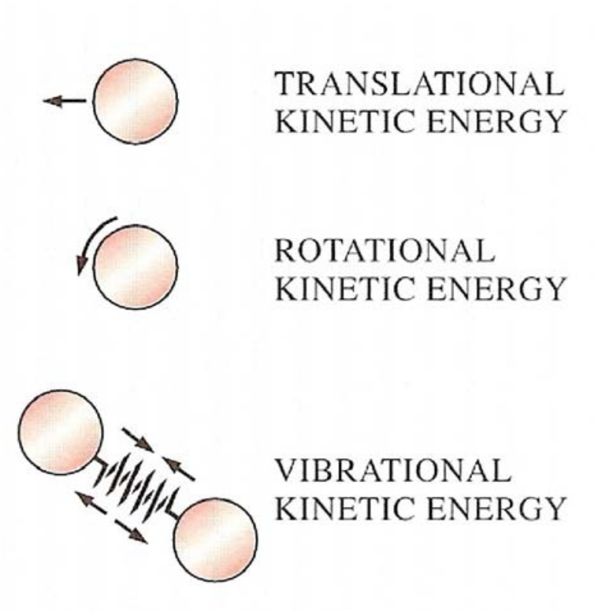
- The change in the total energy ΔE of a stationary system is identical to the change in its internal energy ΔU.

- *In this class* a closed system is assumed to be stationary unless it is specifically stated otherwise.

More about Internal Energy

Internal energy is defined as the sum of all the microscopic forms of energy of a system. It is related to the molecular structure and the degree of molecular activity.

The individual molecules of a system, in general, will move around with some velocity, vibrate about each other, and rotate about an axis during their random motion. Associated with these motions are translational, vibrational, and rotational kinetic energies.



The sum constitutes the kinetic energy of a molecule.

- The portion of the internal energy of a system associated with the kinetic energies of the molecules is called the sensible energy.

The average velocity and the degree of activity of the molecules are proportional to the temperature of the gas.
Thus, at higher temperatures, the molecules will possess higher kinetic energies, and as a result the system will have a higher internal energy.

- The internal energy is also associated with the intermolecular forces between the molecules of a system. These are the forces that bind the molecules to each other, and, as one would expect, they are strongest in solids and weakest in gases. If sufficient energy is added to the molecules of a solid or liquid, they will overcome these molecular forces and break away, turning the system to a gas. This is a phase-change process. Because of this added energy, a system in the gas phase is at a higher internal energy level than it is in the solid or the liquid phase. The internal energy associated with the phase of a system is called latent energy.

- The changes mentioned above can occur without a change in the chemical composition of a system. Most thermodynamic problems fall into this category, and one does not need to pay any attention to the forces binding the atoms in a molecule. The internal energy associated with the atomic bonds in a molecule is called chemical (or bond) energy. During a chemical reaction, such as a combustion process, some chemical bonds are destroyed while others are formed. As a result, the internal energy changes.

- We should also mention the tremendous amount of internal energy associated with the bonds within the nucleus of the atom itself. This energy is called nuclear energy and is released during nuclear reactions.

Obviously, we need not be concerned with nuclear energy in thermodynamics unless, of course, we have a fusion or fission reaction on our hands.

- The above forms of energy can be *contained* or *stored* in a system, and thus can viewed as the static forms of energy.

- The forms of energy that are not stored in a system can be viewed as the dynamic forms of energy, or as energy interactions.

  The dynamic forms of energy are recognized at the system boundary as they cross it, and they represent the energy gained or lost by a system during a process.

- The only two forms of energy interactions associated with a closed system are heat transfer and work.
  - An energy interaction is heat transfer if its driving force is a temperature difference.
  - Otherwise it is work.

- The open systems can also exchange energy via mass transfer, since any time mass is transferred into or out of a system, the energy contained in the mass is also transferred with it.

Properties of a System

Any characteristic of a system is called a property such as

- pressure *P*,
- temperature *T*,
- volume *V*, and
- mass *m*.

- The list can be extended to include less familiar ones such as viscosity, thermal conductivity, modulus of elasticity, thermal expansion coefficient, electric resistivity, and even velocity and elevation.

Not all properties are independent. Some are defined in terms of other ones. For example, density is defined as *mass per unit volume:*

$$\rho = \frac{m}{V}$$

Sometimes the density of a substance is given relative to the density of a better known substance. Then it is called specific gravity, or relative density, and is defined as *the ratio of the density of a substance to the density of some standard substance at a specified temperature* (usually water at 4°C, for which $\rho_{H20} = 1000\ \text{kg/m}^3$). That is,

$$\rho_s = \frac{\rho}{\rho_{H_2O}}$$

Note that specific gravity is a dimensionless quantity.

- A more frequently used property in thermodynamics is the specific volume. It is the reciprocal of density and is defined as *the volume per unit mass:*

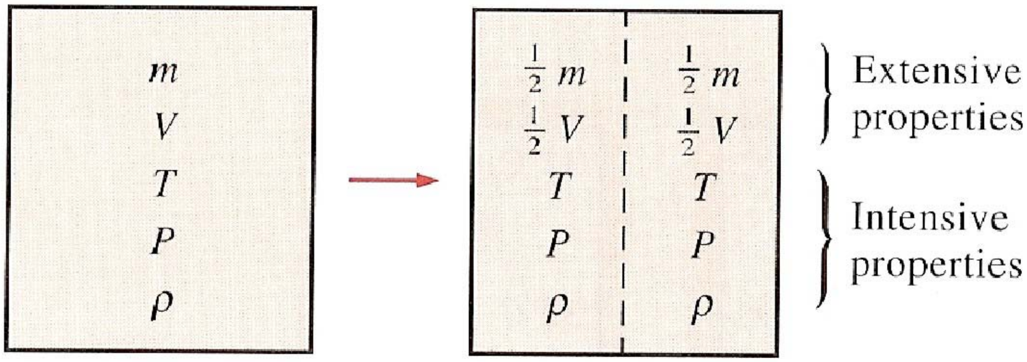
$$v = \frac{V}{m} = \frac{1}{\rho}$$

In classical thermodynamics, the atomic structure of a substance (thus, the spaces between and within the molecules) is disregarded, and the substance is viewed to be a continuous, homogeneous matter with no microscopic holes, i.e., a continuum.

This idealization is valid as long as we work with volumes, areas, and lengths that are large relative to the intermolecular spacing.

Properties are considered to be either *intensive* or *extensive.*

- Intensive properties are those that are independent of the size of a system, such as temperature, pressure, and density.
- Extensive properties are those whose values depend on the size-or extent-of the system. Mass m, volume V, and total energy E are some examples of extensive properties. An easy way to determine whether a property is intensive or extensive is to divide the system into two equal parts with a partition.



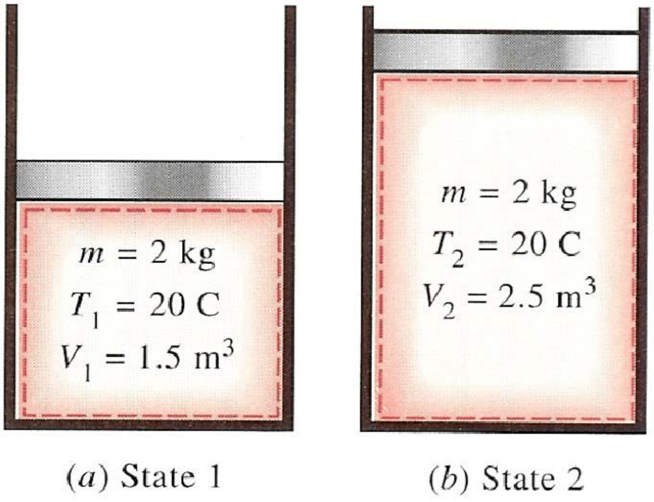
Each part will have the same value of intensive properties as the original system, but half the value of the extensive properties.

- Extensive properties per unit mass are called specific properties. Some examples of specific properties are
  - specific volume ***($v = V/m$),***
  - specific total energy ***($e = E/m$),*** and
  - specific internal energy ***($u = U/m$)***.

State and Equilibrium

Consider a system that is not undergoing any change. At this point, all the properties can be measured or calculated throughout the entire system, which gives us a set of properties that completely describe the condition, or the state, of the system.

- At a given state, all the properties of a system have fixed values.
- If the value of even one property changes, the state will change to a different one.

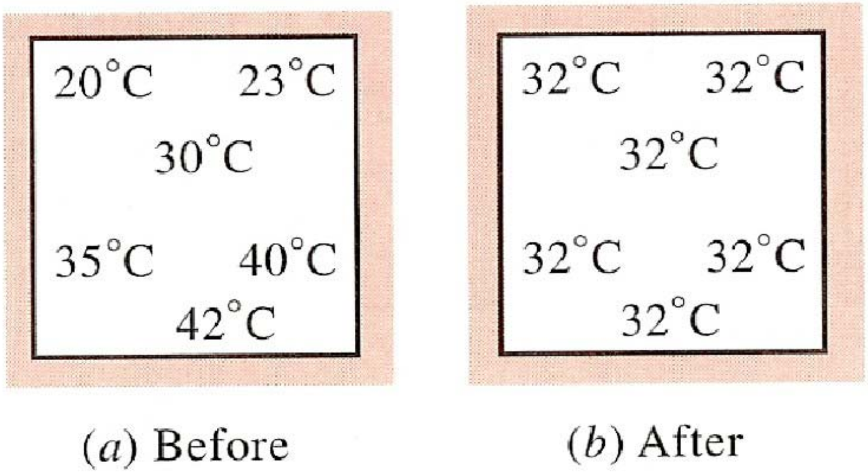


Thermodynamics deals with equilibrium states.

- The word *equilibrium* implies a state of balance.
- In an equilibrium state, there are no unbalanced potentials (or driving forces) within the system.
- A system that is in equilibrium experiences no changes when it is isolated from its surroundings.

There are many types of equilibrium, and a system is not in thermodynamic equilibrium unless the conditions of all the relevant types of equilibrium are satisfied.

- A system is in thermal equilibrium if the temperature is the same throughout the entire system, as shown below.



(a) Before (b) After

The system involves no temperature differentials, which is the driving force for heat flow.

- Mechanical equilibrium is related to pressure, and a system is in mechanical equilibrium if there is no change in pressure at any point of the system with time.

  However, the pressure may vary within the system with elevation as a result of gravitational effects. But the higher pressure at a bottom layer is balanced by the extra weight it must carry, and, therefore, there is no imbalance of forces. The variation of pressure as a result of gravity in most thermodynamic systems is relatively small and usually disregarded.

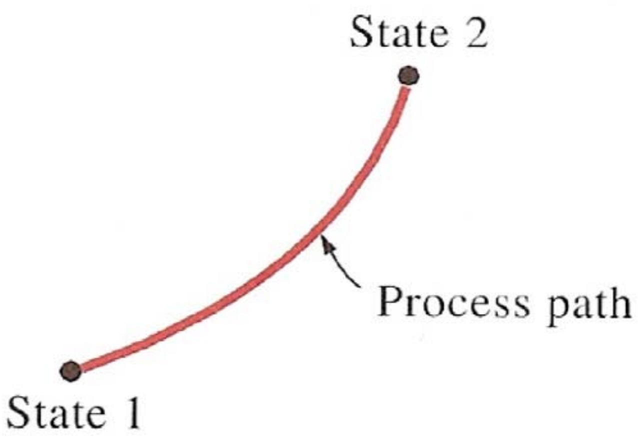
- If a system involves two phases, it is phase equilibrium when the mass of each phase reaches an equilibrium level and stays there.

- Finally, a system is in chemical equilibrium if its chemical composition does not change with time, i.e., no chemical reactions occur.

Processes and Cycles

Any change that a system undergoes from one equilibrium state to another is called a process.

The series of states through which a system passes during a process is called the path of the process.

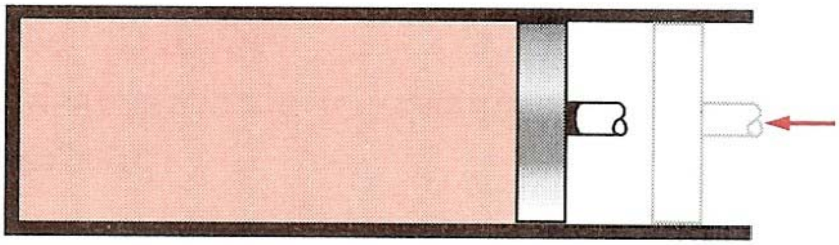


To describe a process completely, one should specify

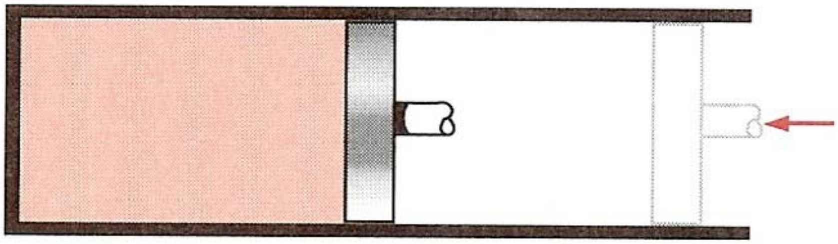
- the initial state and
- final state of the process, as well as
- the path it follows, and
- the interactions with the surroundings.

When a process proceeds in such a manner that the system remains infinitesimally close to an equilibrium state at all times, it is called a quasi-static, or quasi-equilibrium, process.

- A quasi-equilibrium process can be viewed as a sufficiently slow process that allows the system to adjust itself internally so that properties in one part of the system do not change any faster than those at other parts.



(*a*) Slow compression
(quasi-equilibrium)

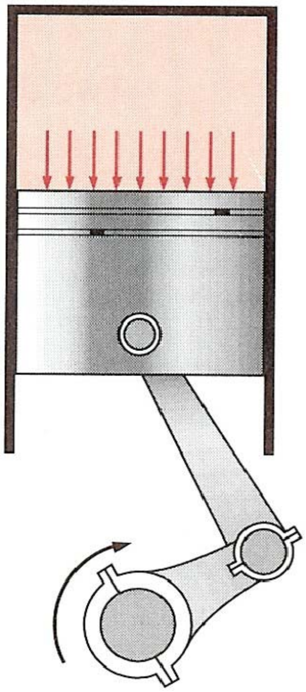


(*b*) Very fast compression
(non-quasi-equilibrium)

- When a gas in a piston-cylinder device is compressed suddenly, the molecules near the face of the piston will not have enough time to escape and they will have to pile up in a small region in front of the piston, thus creating a high-pressure region there. Because of this pressure difference, the system can no longer be said to be in equilibrium, and this makes the entire process non-quasi-equilibrium.

- If the piston is moved slowly, the molecules will have sufficient time to redistribute and there will not be a molecule pileup in front of the piston. As a result, the pressure inside the cylinder will always be uniform and will rise at the same rate at all locations. Since equilibrium is maintained at all times, this is a quasi-equilibrium process.

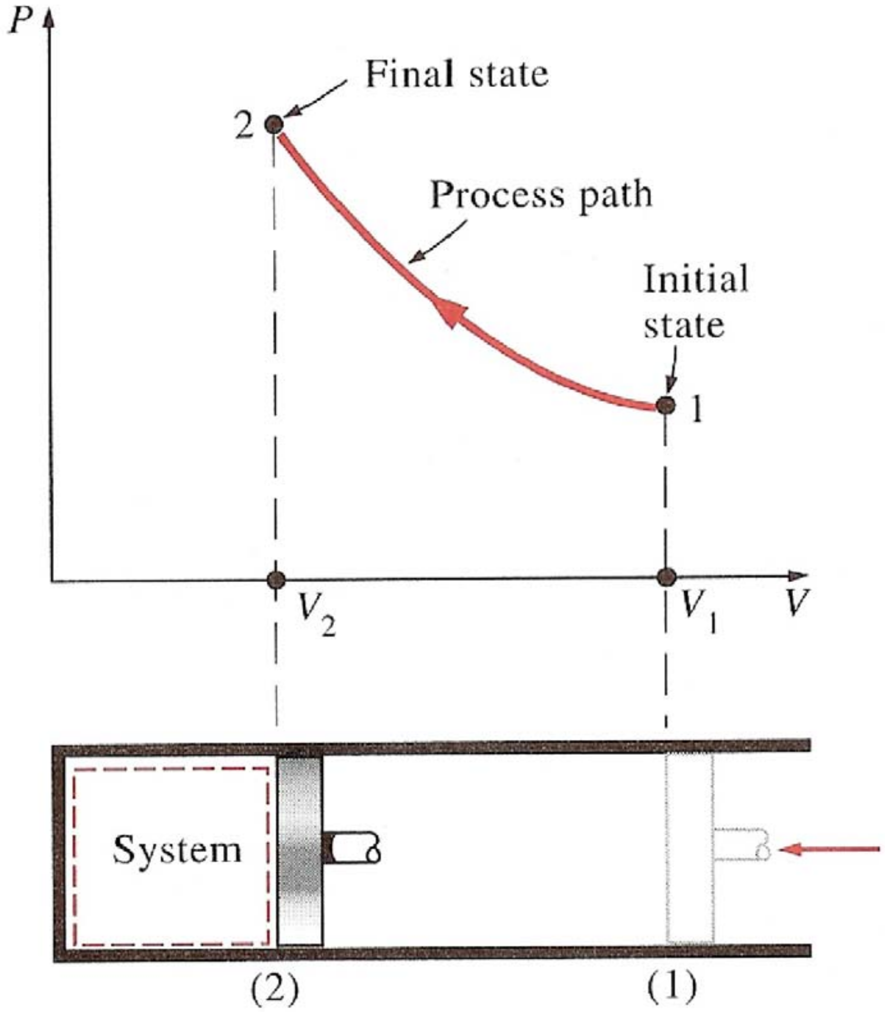
- A quasi-equilibrium process is an idealized process and is not a true representation of an actual process. But many actual processes closely approximate it, and they can be modeled as quasi-equilibrium with negligible error. Engineers are interested in quasi-equilibrium processes for two reasons. First, they are easy to analyze; second, work-producing devices deliver the most work when they operate on quasi-equilibrium processes.



Therefore, quasi-equilibrium processes serve as standards to which actual processes can be compared.

Process diagrams that are plotted by employing thermodynamic properties as coordinates are very useful in visualizing the processes. Some common properties that are used as coordinates are temperature *T*, pressure *P*, and volume *V* (or specific volume *v*).

Figure below shows the *P*- *V* diagram of a compression process of a gas.



Note:

- The process path indicates a series of equilibrium states through which the system passes through during a process and has significance for quasi-equilibrium processes only.

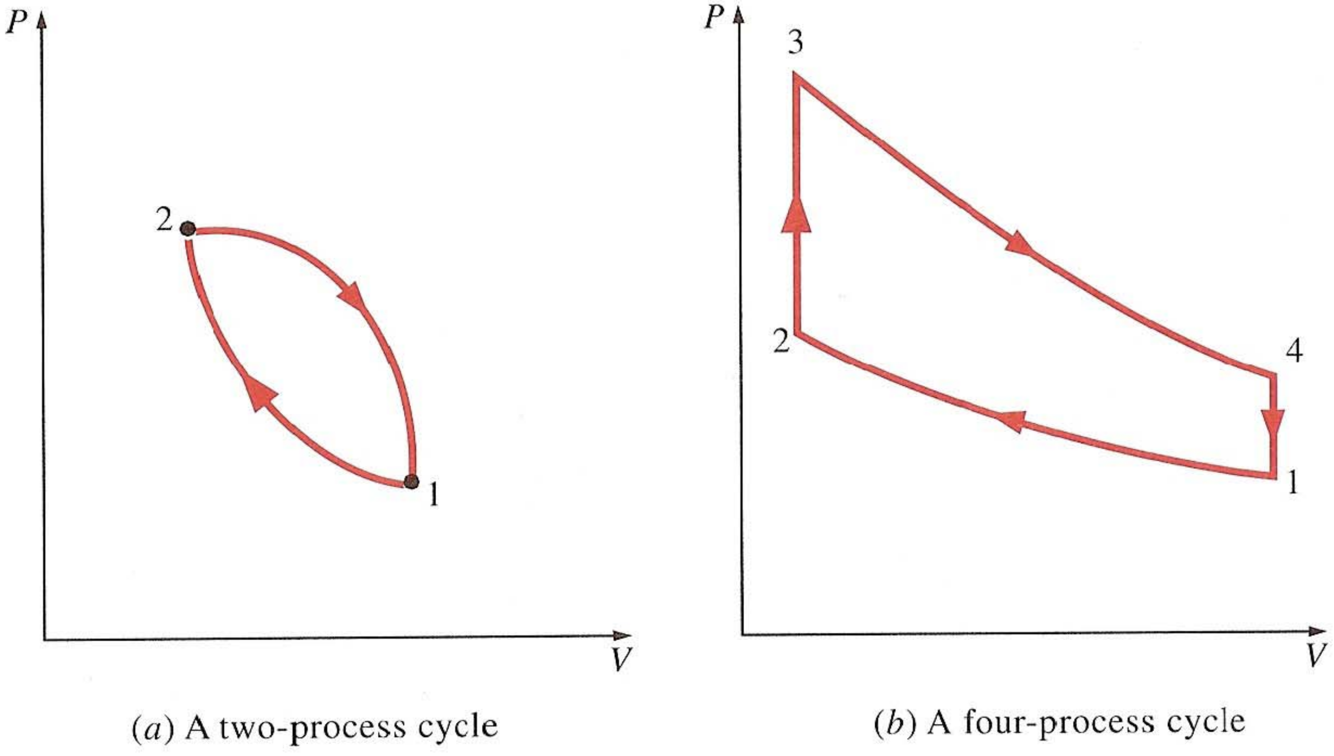
- For non-quasi-equilibrium processes, we are not able to specify the states through which the system passes during the process and so we cannot speak of a process path. A non-quasi-equilibrium process is denoted by a dashed line between the initial and final states instead of a solid line.

The prefix ***iso-*** is often used to designate a process for which a particular property remains constant.

- An isothermal process is a process during which the temperature T remains constant,
- An isobaric process is a process during which the pressure P remains constant, and
- An isochoric (or isometric) process is a process during which the specific volume v remains constant.

A system is said to have undergone a cycle if it returns to its initial state at the end of the process. That is, for a cycle the initial and final states are identical.

Example of cycles:



(a) A two-process cycle

(b) A four-process cycle

The state Postulate

The state of a system can be defined completely by the four observable macroscopic properties of matter known as the variables of state, namely pressure, volume, temperature and composition. How many properties are necessary to specify so that a state of a system is fully determined?

> *The state of a simple compressible system is completely specified by two independent, intensive properties.*

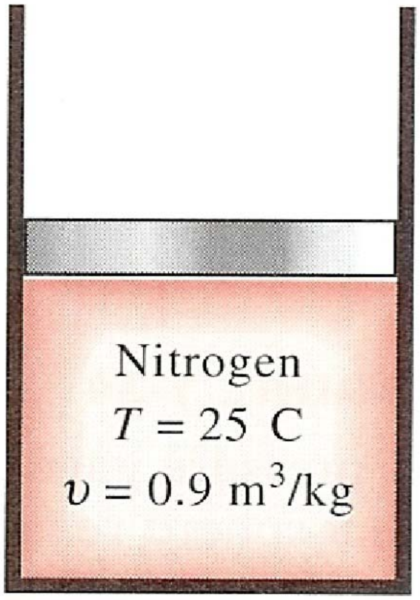
- A system is called a simple compressible system in the *absence* of electrical, magnetic, gravitational, motion, and surface tension effects. These effects are due to external force fields and are negligible for most engineering problems.
- Otherwise, an additional property needs to be specified for each effect which is significant.

  Example: If the gravitational effects are to be considered, for example, the elevation *z* needs to be specified in addition to the two properties necessary to fix the state.

The state postulate requires that the two properties specified be independent to fix the state.

- Two properties are independent if one property can be varied while the other one is held constant.

  Example: Temperature and specific volume are always independent properties, and together they can fix the state of a simple compressible system.



Note: Temperature and pressure are independent properties for single-phase systems, but are dependent properties for multiphase systems. At sea level $(P = 1$ atm), water boils at 100°C, but on a mountaintop where the pressure is lower, water boils at a lower temperature. That is, $T = f(P)$ during a phase-change process; thus, temperature and pressure are not sufficient to fix the state of a two-phase system.

- The chosen independent variables are called the *state variables* or *variables of state* while the other properties which depend on them are called *state functions* or *functions of state*.
- There are two important properties of state functions or variables of state.
  1. Once we specify the state of a system by giving the values of all or a few of the state variables, e.g. $P, V, T,$ and composition, then all other properties such as mass m, density ρ, viscosity η and refractive index μ, are fixed.

The relationship between the dependent and independent variables of state is known as ***the equation of state***.

2. When the state of a system is altered, the change in any state function depends only on the initial and final state of the system, and not on how the change is brought about.

Example: When a gas is compressed from an initial pressure P_1 to a final pressure P_2 the change ΔP in pressure is given by

$$\Delta P=P_2-P_1.$$

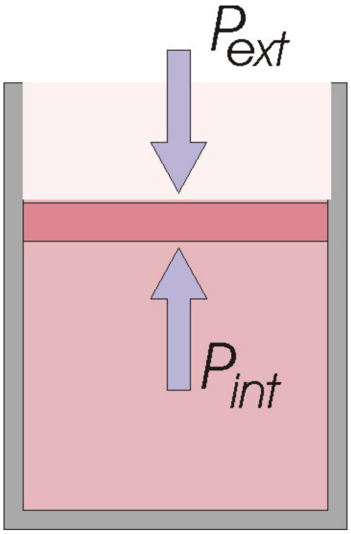
Only the initial and final values of the pressure determine ΔP. Any intermediate values which ΔP may have assumed in changing from P_1 to P_2 are immaterial.

Reversible and Irreversible Paths

These two concepts are of fundamental importance in thermodynamics. Changes of state may be brought about along reversible or irreversible paths.

- A reversible path is one that may be followed in either direction. At any point the direction may be reversed by a small change in a variable such as the temperature or pressure.

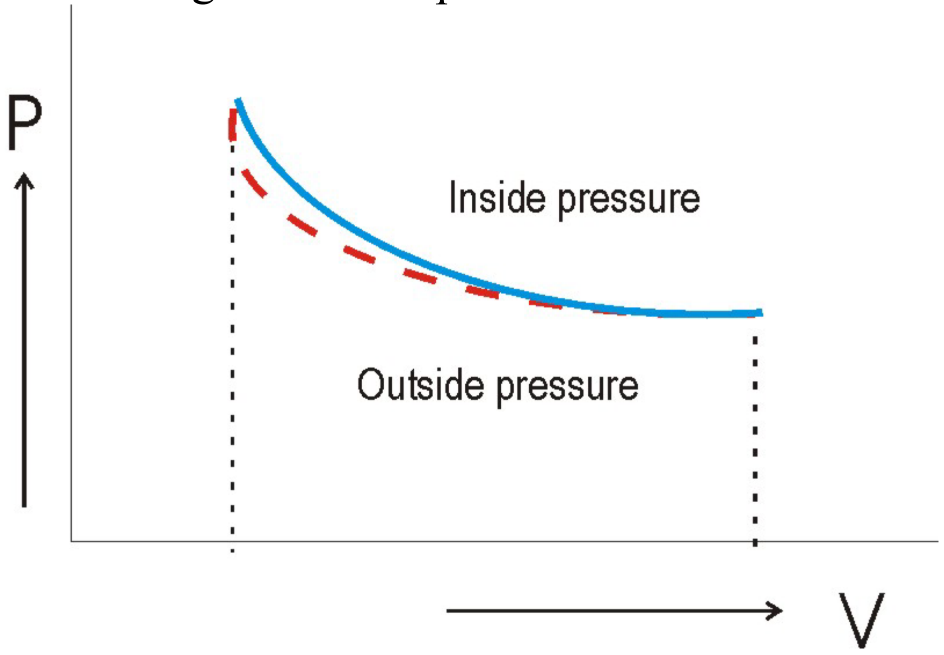
Example:



A cylinder containing a gas and the cylinder has a piston that can move up or down exerting pressure on the gas.

- If the pressure exerted by the gas equals the external pressure, there is equilibrium. At the equilibrium state, by a slight decrease in the piston pressure the gas can be made to expand; also by a slight increase of the piston pressure the gas can be made to contract.
- Assume the gas is expanded by slowly decreasing the piston pressure so that at all times it is very slightly smaller than the pressure exerted by the gas on the piston.

A *P*- *V* diagram of this process is as shown below.



The smaller the difference between P_{int} and P_{ext} , the closer the red curve lies to the blue curve and the slower the rate at which the gas expands.

In the idealized case where the two curves coincide, expansion takes an infinite time, because there is no pressure difference left to act on the piston.

In this limiting case, expansion can be changed into compression by an infinitesimal increase in the outside pressure, and compression into expansion by an infinitesimal decrease in the outside pressure. Only under these circumstances is the expansion of the gas reversible.

Thus we can say that

- Reversible expansion of the gas is an idealized concept that can be carried out in theory only.
- Any actual expansion IS irreversible.

- A reversible process is generally an idealized concept that represents the limit of a sequence of irreversible processes, for which the parameter changes required to reverse the direction become smaller and smaller. At the limit it proceeds infinitely slowly through a sequence of equilibrium states.

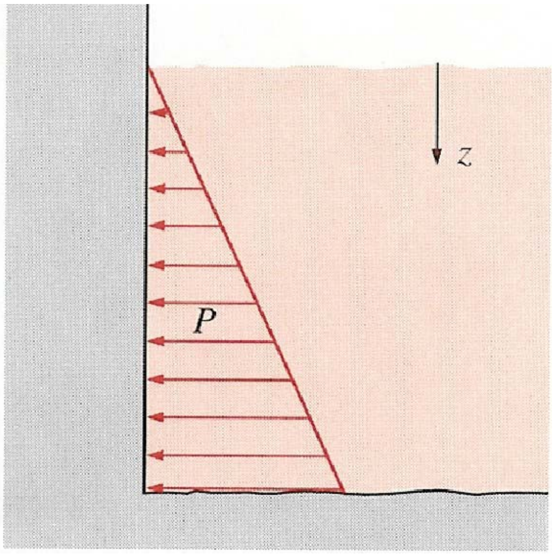
2. Pressure and Temperature

Pressure

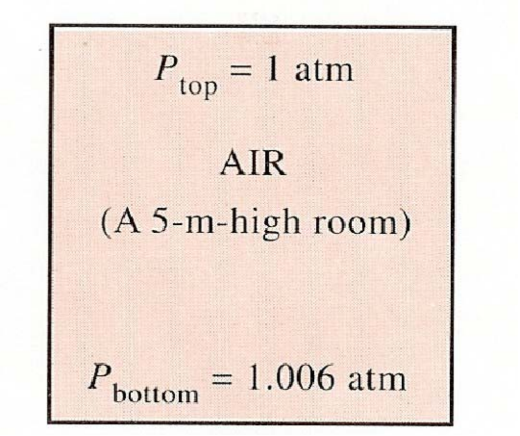
Pressure is *the force exerted by a fluid per unit area*. We speak of pressure only when we deal with a gas or a liquid.

Note: The counterpart of pressure in solids is *stress*.

- For a fluid at rest, the pressure at a given point is the same in all directions.
- The pressure in a fluid increases with depth as a result of the weight of the fluid.
- The pressure varies in the vertical direction as a result of gravitational effects, but there is no variation in the horizontal direction.



- The pressure in a tank containing a gas may be considered to be uniform since the weight of the gas is too small to make a significant difference.



Units: 1 Pa = 1 N/m^2

Other units:

- *kilopascal* (1 kPa = 10^3 Pa);
- *megapascal* (1 MPa = 10^6 Pa);
- *bar* (1 bar = 10^5 Pa);
- *standard atmosphere* (1 atm = 101,325 Pa);
- In the English system, the pressure unit is *pound-force per square inch* (Ibf/in^2, or psi), and 1 atm = 14.696 psi.

- The actual pressure at a given position is called the absolute pressure, and it is measured relative to absolute vacuum, i.e., absolute zero pressure.

- Most pressure-measuring devices, however, are calibrated to read zero in the atmosphere, and so they indicate the difference between the absolute pressure and the local atmospheric pressure. This difference is called the gage pressure.

  - Pressures below atmospheric pressure are called vacuum pressures and are measured by vacuum gages which indicate the difference between the atmospheric pressure and the absolute pressure.

Absolute, gage, and vacuum pressures are all positive quantities and are related to each other by

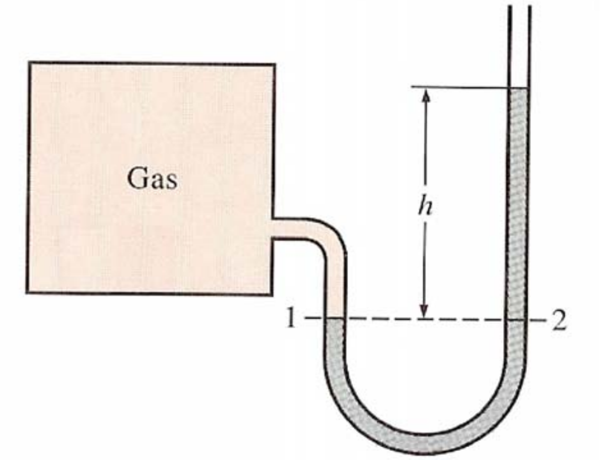
$P_{gage} = P_{abs} - P_{atm}$ for pressures above P_{atm}

$P_{vac} = P_{atm} - P_{abs}$ for pressures below P_{atm}

Thermodynamics uses the absolute pressure denoted P.

Measuring pressure

Manometer is used to measure small and moderate pressure differences.



Note: Since the gravitational effects of gases are negligible, the pressure anywhere in the tank and at position 1 has the same value. Furthermore, since pressure in a fluid does not vary in the horizontal direction within a fluid, the pressure at 2 is the same as the pressure at 1.

$$P_2 = P_1,$$

The pressure exerted by the column *h* plus the atmospheric pressure above it equals the pressure in the tank.

For a cross-section in the tube A, we have:

$$AP_1 = AP_{atm} + W$$

Where

$$W = mg = \rho Vg = \rho Ahg$$

Thus,

$$P_1 = P_{atm} + \rho hg$$

In the above relations, W is the weight of the fluid column, ρ is the density of the fluid and is assumed to be constant, g is the local gravitational acceleration, A is the cross-sectional area of the tube, and P_{atm} is the atmospheric pressure.

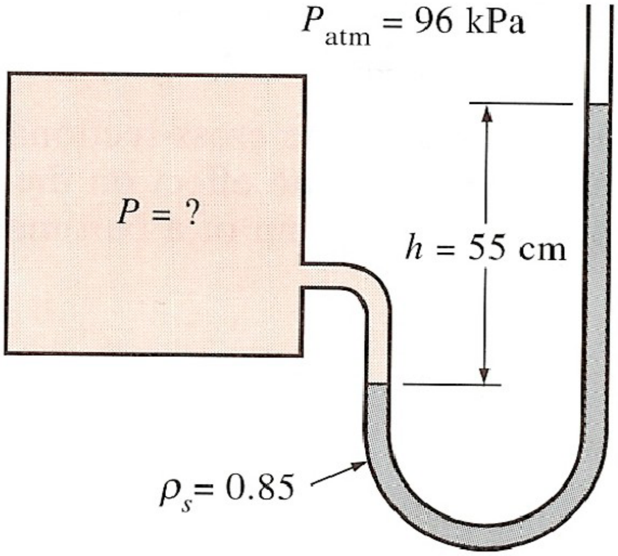
The pressure difference can be expressed as

$$\Delta P = P_1 - P_{atm} = \rho hg$$

Note: the cross-sectional area of the tube has no effect on the height differential *h,* and thus the pressure exerted by the fluid.

Example

A manometer is used to measure the pressure in a tank. The fluid used has a specific gravity of 0.85, and the manometer column height is 55 cm, as shown



If the local atmospheric pressure is 96 kPa, determine the absolute pressure within the tank.

Solution The gravitational acceleration is not specified, so we assume the standard value of 9.81 m/s^2. The density of the fluid is obtained by multiplying its specific gravity by the density of water, which is taken to be 1000 kg/m^3:

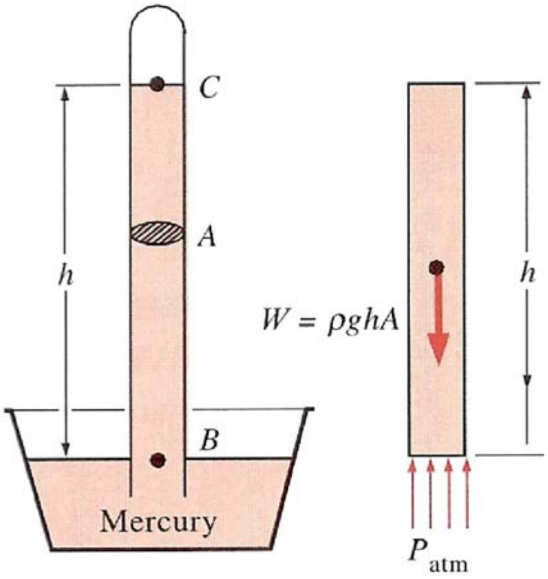
$$\rho = (\rho_S)(\rho_{H20}) = (0.85)(1000\ \text{kg/m}^3) = 850\ \text{kg/m}^3$$

Recall

$$P = P_{atm} + \rho g h$$

$= 96\ \text{kPa} + (850\ \text{kg/m}^3)(9.81\ \text{m/s}^2)(0.55\ \text{m}) = 100.6\ \text{kPa}$

Barometer measures the atmospheric pressure, thus the atmospheric pressure is often called the *barometric pressure.*



As Torricelli (1608-1647) discovered some centuries ago, the atmospheric pressure can be measured by inverting a mercury-filled tube into a mercury container that is open to the atmosphere, as shown above. The pressure at point *B* is equal to the atmospheric pressure, and the pressure at C can be taken to be zero since there is only mercury vapor above point C and the pressure it exerts is negligible.

At level B

$$P_{atm} = \rho g h \quad \text{(kPa)}$$

where ρ is the density of mercury, g is the local gravitational acceleration, and h is the height of the mercury column above the free surface.

Note that the length and the cross-sectional area of the tube have no effect on the height of the fluid column of a barometer.

The *standard atmosphere,* is the pressure produced by a column of mercury 760 mm in height at 0°C ($\rho_{Hg} = 13{,}595\ \text{kg/m}^3$) under standard gravitational acceleration ($g = 9.807\ \text{m/s}^2$).

Note: If water instead of mercury were used to measure the standard atmospheric pressure, a water column of about 10.3 m would be needed.

Units: Pressure is sometimes expressed (especially by weather forecasters) in terms of the height of the mercury column. The standard atmospheric pressure, for example, is 760 mmHg (29.92 in Hg) at 0°C.

Exercise: Calculate the standard atmospheric pressure in kPa

The average atmospheric pressure P_{atm} changes from 101.325 kPa at sea level to 89.88, 79.50, 54.05, 26.5, and 5.53 kPa at altitudes of 1000, 2000, 5000, 10,000, and 20,000 m, respectively. The average atmospheric pressure in Denver (elevation = 1610 m), for example, is 83.4 kPa.

Remember that the atmospheric pressure at a location is simply the weight of the air above that location per unit surface area. Therefore, it changes not only with elevation but also with weather conditions.

Example

Determine the atmospheric pressure at a location where the barometric reading is 740 mmHg and the gravitational acceleration is g = 9.7 m/s^2. Assume the temperature of mercury to be 10°C, at which its density is 13,570 kg/m^3.

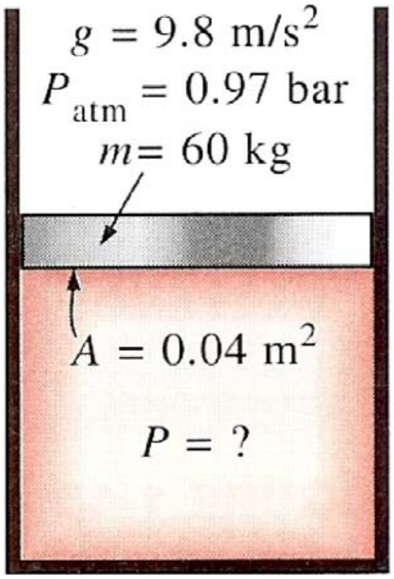
Solution: 97.4 kPa

Example

The piston of a piston-cylinder device containing a gas has a mass of 60 kg and a cross-sectional area of 0.04 m^2, as shown below. The local atmospheric pressure is 0.97 bar, and the gravitational acceleration is 9.8 m/s^2.

(a) Determine the pressure inside the cylinder.

(b) If some heat is transferred to the gas and its volume doubles, do you expect the pressure inside the cylinder to change?


$g = 9.8\ \text{m/s}^2$
$P_{\text{atm}} = 0.97$ bar
$m = 60$ kg
$A = 0.04\ \text{m}^2$
$P = ?$

Temperature

The central concept of thermodynamics is temperature.

Although we are familiar with **temperature** as a measure of "hotness" or "coldness," it is not easy to give an exact definition for it. Based on our physiological sensations, we express the level of temperature qualitatively with words like *freezing cold, cold, warm, hot,* and *red-hot.* However, we cannot assign numerical values to temperatures based on our sensations alone. Furthermore, our senses may be misleading. A metal chair, for example, will feel much colder than a wooden one even when both are at the same temperature.

Fortunately, *several properties of materials change with temperature in a repeatable and predictable way*, and this forms the basis for accurate temperature measurement. The commonly used mercury-in-glass thermometer, for example, is based on the expansion of mercury with temperature. Temperature is also measured by using several other temperature-dependent properties.

Temperature scales

Temperature scales enable scientists to use a common basis for temperature measurements, and several have been introduced throughout history.

All temperature scales are based on some easily reproducible states such as the freezing and boiling points of water, which are also called the *ice point* and the *steam point,* respectively.

- A mixture of ice and water that is in equilibrium with air saturated with vapor at 1-atm pressure is said to be at the ice point, and
- a mixture of liquid water and water vapor (with no air) in

equilibrium at 1-atm pressure is said to be at the steam point.

The temperature scales used in the SI and in the English system today are the

- Celsius scale (formerly called the *centigrade scale;* in 1948 it was renamed after the Swedish astronomer A. Celsius, 1701-1744, who devised it) and the

- Fahrenheit scale (named after the German instrument maker G. Fahrenheit, 1686-1736).

- On the Celsius scale, the ice and steam points are assigned the values of 0 and 100°C, respectively.
- The corresponding values on the Fahrenheit scale are 32 and 212°F. These are often referred to as *two-point scales* since temperature values are assigned at two different points.

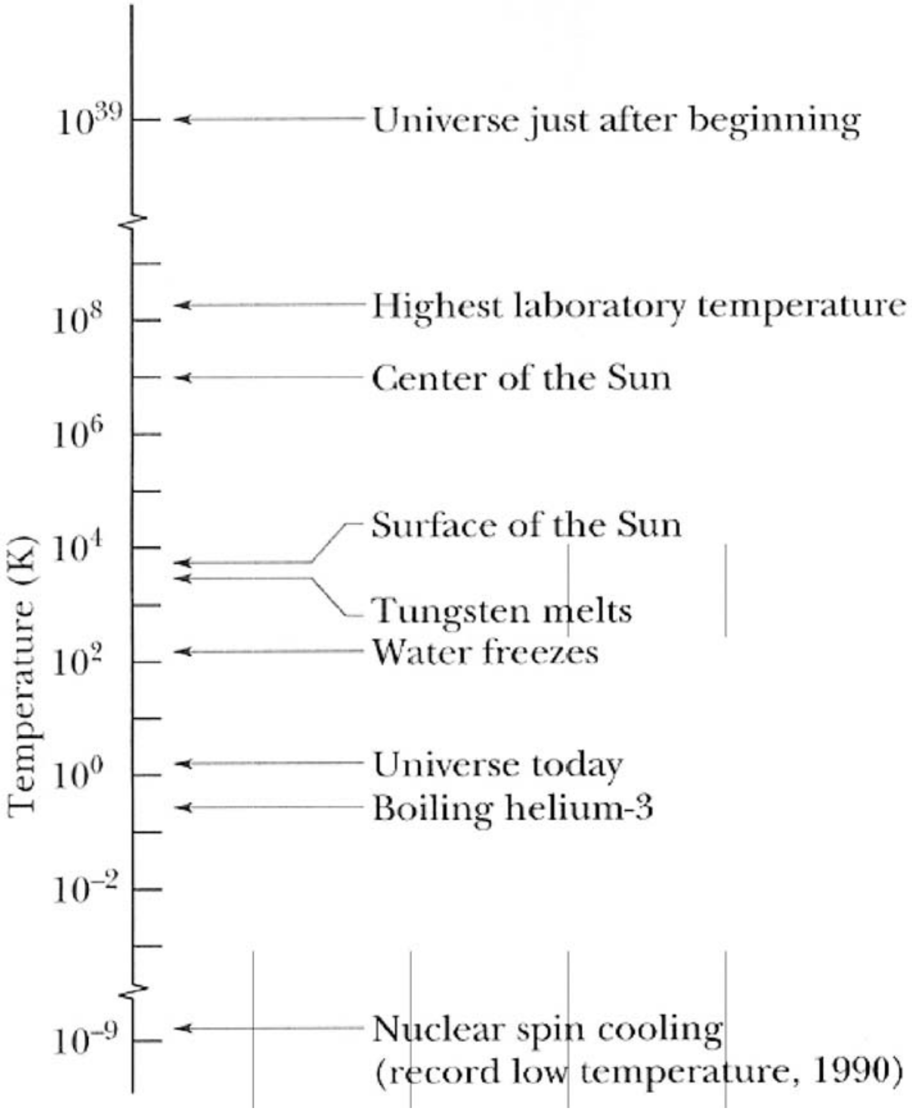
In thermodynamics, it is very desirable to have a temperature scale that is independent of the properties of any substance or substances. Such a temperature scale is called a *thermodynamic temperature scale*.

- The thermodynamic temperature scale in the SI is the Kelvin scale, named after Lord Kelvin (1824-1907). The temperature unit on this scale is the kelvin, which is designated by K.

- The lowest temperature on the Kelvin scale is 0 K.

- Using nonconventional refrigeration techniques, scientists have approached absolute zero kelvin (they achieved 0.000000002 K in 1989).

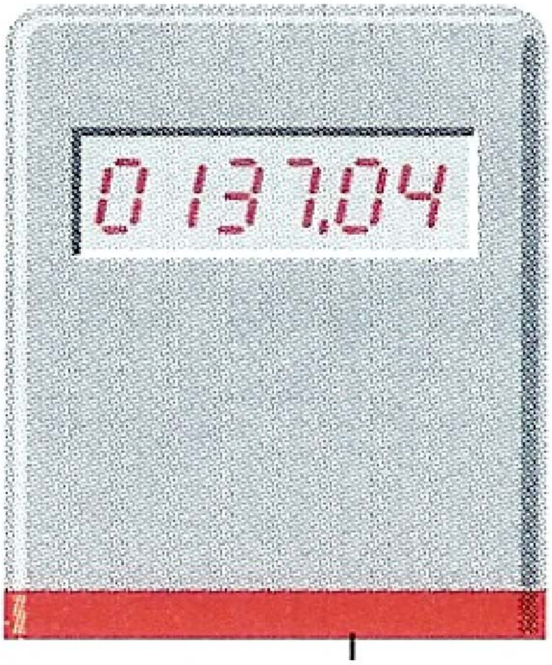
- Although the temperature of a body apparently has no upper limit, it does have a lower limit; this limiting low temperature is taken as the zero of the Kelvin temperature scale. Room temperature is about 290 kelvins (or 290 K), above this *absolute zero.*



- When the universe began, some 14 billion years ago, its temperature was about 10^{39} K. As the universe expanded it cooled, and it has now reached an average temperature of about 3 K. We on Earth are a little warmer than that because we happen to live near a star. Without our Sun, we too would be at 3 K (or rather, we could not exist).

The Zeroth Law of Thermodynamics

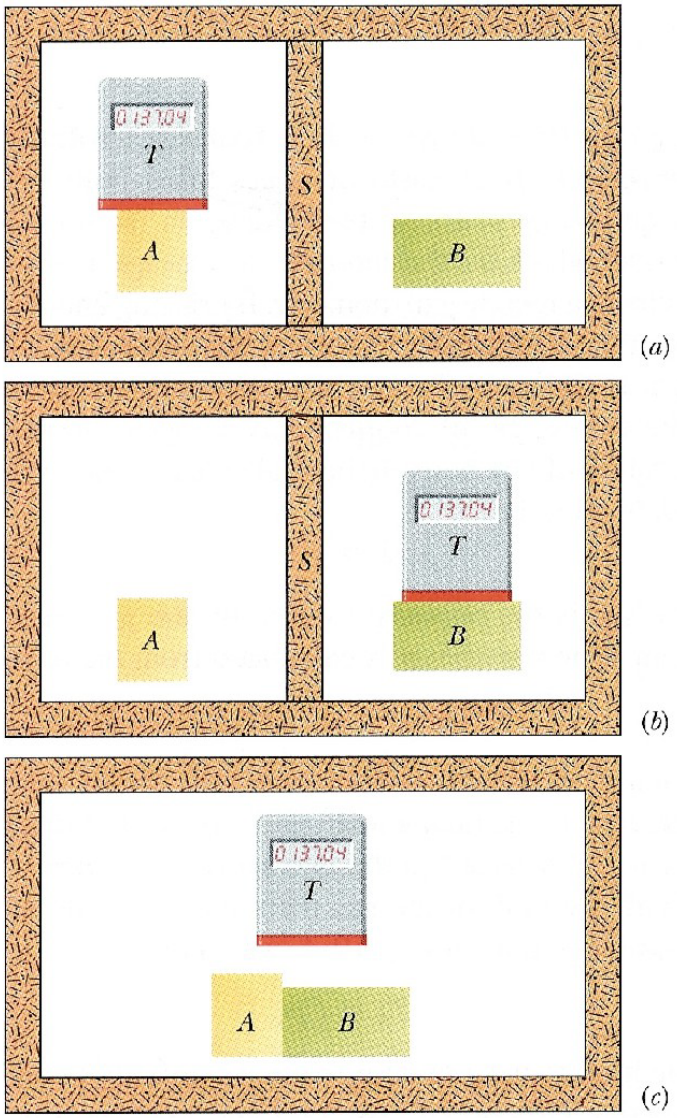
As shown earlier, the properties of many bodies change as we alter their temperature. We can use anyone of these properties as the basis of an instrument that will help us to pin down the concept of temperature. The figure shows such an instrument.



Thermally sensitive element

Any resourceful engineer could design and construct it, using anyone of the properties temperature dependent. The instrument is fitted with a digital readout display and has the following properties: if you heat it with a Bunsen burner, the displayed number starts to increase; if you then put it into a refrigerator, the displayed number starts to decrease. The instrument is not calibrated in any way, and the numbers have (as yet) no physical meaning. The device is a *thermoscope* but not (as yet) a *thermometer.*

- Suppose that we put the thermoscope (body *T)* into intimate contact with another body (body *A).* The entire system is confined within a thick-walled insulating box. The numbers displayed by the thermoscope roll by until, eventually, they come to rest (let us say the reading is "137.04") and no further change takes place. In fact, we suppose that every measurable property of body *T* and of body *A* has assumed a stable, unchanging value. Then we say that the two bodies are in *thermal equilibrium* with each other.



Even though the displayed readings for body *T* have not been calibrated, we conclude that bodies *T* and *A* must be at the same (unknown) temperature.

- Suppose that we next put body *T* in intimate contact with body *B*

> and find that the two bodies come to thermal equilibrium ***at the same reading of the thermoscope***. Then bodies *T* and *B* must be at the same (still unknown) temperature. If we now put bodies *A* and *B* into intimate contact, will they immediately be in thermal equilibrium with each other? Experimentally, we find that they are.

Thus the above experimental facts are summed up in the zeroth law of thermodynamics:

If bodies A and B are each in thermal equilibrium with a third body T, then they are in thermal equilibrium with each other.

- In less formal language, the message of the zeroth law is: "Every body has a property called temperature. When two bodies are in thermal equilibrium, their temperatures are equal." And vice versa.

- We can now make our thermoscope (the third body *T)* into a thermometer, confident that its readings will have physical meaning. All we have to do is calibrate it.

- We use the zeroth law constantly in the laboratory. If we want to know whether the liquids in two beakers are at the same temperature, we measure the temperature of each with a thermometer. We do not need to bring the two liquids into intimate contact and observe whether they are or are not in thermal equilibrium.

Note: *The zeroth law of thermodynamics states that if two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other. It may seem silly that such an obvious fact is called one of the basic laws of thermodynamics. However, it cannot be concluded from the other laws of thermodynamics, and it serves as a basis for the validity of temperature measurement. The zeroth law, which has been called a logical afterthought, came to light only in the 1930s, long after the first and the second law of thermodynamics had been discovered and numbered. Because the concept of temperature is fundamental to those two laws, the law that establishes temperature as a valid concept should have the lowest number. Hence the zero.*

Measuring Temperature

- How do we define and measure temperatures on the Kelvin scale?
- How do we calibrate a thermoscope so as to make it into a usable thermometer?

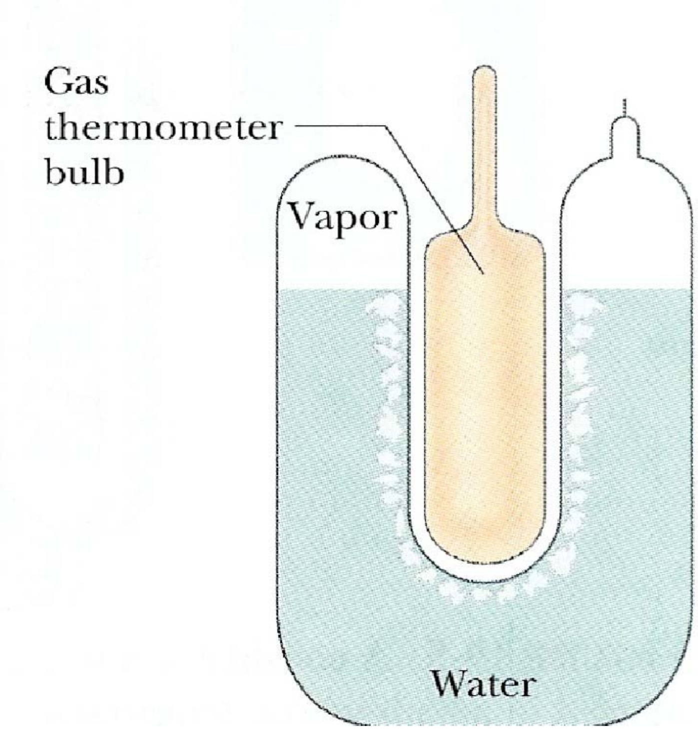
The Triple Point of Water

To set up a temperature scale, we pick some reproducible thermal phenomenon and, quite arbitrarily, assign a certain Kelvin temperature to its thermal environment. That is, we select a *standard fixed point* and give it a standard fixed-point temperature.

We could, for example, select the freezing point or the boiling point of water but, for various technical reasons, we do not. Instead we select the triple point of water.

Liquid water, *solid ice*, and *water vapor* (gaseous water) can coexist, in thermal equilibrium, at only one set of values of pressure and temperature.

Figure below shows a triple-point cell, in which this so-called triple point of water can be achieved in the laboratory.



By international agreement, the triple point of water has been assigned a value of **273.16 K** as the standard fixed-point temperature for the calibration of thermometers. That is,

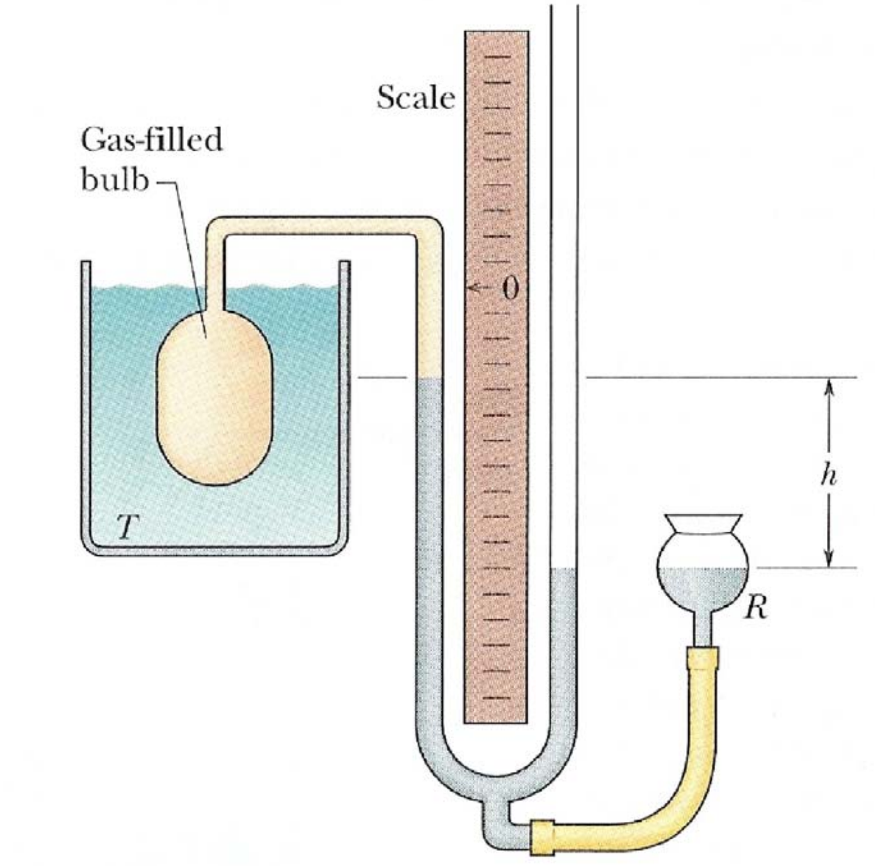
$$T_3 = 273.16 \text{ K}$$

in which the subscript 3 reminds us of the triple point. This agreement also sets **the size of the kelvin** as 1/273.16 of the difference between absolute zero and the triple-point temperature of water.

The Constant-Volume Gas Thermometer

Choosing the temperature-sensitive physical property on which, by international agreement, one should base the thermometer.

- Should it be the length of a metal rod, the electrical resistance of a wire, the pressure exerted by a confined gas, or something else? The choice is important because different choices lead to different temperatures for-to give one example-the boiling point of water. For reasons that will emerge below, the standard thermometer, against which all other thermometers are to be calibrated, is based on the pressure exerted by a gas confined to a fixed volume.



This is called constant-volume gas thermometer

- It consists of a gas-filled bulb made of glass, quartz, or platinum (depending on the temperature range over which the thermometer is to be used) connected by a tube to a mercury manometer. By raising and lowering reservoir *R,* the mercury level on the left can always be brought to the zero of the manometer scale, thus assuring that the volume of the confined gas remains constant.

- The temperature of any body in thermal contact with the bulb is then defined to be

$$T = C\,P \qquad 1$$

in which P is the pressure exerted by the gas and C is a constant. The pressure P is calculated from the relation

$$P = P_0 - \rho g h \qquad \mathbf{2}$$

in which P_o is the atmospheric pressure, ρ is the density of the mercury in the manometer, and h is the measured level difference of mercury in the two arms of the tube.

With the bulb of the gas thermometer immersed in a triple-point cell, as shown above, we have

$$T_3 = C\,P_3 \qquad 3$$

in which P_3 is the pressure reading under this condition.

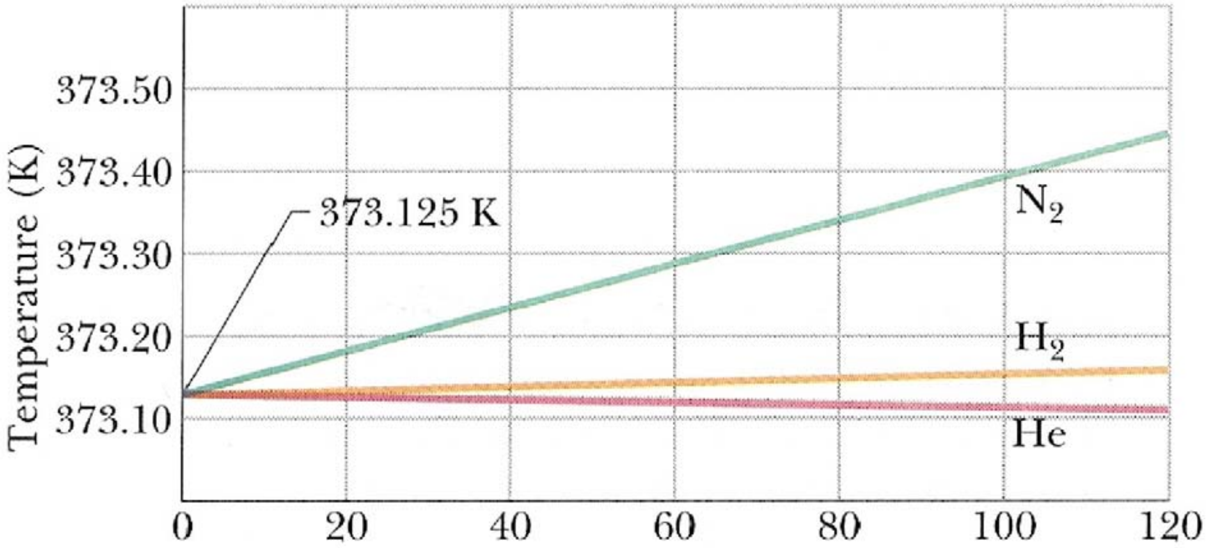
Eliminating C between *1* and *3* leads to

$$T = T_3 \frac{P}{P_3}$$

$$T = (273.16)\left(\frac{P}{P_3}\right) \qquad 4$$

- Equation *4* is not yet our final definition of a temperature measured with a gas thermometer. We have said nothing about what gas (or how much gas) we are to place in the thermometer. If our thermometer is used to measure some temperature, such as the boiling point of water, we find that different gases in the bulb give slightly different measured temperatures. However, <u>as we use smaller and smaller amounts of gas to fill the bulb, the readings converge nicely to a single temperature, no matter what gas we use.</u>

(Temperatures calculated from Eq. 4 for a constant-volume gas thermometer whose bulb is immersed in boiling water. the pressure in the figure is given in kPa)



In other words, Eq. *4* should be written as:

$$T = (273.16)\left(\lim_{m\to 0} \frac{P}{P_3}\right) \qquad 5$$

Note: all readings for the gases in figure converge in the limit of zero density to a temperature of 373.125 K.

- Thus, how would you measure the temperature of an unknown gas? As follows:
  - Fill the bulb with an arbitrary mass *m* of *any* gas (for example, nitrogen) and measure P_3 (using a triplepoint cell) and *P,* the gas pressure at the temperature being

measured. Calculate the ratio P/P_3.

- Then repeat both measurements with a smaller amount of gas in the bulb, and again calculate this ratio. Continue this way, using smaller and smaller amounts of gas, until you can extrapolate to the ratio P/P_3 that you would find if there were approximately no gas in the bulb.

- Calculate the temperature T by substituting that extrapolated ratio into Eq. *5*. (The temperature measured in this way is the *ideal gas temperature.)*

Note: If temperature is to be a truly fundamental physical quantity, one in which the laws of thermodynamics may be expressed, it is absolutely necessary that its definition be independent of the properties of specific materials. It would not do, for example, to have a quantity as basic as temperature depend on the expansivity of mercury, the electrical resistivity of platinum, or any other such ‘handbook" property. We chose the gas thermometer as our standard instrument precisely because no such specific properties of materials are involved in its operation. Use *any* gas-you will always get the same result.

Example

The bulb of a gas thermometer is filled with nitrogen to a pressure of 120 kPa. What provisional value (see figure above) would this thermometer yield for the boiling point of water
and what is the error in this value?

Solution: From figure above, the curve for nitrogen shows I
that, at 120 kPa, the provisional temperature for the boiling point of water would be about 373.44 K. The actual boiling point of water (found by extrapolation in figure) is 373.125 K. Thus using the provisional temperature leads to an error of 0.315 K, or 315 mK.

The Celsius and Fahrenheit scales

- So far, we have discussed only the Kelvin scale, used in basic scientific work. In nearly all countries of the world, the Celsius scale is the scale of choice for popular and commercial use and much scientific use. Celsius temperatures are measured in degrees, and the Celsius degree has the same size as the kelvin. However, the zero of the Celsius scale is shifted to a more convenient value than absolute zero. If T_C represents a Celsius temperature, then

$$T_C = T - 273.15^o \qquad 6$$

In expressing temperatures on the Celsius scale, the degree symbol is commonly used. Thus we write 20.00°C for a Celsius reading but 293.15 K for a Kelvin reading.

- The Fahrenheit scale, used in the United States, employs a smaller degree than the Celsius scale and a different zero of temperature. You can easily verify both these differences by examining an ordinary room thermometer on which both scales are marked. The relation between the Celsius and Fahrenheit scales is

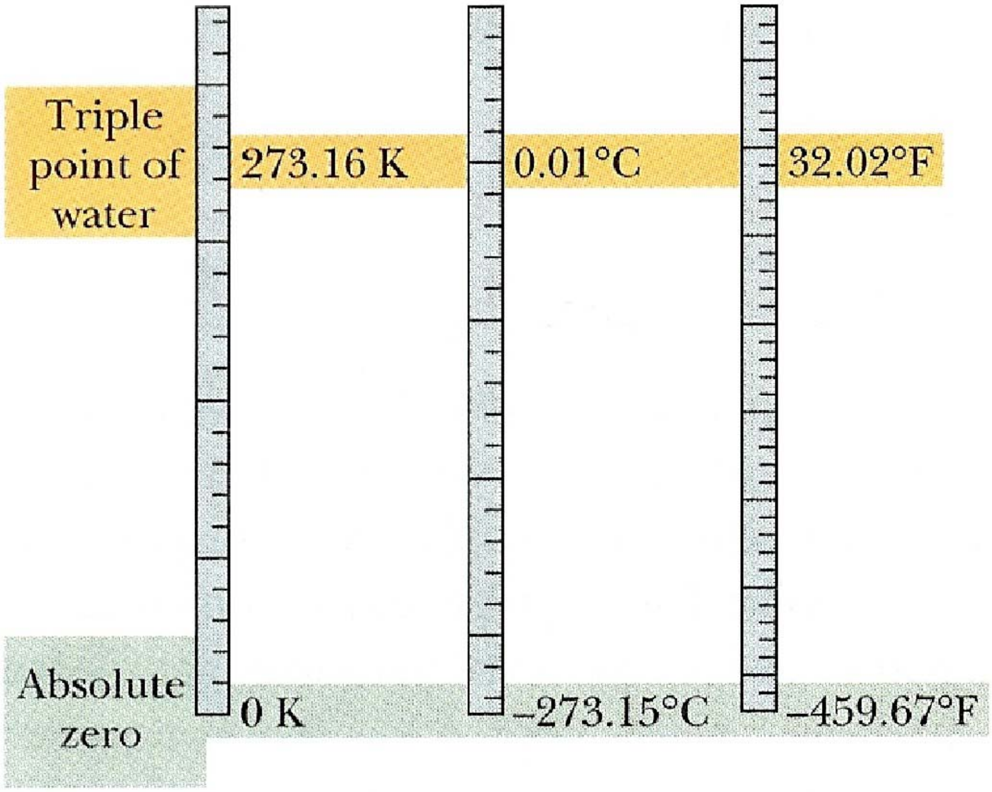
$$T_F = 9/5\ T_C + 32^o \qquad 7$$

where T_F is Fahrenheit temperature.

Transferring between these two scales can be done easily by remembering a few corresponding points (such as the freezing and boiling points of water) and by making use of the fact that 9 degrees on the Fahrenheit scale equals 5 degrees on the Celsius scale. Figure below compares the Kelvin, Celsius, and Fahrenheit scales.

We use the letters *C* and *F* to distinguish measurements and degrees on the two scales. Thus,

O°C = 32°F



3. Basic Concepts of Thermodynamics – Part 2

Temperature and Heat

If you take a can of cola from the refrigerator and leave it on the kitchen table, its temperature will rise-rapidly at first but then more slowly-until the temperature of the cola equals that of the room (the two are then in thermal equilibrium). In the same way, the temperature of a cup of hot coffee, left sitting on the table, will fall until it also reaches room temperature.

In generalizing this situation, we describe the cola or the coffee as a *system* (with temperature T_S) and the relevant parts of the kitchen as the *environment* (with temperature T_E) of that system. Our observation is that if T_S is not equal to T_E, then T_S will change (T_E may also change some) until the two temperatures are equal and thus thermal equilibrium is reached.

Such a change in temperature is due to the transfer of a form of energy between the system and its environment. This energy is *internal energy* (or *thermal energy*).

The transferred internal energy is called **heat** and is symbolized Q.

- Heat is *positive* when internal energy is transferred to a system from its environment (we say that heat is absorbed). Thus, when $T_S < T_E$, $Q > 0$.

- Heat is *negative* when internal energy is transferred from a system to its environment (we say that heat is released or lost). Thus, when $T_S > T_E$, $Q < 0$.
- When $T_S = T_E$, $Q = 0$; there will be no heat transfer between the system and the environment*; they are in thermal equilibrium.*

Heat is the energy that is transferred between a system and its environment because of a temperature difference that exists between them.

Recall that energy can also be transferred between a system and its environment by means of *work W,* which we always associate with a force acting on a system during a displacement of the system. Heat and work, unlike temperature, pressure, and volume, are not intrinsic properties of a system. They have meaning only as they describe the transfer of energy into or out of a system.

Units for heat

Before scientists realized that heat is transferred energy, heat was measured in terms of its ability to raise the temperature of water.

- Thus the calorie (cal) was defined as the amount of heat that would raise the temperature of 1 g of water from 14.5°C to 15.5°C.
- In the British system, the corresponding unit of heat was the British thermal unit (Btu), defined as the amount of heat that would raise the temperature of I Ib of water from 63°F to 64°F.
- In 1948, the scientific community decided that since heat (like work) is transferred energy, the SI unit for heat should be the same as that for energy, namely, the joule.

The calorie is now defined to be 4.1860 J (exactly) with no reference to the heating of water. (The "calorie" used in nutrition, sometimes called the Calorie (Cal), is really a kilocalorie.) The relations among the various heat units are

$$1 \text{ cal} = 3.969 \text{ X } 10^{-3} \text{ Btu} = 4.186 \text{ J}.$$

The Absorption of Heat by Solids and Liquids

Heat Capacity

The heat capacity C of an object (for example, a Pyrex coffee pot or a marble slab) is the proportionality constant between an amount of heat and the change in temperature that this heat produces in the object. Thus

$$Q = C\,(T_f - T_i). \qquad 1$$

in which T_i and T_f are the initial and final temperatures of the object.

- Heat capacity C has the unit of energy per degree (J/C^o) or energy per kelvin (J/K).

Specific Heat

Two objects made of the same material, say marble, will have heat capacities proportional to their masses. It is therefore convenient to define a "heat capacity per unit mass" or specific heat c that refers not to an object but to a unit mass of the material of which the object is made. Eq. *1* then becomes

$$Q = cm\,(T_f - T_i). \qquad 2$$

- Specific heat has the unit J/kg.K.

SPECIFIC HEATS OF SOME SUBSTANCES
AT ROOM TEMPERATURE

	SPECIFIC HEAT		MOLAR SPECIFIC HEAT
SUBSTANCE	cal/g.K	J/kg. K	J/mol. K
Elemental Solids			
Lead	0.0305	128	26.5
Tungsten	0.0321	134	24.8
Silver	0.0564	236	25.5
Copper	0.0923	386	24.5
Aluminum	0.215	900	24.4
Other Solids			
Brass	0.092	380	
Granite	0.19	790	
Glass	0.20	840	
Ice (-lO°C)	0.530	2220	
Liquids			
Mercury	0.033	140	
Ethyl alcohol	0.58	2430	
Seawater	0.93	3900	
Water	1.00	4190	

Example: of specific heats (in J/kg.K):
Lead: 128
Water: 4190
Seawater: 3900

What material will require more heat to raise its temperature by 1K?

Molar Specific Heat

In many instances the most convenient unit for specifying the amount of a substance is the mole (mol), where

I mol = 6.02 X 10^{23} elementary units of *any* substance

Example: 1 mol of aluminum means 6.02 X 10^{23} atoms (the atom being the elementary unit), and 1 mol of aluminum oxide means 6.02 X 10^{23} molecules of the oxide (because the molecule is the elementary unit of a compound).

When quantities are expressed in moles, the specific heat must also involve moles (rather than a mass unit); it is then called a molar specific heat (the unit in this case is J / mol.K).

The table shows the values for some elemental solids (each consisting of a single element) at room temperature.

	SPECIFIC HEAT		MOLAR SPECIFIC HEAT
SUBSTANCE	cal/g.K	J/kg. K	J/mol. K
Elemental Solids			
Lead	0.0305	128	26.5
Tungsten	0.0321	134	24.8
Silver	0.0564	236	25.5
Copper	0.0923	386	24.5
Aluminum	0.215	900	24.4

Note that the molar specific heats of all the elements listed in the table have about the same value at room temperature, namely, **25 J/mol. K**.

- As a matter of fact, the molar specific heats of all solids increase toward that value as the temperature increases.
- Some substances, such as carbon and beryllium, do not reach this limiting value until temperatures well above room temperature.
- Other substances may melt or vaporize before they reach this limit.

When we compare two substances on a molar basis, we are comparing samples that contain the same number of elementary units. The fact that at high enough temperatures, all solid elements have the same molar specific heat tells us that atoms of all kinds-whether they are aluminum, copper, uranium, or anything else-absorb heat in the same way.

Note: In determining and then using the specific heat of any substance, we need to know the conditions under which heat transfer occurs. For solids and liquids, we usually assume that the sample is under constant pressure (usually atmospheric) during the heat transfer. It is also conceivable that the sample is held at constant volume while the heat is absorbed. This means that thermal expansion of the sample is prevented by applying external pressure. For solids and liquids, this is very hard to arrange experimentally but the effect can be calculated, and it turns out that

- The specific heats under constant pressure and constant volume for any solid or liquid differ usually by no more than a few percent.
- Gases, as you will see, have quite different values for their specific heats under constant-pressure conditions and under constant-volume conditions.

Heats of Transformation

When heat is absorbed by a solid or liquid, the temperature of the sample does not necessarily rise. Instead, the sample may change from one *phase,* or *state,* (that is, solid, liquid, or gas) to another. Thus ice may melt and water may boil, absorbing heat in each case without a temperature change. In the reverse processes (water freezing, steam condensing), heat is released by the sample, again while the temperature of the sample remains constant.

The amount of heat per unit mass that must be transferred when a sample completely undergoes a phase change is called the heat of transformation L.

So when a sample of mass m completely undergoes a phase change, the total heat transferred is

$$Q = Lm.$$

- When the phase change is from solid to liquid (then the sample must absorb heat) or from liquid to solid (then the sample must release heat), the heat of transformation is called the heat of fusion L_F. For water at its normal freezing or melting temperature, $L_F = 333$ kJ/kg.

- When the phase change is from liquid to gas (then the sample must absorb heat) or from gas to liquid (then the sample must release heat), the heat of transformation is called the heat of vaporization L_V. For water at its normal boiling or condensation temperature $L_V = 2256$ kJ/kg.

Example: A candy bar has a marked nutritional value of 350 CaI. How many kilowatt-hours of energy will it deliver to the body as it is digested?

Answer: 0.407 kW.h

Note: This amount of energy would keep a 100 W light bulb burning for 4.1 h. To burn up this much energy by exercise, a person would have to jog about 3 or 4 mi.

A generous human diet corresponds to about 3.5 kW.h per day, which represents the absolute maximum amount of work that a human can do in one day. In an industrialized country, this amount of energy can be purchased (perhaps as electrical energy) for about 35 cents.

Example: How much heat is needed to take ice of mass $m = 720$ g at -10^{o}C to a liquid state at 15°C?

Answer: 300 kJ.

Example: A copper slug whose mass m_c is 75 g is heated in a laboratory oven to a temperature T of 312°C. The slug is then dropped into a glass beaker containing a mass $m_W = 220$ g of water. The heat capacity C_b of the beaker is 45 cal/K. The initial temperature T_j of the water and the beaker is 12°C. What is the final temperature T_f of the slug, the beaker, and the water when thermal equilibrium is reached?

Answer: 20^{o}C

The Absorption of Heat by gases

The heat capacity can be written as:

$$C = \frac{dQ}{dT} \qquad 1$$

The heat absorbed by a gas depends on the path.

Heat capacity at constant volume

If a gas is heated with its volume constant, then the measured heat capacity is called the heat capacity at constant volume and is denoted by the symbol C_V.

At constant volume the heat absorbed increases the energy of the system when the temperature is raised from T_1 to T_2, i.e.

$$C_V\,(T_2 - T_1) = U_2 - U_1. \qquad 2$$

For a very small change dT in temperature, the heat capacity at constant volume is equal to the rate of change of internal energy with temperature, i.e.

$$C = \frac{dU}{dT} \qquad 3$$

Heat capacity at constant pressure

If a gas is heated with the pressure fixed, the measured heat capacity is called the heat capacity at constant pressure, C_P . When heat is supplied to a system at constant pressure, expansion occurs and therefore work is done against the applied (external) pressure. Consequently, more heat is required to produce a 1°C rise in temperature at constant pressure than at constant volume. The extra heat needed goes into the work done in expansion, i.e.

$$C_P = C_V + \textit{heat for}\ \text{work done in expansion.} \qquad 4$$

Experimental information about the C_P of a substance may often be represented with considerable precision by an empirical equation. With some substances, such as H_20, the value of C_P is nearly a linear function of temperature and, therefore, may be represented by the equation

$$C_P = a + bT \qquad 5$$

In order to represent the data for other substances it may be necessary to add a third term to Eq. *5*

$$C_P = a + bT + cT^{\alpha} \qquad 6$$

Where α can have values of 2 or -1 or -2, etc.

It is possible to compute the heat required to increase the temperature of a substance over any interval within the range of experimental temperatures. Thus, Eq. *1* becomes:

$$Q = \int_{T_1}^{T_2} C dT \qquad 7$$

If the experimental values of C are available over the temperature interval of interest, the value of Q in Eq. 7 may be obtained graphically. When the heat capacity is known as a function of temperature in the form of an empirical equation such as Eq. *6*, the integral in Eq. *7* becomes

$$Q = \int_{T_1}^{T_2} (a + bT + cT^{\alpha}) dT \qquad 8$$

The molar heat capacity of a substance depends on its temperature. **Example**: it takes 75.22 J/mol °C to raise the temperature of 1 mol of water from 25 to 26°C, and 75.8 J/mol °C to raise it from 95 to 96°C. It is, therefore, more precise to define the molar heat capacity C_X by the differential relationship

$$\mathrm{d}Q_x = nC_{\mathrm{x}}\mathrm{d}T \qquad 9$$

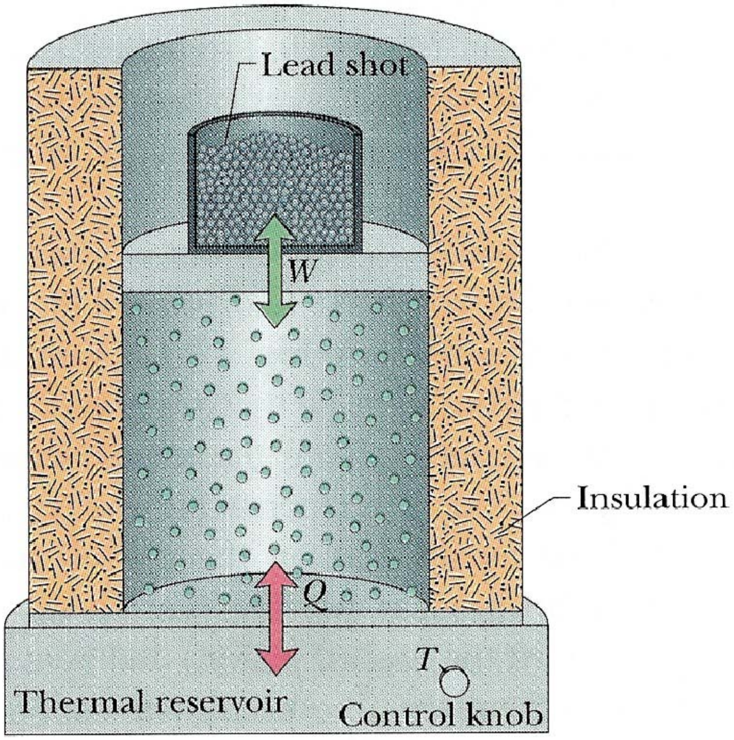
where $\mathrm{d}Q_x$ is the heat required to raise the temperature of n moles of substance from T to $T + dT$ along the path x.

The change in C_P and C_V with temperature, in a range of some ten or even hundred degrees Celsius, is usually small and neglected unless indicated otherwise. Thus, if n moles of a substance are to be heated (or cooled) isobarically from T_1 to T_2, the amount of heat involved is

$$Q \simeq n\, C_P\, (T_2 - T_1) = n\, C_P \Delta T \qquad 10$$

Heat and work

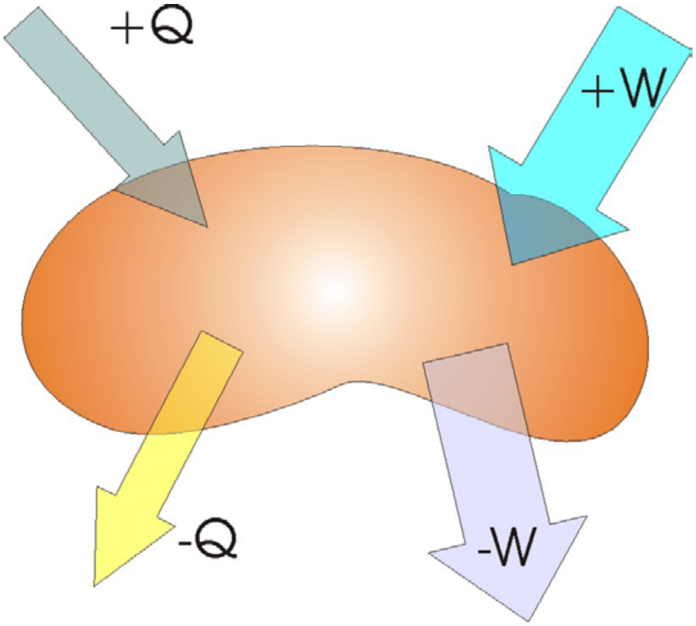
Here we look in some detail at how heat and work are exchanged between a system and its environment. Let us take as our system a gas confined to a cylinder with a movable piston, as in figure below.



- The upward force on the piston due to the pressure of the confined gas is equal to the weight of lead shot loaded onto the top of the piston (atmospheric pressure is neglected here).
- The walls of the cylinder are made of insulating material that does not allow any heat transfer.
- The bottom of the cylinder rests on a reservoir for thermal energy, a *thermal reservoir* (perhaps a hot plate) whose temperature T you can control by turning a knob.
- The system (the gas) starts from an *initial state i,* described by a pressure P_i a volume V_i, and a temperature T_i.
- You want to change the system to *a final state f* described by a pressure

P_f a volume V_f and a temperature T_f.

- During the change from state *i* to state *f*, heat may be transferred into the system from the thermal reservoir (positive heat) or vice versa (negative heat). And work is done by the system to raise the loaded piston (negative work) or lower it (positive work).



- We assume that all such changes occur slowly, with the result that the system is always in (approximate) thermal equilibrium, (that is, every part of the system is always in thermal equilibrium with every other part).

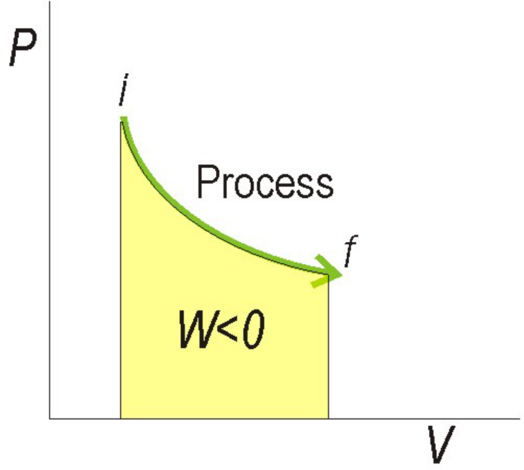
- Suppose that you remove a few lead shot from the piston, allowing the gas to push the piston and remaining shot upward through a differential displacement *ds* with an upward force *F*. Since the displacement is tiny, we can assume that *F* is constant during the displacement. Then *F* has a magnitude that is equal to *PA,* where *P* is the pressure of the gas and *A* is the face area of the piston. The differential work *dW* done by the gas during the displacement is

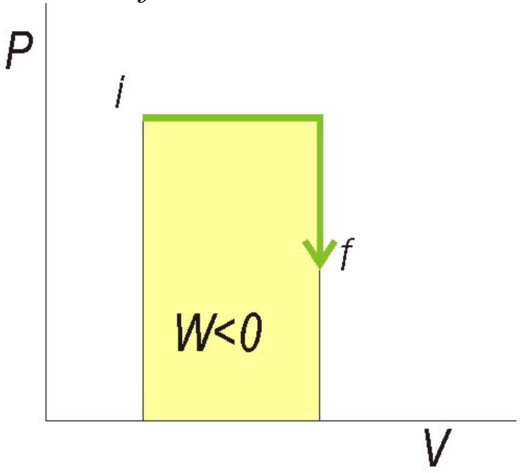
$$dW = F\,ds = (PA)(ds) = PdV \tag{11}$$

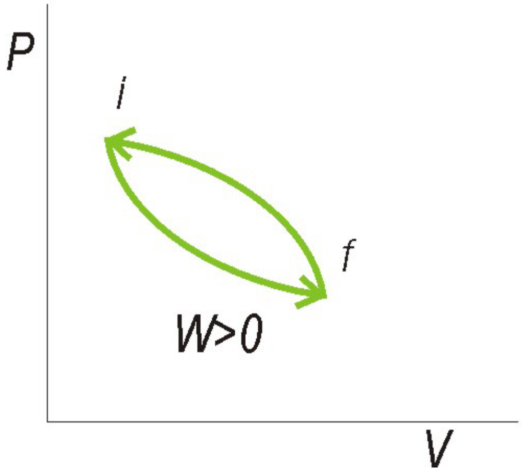
When the overall volume changes from V_i to V_f, the total work done by the gas is:

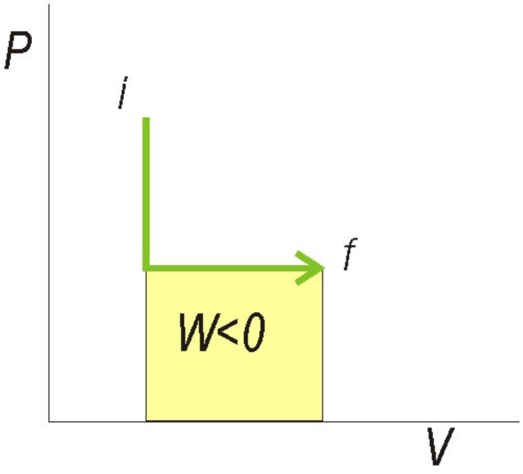
$$W = \int dW = \int_{V_1}^{V_2} PdV \tag{12}$$

- During the change in volume, the pressure and temperature of the gas may also change. To evaluate the integral in Eq. *12* directly, we would need to know how pressure varies with volume for the actual process by which the system changes from state *i* to state *f*.

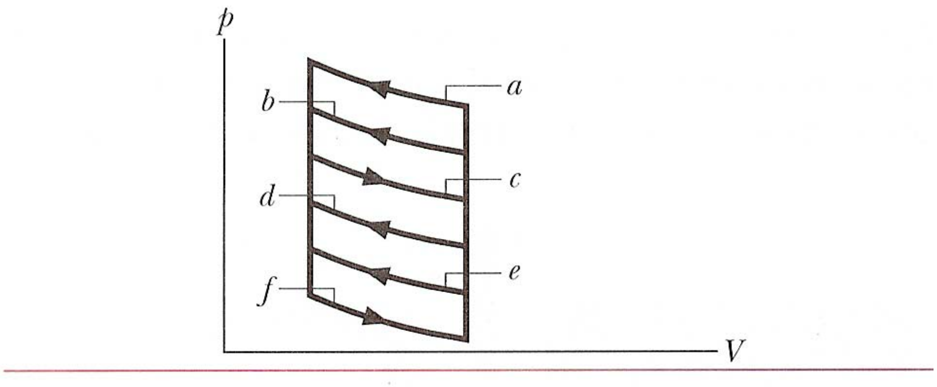








Example: The P- V diagram shows six curved paths (connected by vertical paths) that can be followed by a gas. Which two of them should be part of a closed cycle if the net work done on the gas is to be at its maximum positive value?

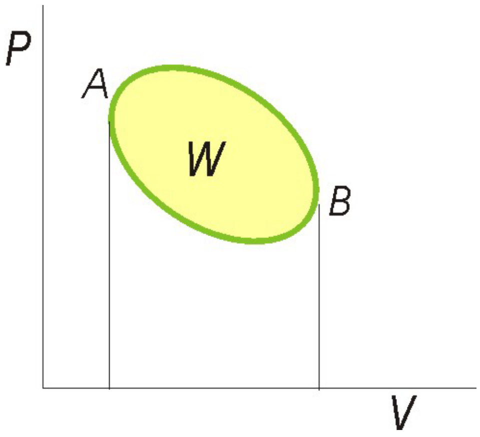


In the important special case in which the outside pressure remains constant during a finite expansion of the system, P may be brought outside the integral sign, so that

$$W = P\int_1^2 dV = P\Delta V \qquad 13$$

This equation shows that, when $P = 0$, i.e. when the external pressure is zero, the work $W = 0$. *A system that expands into a vacuum therefore performs no work*.

- When a system contracts, W is positive because the surroundings now perform work on the system.
- For a cyclic process involving pressure-volume work only, W is the area enclosed by the path in a P- V diagram. W is a positive area when the path corresponds to counter-clockwise rotation, and a negative area for clockwise rotation.



Note: When a gas is changed from V_1 and P_1 to V_2 and P_2 at constant *T it can be done many ways.* and the *W* values obtained may be different for any two of these ways.

- The gas may be expanded along a reversible path. This is indeed the path for which the integral of $P_{ext}\, dV$ *for* the change in state considered is a maximum. All along this path, $P_{ext} = P_{int}$ (except for an infinitesimal amount), and at no point could P_{ext} be increased (thus increasing the integral) without changing the expansion into a compression. The outside pressure may, however, be made smaller than P_{int} for any portion of the path. For this changed portion of the path the contribution to the integral would be decreased, and in addition the expansion would not be reversible because it could not be changed into a compression by an infinitesimal increase of P_{ext}. It is apparent that the reversible path is the only path for which the integral has its maximum value. For any actual path, this integral, the work - *W* performed by the system on the surroundings, is less than this maximum value. Therefore,

$$- W_{actual} \leq - W_{reversible} \qquad 14$$

- Expansion and compression

  During expansion the external pressure is always smaller than the internal pressure. During a compression, the external pressure is always larger than the internal pressure, except in the idealized limit of reversible compression.

  In any actual (real) situation, P_{ext} must be larger than P_{int} to overcome frictions and to make the piston move. The work W_{act} performed on the system is, therefore, larger than the work that would be necessary for compression along the idealized path of a continuous chain of equilibrium states. Therefore, in this case

$$W_{actual} \geq W_{reversible} \qquad 15$$

Eq. *14* and *15* are the same when the sign is taken into account. Thus, for both compressions and expansions for a given change in state the work performed by the system is a maximum for a reversible path.

Kinetic Theory of Gases

A gas is made up of atoms or molecules

- The pressure exerted by a gas is related to the steady drumbeat of its molecules on the walls of its container.

- The ability of a gas to take on the volume of its container is due to the freedom of motion of its molecules.

- The temperature and internal energy of a gas is related to the kinetic energy of these molecules.

The idea that the properties of gases such as diffusibility, expansibility and compressibility could be explained by considering the gas molecules to be in continuous motion occurred to several scientists as far back as the mid-eighteenth century (Bernoulli in 1738, Poule in 1851 and Kronig in 1856). In the second half of the nineteenth century, Boltzmann, Maxwell, Clausius and others developed this hypothesis into the detailed kinetic theory of gases.

The molecular theory of gases was developed under the following assumptions:

For an ideal gas

1. A gas is composed of separate particles called molecules and it can be represented by a simple 'model'.

2. Gaseous particles, whether atoms or molecules, behave like point centers of mass, i.e. the volume actually occupied by the individual molecules of an ideal gas under ordinary conditions is insignificant compared with the total volume of the gas.

3. These point centers of mass are far apart and most of the time do not exert any force (attraction or repulsion) on one another, except when near the temperature at which they become liquids.

4. They are in continuous, completely random motion in a straight line.

For a real gas

a. The volume occupied by the molecules under ordinary conditions may not be negligible compared with the total volume of the gas.

b. The forces (attractive or repulsive) exerted by the molecules on one another may not be negligible.

Avogadro's number

The *mole* is one of the seven SI base units and is defined as follows:

One mole is the number of atoms in a 12 g sample of carbon-12.

The number of elementary units in one mole is equal to Avogadro's number and it was determined experimentally:

$$N_A = 6.02 \text{ X } 10^{23} \text{ mol}^{-1} \qquad 1$$

Italian scientist Amadeo Avogadro (1776-1856), suggested that all gases contain the same number of molecules or atoms when they occupy the same volume under the same conditions of temperature and pressure.

- The number of moles n contained in a sample of any substance can be found from

$$n = N / N_A \qquad 2$$

where N is the number of molecules in the sample.

- The number of moles in a sample can also be found from the mass M_{sam} of the sample and either the molar mass M (the mass of 1 mole of that substance) or the mass m of one molecule:

$$N = M_{sam} / M = M_{sam} / mN_A \qquad 3$$

Note: The enormously large value of Avogadro's number suggests how tiny and how numerous atoms must be. A mole of air, for example, can easily fit into a suitcase. Yet, if these molecules were spread uniformly over the surface of Earth, there would be about 120,000 of them per square centimeter. A second example: one mole of tennis balls would fill a volume equal to that of seven Moons!

Ideal Gases

Experimenters have found that if we confine 1 mole samples of various gases in boxes of identical volume and hold the gases at the same temperature, then their measured pressures are nearly - though not exactly - the same. If we repeat the measurements at lower gas densities, then these small differences in the measured pressures tend to disappear. Further experiments show that, at low enough densities, all real gases tend to obey the relation

$$PV = nRT \qquad 4$$

which is called **the ideal gas law.** Here P is the absolute pressure; T is the absolute temperature, n the number of moles and R the gas constant, which has the same value for all the gases;

$$\boldsymbol{R = 8.31\ \mathrm{J/mol.K}}$$

Provided the gas density is reasonably low, Eq. *4* holds for any type of gas, or a mixture of different types, with n being the total number of moles present.

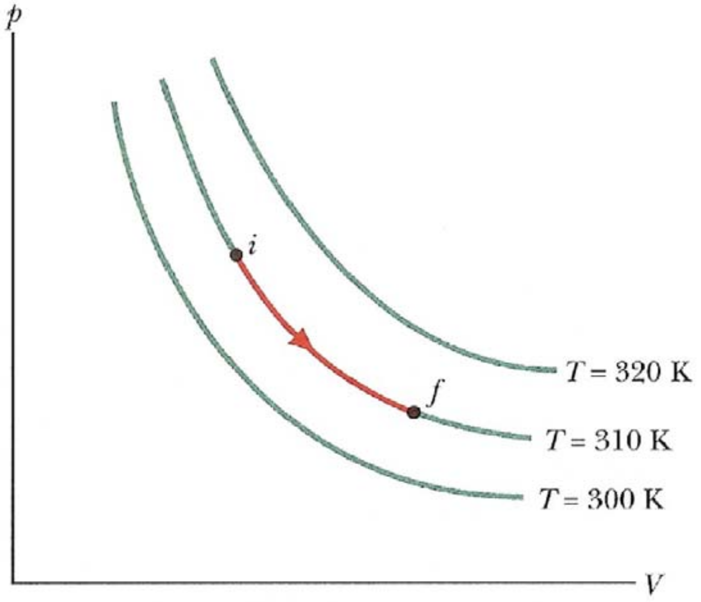
Work done by an Ideal Gas at constant temperature

Suppose that a sample of n moles of an ideal gas, confined to a piston-cylinder arrangement, is allowed to expand from an initial volume V_i to a final volume V_f. Suppose further that the temperature T of the gas is held constant throughout the process. Such a process is called an isothermal expansion (and the reverse is called an isothermal compression).

$$W = \int dW = \int_{V_i}^{V_f} P dV \qquad 5$$

On a p-V diagram, an isotherm is a curve that connects points that have the same temperature. It is then a graph of pressure versus volume for a gas whose temperature T is held constant, that is, a graph of

$$P = nRT\frac{1}{V} = (const)\frac{1}{V} \qquad 6$$



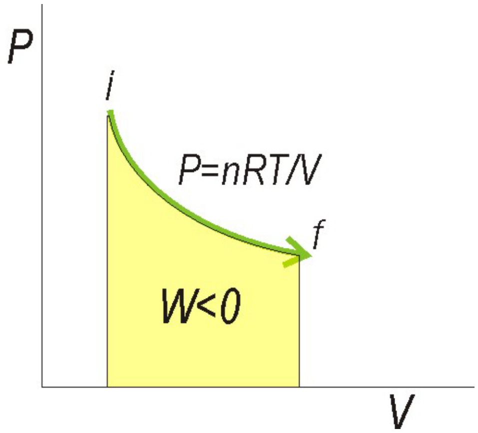
Let us consider the reversible expansion of an ideal gas at constant temperature T, in which the external pressure P_{ext} is successively reduced so that it always balances the internal pressure P_{int}.

By the ideal gas equation:

$$P_{ext} = P_{\text{int}} = \frac{nRT}{V}$$

thus,

$$W = -\int_i^f P_{ext} dV = -nRT \int_i^f \frac{dV}{V} = -nRT \ln \frac{V_f}{V_i} \qquad 7$$



The yellow area represents the work performed by the system and is, therefore, equal to - W. As will be seen later, heat has to be supplied to the system to keep the temperature of the expanding gas constant.

- For an expansion, $V_f > V_i$ by definition, so the ratio V_f / V_i in Eq. 7 is greater than unity. The natural logarithm of a quantity greater than unity is positive, and so the work W done by an ideal gas during an isothermal expansion is negative, as we expect. For a compression, we have $V_f < V_i$, so the ratio of volumes in Eq. 6 is less than unity. The natural logarithm in that equation - hence the work W-*is* positive, again as we expect.

Work done by an Ideal Gas at constant volume

If the volume of the gas is constant, then Eq. *5* yields

$$W = 0 \tag{8}$$

Work done by an Ideal Gas at constant pressure

If, instead, the volume changes while the pressure P of the gas is held constant, then Eq. 5 becomes

$$W = P\,(V_f - V_i) = P\,\Delta V \tag{9}$$

Example: A cylinder contains 12 L of oxygen at 20°C and 15 atm. The temperature is raised to 35°C, and the volume reduced to 8.5 L. What is the final pressure of the gas in atmospheres? Assume that the gas is ideal.

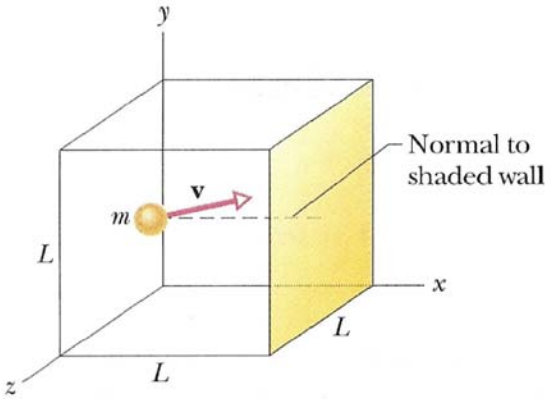
Hint: use Eq. 4: $PV = nRT$
Answer: 22 atm

Example: One mole of oxygen (assume it to be an ideal gas) expands at a constant temperature T of 310 K from an initial volume V_i of 12 L to a final volume V_f of 19 L. How much work is done by the expanding gas?

Answer: 1180 J

Pressure, Temperature and RMS Speed

. Assume n moles of an ideal gas are confined in a cubical box of volume V, as in figure. The walls of the box are held at temperature T. What is the connection between the pressure P exerted by the gas on the walls and the speeds of the molecules?



- The molecules of gas in the box are moving in all directions and with various speeds, bumping into each other and bouncing from the walls of the box like balls in a racquetball court. We ignore (for the time being) collisions of the molecules with one another and consider only elastic collisions with the walls.

- Figure shows a typical gas molecule, of mass m and velocity v, that is about to collide with the shaded wall. Because we assume that any collision of a molecule with a wall is elastic, when this molecule collides with the shaded wall, the only component of its velocity that is changed is the x component, and that component is reversed. This means that the only change in the particle's momentum is then along the x axis, and that change is

$$\Delta p_x = (-mv_x) - (mv_x) = -2mv_x$$

So, the momentum delivered by the molecule to the wall is $2mv_x$

- The molecule will hit the shaded wall repeatedly. The time Δt between collisions is the time the molecule takes to travel to the opposite wall and back again (a distance of $2L$) at speed v_x.Thus

- Δt is equal to $2L / v_{x'}$ (Note that this result holds even if the molecule bounces off any of the other walls along the way, because those walls are parallel to x and so cannot change v_x .) Thus the average rate at which momentum is delivered to the shaded wall by this single molecule is

$$\Delta p_x / \Delta t = 2mv_x / (2L/v_x) = mv_x^2 / L$$

Newton’s second law gives:

$$\boldsymbol{F} = d\boldsymbol{p} / dt$$

Where ***F*** is the force acting on the wall.

The pressure P on the wall is equal to the total force F_x divided by the area of the wall and it contains the contributions of all the molecules

$$P = \frac{F_x}{L^2} = \frac{\sum_{i=1}^{N} \frac{m v_{x_i}^2}{L}}{L^2} = \frac{m}{L^3} \sum_{i=1}^{N} v_{x_i}^2 \tag{10}$$

We can replace the sum by

$$\sum_{i=1}^{N} v_{x_i}^2 = n N_A \overline{v_x^2}$$

where $\overline{v_x^2}$ is the average value of the square of the x components of all the molecular speeds.

Eq. *10* becomes

$$P = \frac{n m N_A}{L^3} \overline{v_x^2}$$

or, by replacing mN_A with the molecular mass M, we get:

$$P = \frac{nM}{L^3} \overline{v_x^2} \tag{11}$$

For any molecule,

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

Because there are many molecules and because they are all moving in random directions, the average values of the squares of their velocity components are equal, so that

$$v_x^2 = \frac{1}{3} v^2$$

and the pressure Eq. *11* becomes

$$P = \frac{nM}{3V} \overline{v^2}$$

The square root of $\overline{v^2}$ is called root mean square $\boldsymbol{v_{rms}}$

The equation for the pressure becomes:

$$P = \frac{nM}{3V} v_{rms}^2 \qquad 12$$

Combining the law of ideal gases ($PV = nRT$) with Eq. *12* we get:

$$v_{rms} = \sqrt{\frac{3RT}{M}} \qquad 13$$

Note:

- The speeds are surprisingly high. For hydrogen molecules at room temperature (300 K), the rms speed is 1920 m/s or 4300 rni/h - faster than a speeding bullet!

- On the surface of the Sun, where the temperature is 2 X 10^6 K, the rms speed of hydrogen molecules would be 82 times larger than at room temperature were it not for the fact that at such high speeds, the molecules cannot survive the collisions among themselves.

- Remember too that the rms speed is only a kind of average speed; many molecules move much faster than this, and some much slower.

- The speed of sound in a gas is closely related to the rms speed of the molecules of that gas. In a sound wave, the disturbance is passed on from molecule to molecule by means of collisions. The wave cannot move any faster than the "average" speed of the molecules. In fact, the speed of sound must be somewhat less than this "average" molecular speed because not all molecules are moving in exactly the same direction as the wave. As examples, at room temperature, the rms speeds of hydrogen and nitrogen molecules are 1920 m/s and 517 m/s, respectively. The speeds of sound in these two gases at this temperature are 1350 *m/s* and 350 m/s, respectively.

- A question often arises: If molecules move so fast, why does it take as long as a minute or so before you can smell perfume if someone opens a bottle across a room? Although the molecules move very fast between collisions -a given molecule will wander only very slowly away from its release point.

Translational Kinetic Energy

We again consider a single molecule of an ideal gas as it moves around in a box, but we now assume that its speed changes when it collides with other molecules.

- Its translational kinetic energy at any instant is

$$KE = \tfrac{1}{2} mv^2$$

- Its *average* translational kinetic energy over the time that we watch it is

$$\overline{KE} = \overline{\tfrac{1}{2} mv^2} = \tfrac{1}{2} m\overline{v^2} = \tfrac{1}{2} mv_{rms}^2 \qquad 14$$

Here we make the assumption that the average speed of the molecule during our observation is the same as the average speed of all the molecules at any given time. (Provided the total energy of the gas is not changing and we observe our molecule for long enough, this assumption is appropriate.)

- Substituting for v_{rms} from Eq. *13* we get

$$\overline{KE} = \frac{3RT}{2N_A}$$

or

$$\overline{KE} = \frac{3}{2}kT \qquad 15$$

$k = R/N_A$ is Boltzmann constant

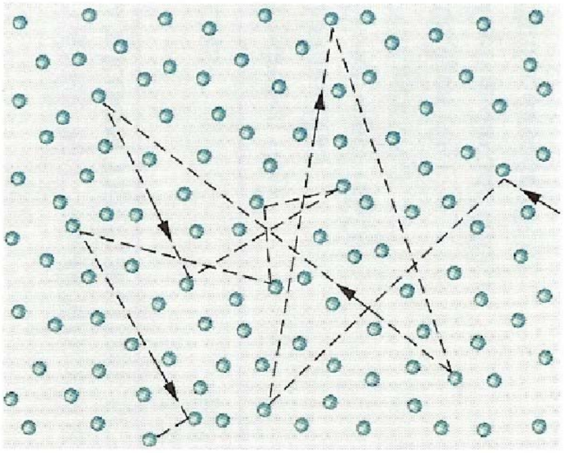
$$k = 1.38 \times 10^{-23}\ \text{J/K}$$

At a given temperature *T,* all ideal gas molecules - no matter what their mass - have the same average translational kinetic energy, namely, *3/2 kT.* When we measure the temperature of a gas, we are also measuring the average translational kinetic energy of its molecules.

Example: A gas mixture consists of molecules of types I, 2, and 3, with molecular masses $m_1 > m_2 > m_3$. Rank the three types according to (a) average kinetic energy and (b) rms speed, greatest first.

Mean Free Path

A typical molecule as it moves through the gas, changes both speed and direction abruptly as it collides elastically with other molecules. Between collisions, the molecule moves in a straight line at constant speed. Although the figure shows all the other molecules as stationary, they too are moving in much the same way.



One useful parameter to describe this random motion is the mean free path λ. As its name implies, λ is the average distance traversed by a molecule between collisions.

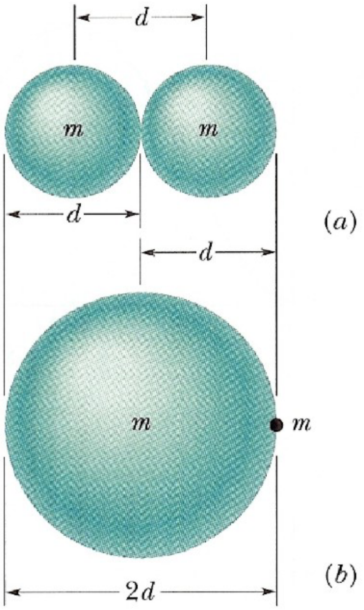
- We expect λ to vary inversely with N / V, the number of molecules per unit volume (or density of molecules). The larger N / V is, the more collisions there should be and the smaller the mean free path.
- We also expect λ to vary inversely with the size of the molecules. (If the molecules were true points, they would never collide and the mean free path would be infinite.) Thus the larger the molecules, the smaller the mean free path.
- We can even predict that λ should vary (inversely) as the square of the molecular diameter because the cross section of a molecule - not its diameter - determines its effective target area.

The expression for the mean free path is:

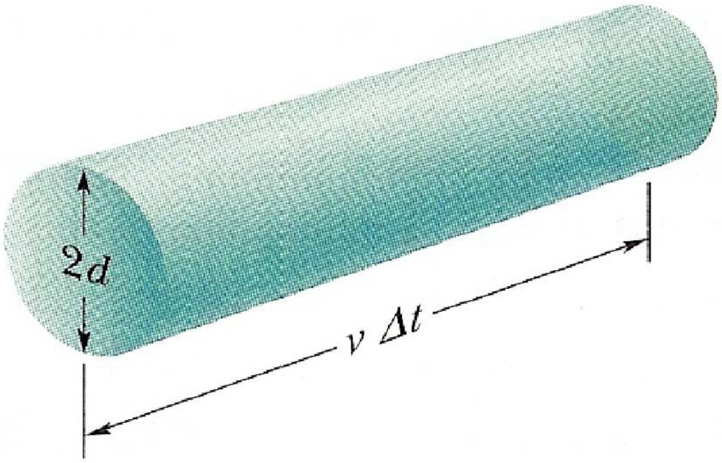
$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \, N/V} \qquad 16$$

- To justify Eq. *16*, we focus attention on a single molecule and assume that the molecule is traveling with a constant speed v and that all the other molecules are at rest. Later, we shall relax this assumption.

- We assume further that the molecules are spheres of diameter d. A collision will then take place if the centers of the molecules come within a distance d of each other (see figure below). Another, more helpful way to look at the situation is to consider the single molecule to have a ***radius*** of d and all the other molecules to be ***points***. This does not change our criterion for a collision.



- As the single molecule zigzags through the gas, it sweeps out a short cylinder of cross-sectional area πd^2 between successive collisions. If we watch this molecule for a time interval Δt, it moves a distance $v \Delta t$, where v is its assumed speed. Thus, if we align all the short cylinders swept out in Δt, we form a composite cylinder (see figure) of length $v \Delta t$ and volume $(\pi d^2)(v \Delta t)$. The number of collisions that occur is then equal to the number of (point) molecules that lie within this cylinder.



- Since N/V is the number of molecules per unit volume, the number of collisions is N/V times the volume of the cylinder, or

$$(N/V)\ (\pi d^2)(v\ \Delta t).$$

- The mean free path is the length of the path (and of the cylinder) divided by this number:

$$\lambda = \frac{length.of.path}{number.of.collisions} \approx \frac{v\Delta t}{\pi d^2 v\Delta t\, N/V} = \frac{1}{\pi d^2\ N/V} \qquad 17$$

- This equation is only approximate because it is based on the assumption that all the molecules except one are at rest. In fact, *all* the molecules are moving; when this is taken properly into account, Eq. *16* results. Note that it differs from the (approximate) Eq. *17* only by a factor of 1/√2.

- We can even get a glimpse of what is "approximate" about Eq. *17*. The v in the numerator and that in the denominator are-strictly-not the same. The v in the numerator is the mean speed of the molecule *relative to the container.* The v in the denominator is the mean speed of the single molecule *relative to the other molecules,* which are moving. It is this latter average speed that determines the number of collisions. A detailed calculation, taking into account the actual speed distribution of the molecules, gives

$$\overline{v_{rel}} = \sqrt{2}\,\overline{v}$$

and thus the factor √2.

- The mean free path of air molecules at sea level is about 0.1 μm. At an altitude of 100 km, the density of air has dropped to such an extent that the mean free path rises to about 16 cm. At 300 km, the mean free path is about 20 km.

  Note: A problem faced by those who would study the physics and chemistry of the upper atmosphere in the laboratory is the unavailability of containers large enough to hold gas samples that simulate upper atmospheric conditions. Yet studies of the concentrations of Freon, carbon dioxide, and ozone in the upper atmosphere are of vital public concern.

Example: The molecular diameters of gas molecules of different kinds can be found experimentally by measuring the rates at which the different gases diffuse (spread) into each other. For oxygen, $d = 2.9 \text{ X } 10^{-10}$ m has been reported.

(a) What is the mean free path for oxygen at room temperature (T = 300 K) and at an atmospheric pressure of 1.0 atm? Assume it is an ideal gas under these conditions.

Answer: $1.1\text{x}10^{-7}\text{m}$

(b) If the average speed of an oxygen molecule is 450 m/s, what is the average collision rate?

Hint: the average collision rate is found by dividing the average speed by the mean free path.

The molar specific heat of an ideal gas

Internal Energy U

- Assume that the ideal gas is a *monatomic gas* (which has individual atoms rather than molecules), such as helium, neon, or argon.

- The internal energy is the energy associated with random motions of atoms and molecules. So let us assume that the internal energy U of the ideal gas is simply the sum of the translational kinetic energies of its atoms. (Individual atoms do not have rotational kinetic energy.)

- The average translational kinetic energy of a single atom depends only on the gas temperature and is given by

$$\overline{KE} = \frac{3}{2}kT$$

- A sample of n moles of such a gas contains nN_A atoms. The internal energy U of the sample is then

$$U = (nN_A)\overline{KE}$$

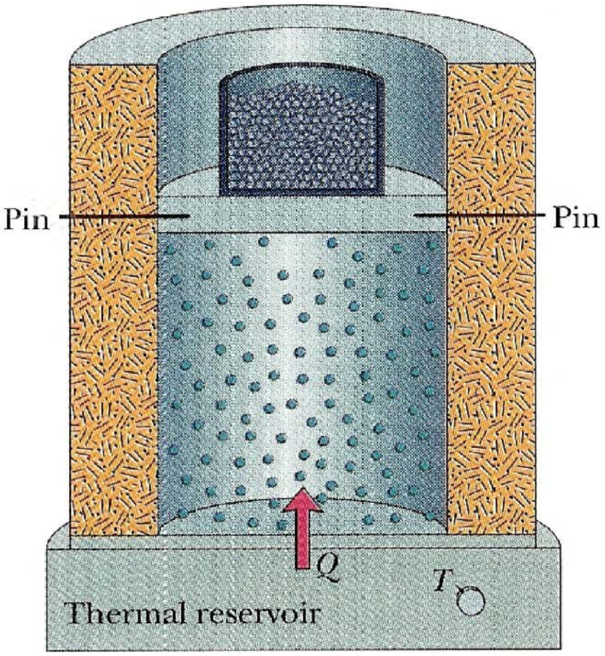
or

$$U = \frac{3}{2}nRT \tag{18}$$

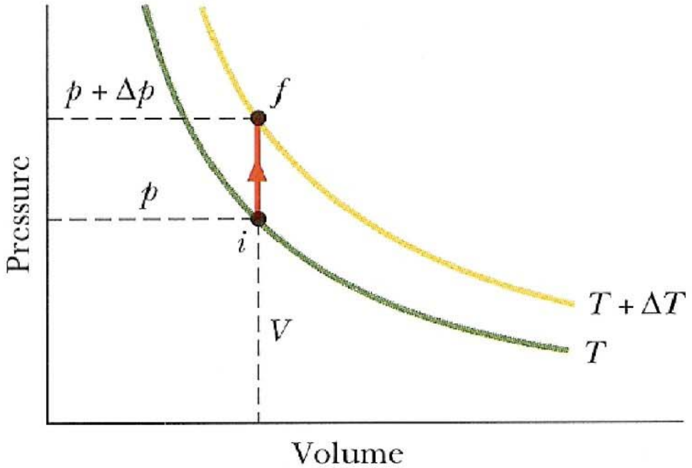
The internal energy U of an ideal gas is a function of the gas temperature only; it does not depend on any other variable.

Molar specific heat at constant volume

Figure shows n moles of an ideal gas at pressure P and temperature T, confined to a cylinder of fixed volume V.



(a)



(b)

- By adding a small amount of heat Q to the gas, its temperature rises a small amount to $T + \Delta T$, and its pressure to $P + \Delta P$, bringing the gas from the initial state I to *final state f.*

- The molar specific heat at constant volume is defined from:

$$Q = nC_v \Delta T$$

- Because the volume does not change, the added heat increases the internal energy of the gas

$$C_v = \frac{1}{n}\frac{\Delta U}{\Delta T}$$

but

$$U = \frac{3}{2} nRT$$

thus

$$C_v = 3/2\, R \text{ J/mol.K} \qquad 19$$

- The prediction for the monatomic gases agrees very well with the experimental results. ($C_v = 12.5$ J / mol.K)

Note: For diatomic and polyatomic gases the values are different.

- Alternately, the internal energy of any ideal gas can be written as

$$U = n\, C_v T \qquad 20$$

and

$$\Delta U = n\, C_v \Delta T \qquad 21$$

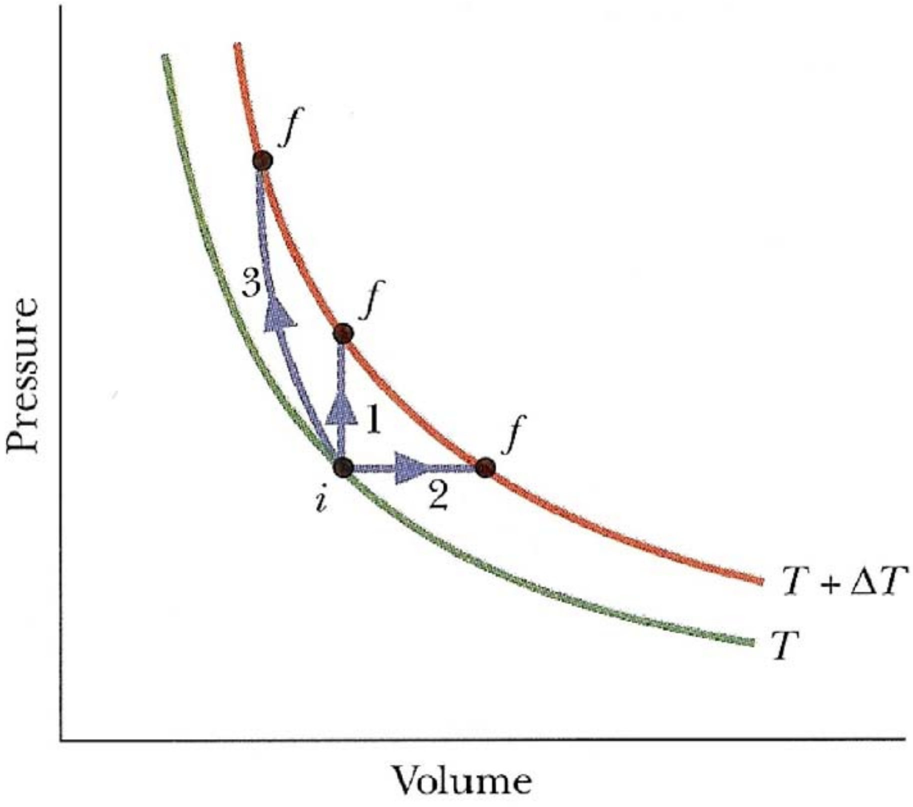
This equation applies not only to an ideal monatomic gas but also to diatomic and polyatomic ideal gases, provided the appropriate value of C_v is used.

Conclusion:

- **The internal energy depends on the temperature of the gas but not on its pressure or density.**

- **A change in the internal energy *U* of a confined ideal gas depends on the change in the gas temperature only; it does not depend on what type of process produces the change in the temperature.**

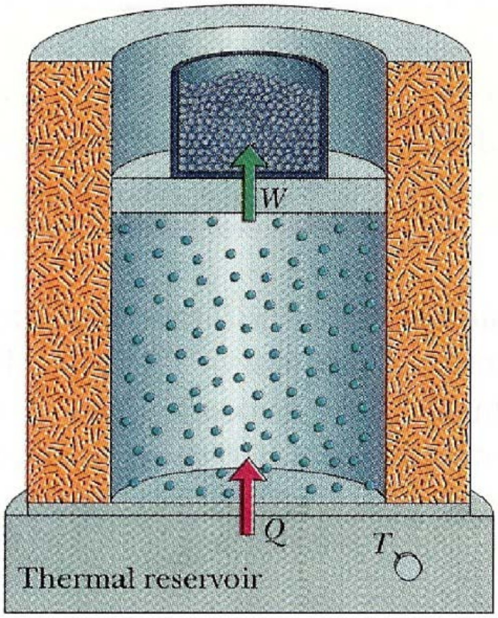
Note: Consider the three paths between the two isotherms in the *P- V* diagram in figure below. Path 1 represents a constant-volume process. Path 2 represents a constant-pressure process, and as we will see shortly, path 3 represents an adiabatic process.



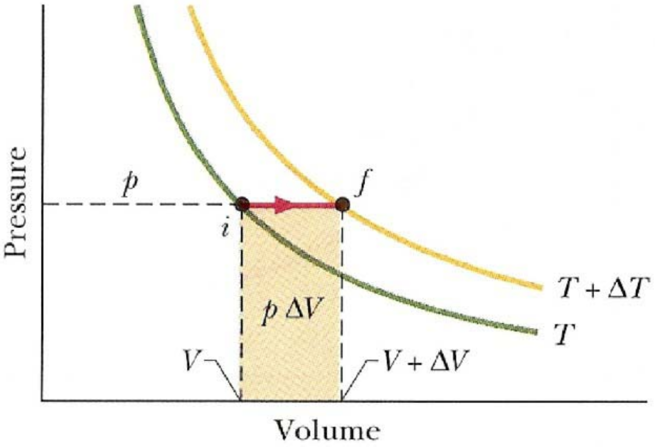
Although the values of heat Q and work *W* associated with these three paths differ, as do P_f and V_f, the values of ΔU associated with the three paths are identical and are all given by Eq. *21*, because they all involve the same temperature change ΔT. So, no matter what path is actually traversed between *T* and $T + \Delta T$, we can always use path 1 and Eq. *21* to compute ΔU easily.

Molar specific heat at constant pressure

We now assume that the temperature of the ideal gas is increased by the same small amount ΔT as previously, but that the necessary heat Q is added with the gas under constant pressure. A mechanism for doing this is shown in figure below.



(a)



- We can guess at once that the molar specific heat at constant pressure C_p which we define with

$$Q = n\, C_P\, \Delta T \qquad 22$$

is *greater* than the molar specific heat at constant volume, because energy must now be supplied not only to raise the temperature of the gas but also for the gas to do work, that is, to lift the weighted piston.

- The heat provided by the environment is used to increase the temperature of the gas and do work on the system:

$$Q = \Delta U + W \qquad 23$$

By writing

$$W = P\Delta V = n\,R\,\Delta T$$

We get

$$n\,C_P\,\Delta T = n\,C_v\,\Delta T + n\,R\,\Delta T$$

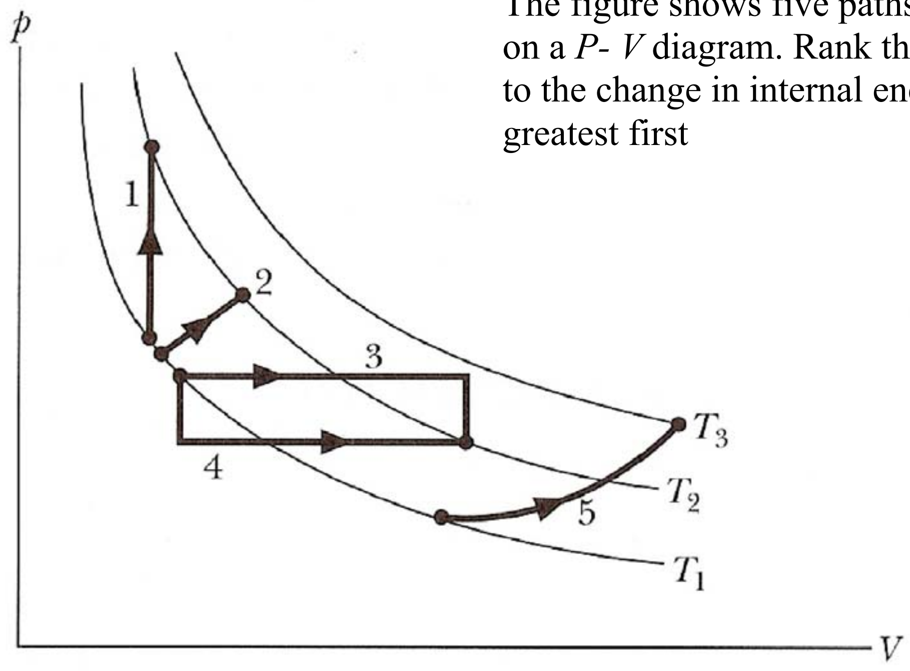
which gives

$$C_P = C_v + R \qquad 24$$

Note: This prediction of kinetic theory agrees well with experiment, 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.

Example:

The figure shows five paths traversed by a gas on a *P*- *V* diagram. Rank the paths according to the change in internal energy of the gas, greatest first



Example: A bubble of 5.00 mol of (monatomic) helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase ΔT of 20.0 C° at constant pressure. As a result, the bubble expands.

(a) How much heat Q is added to the helium during the expansion and temperature increase?

Answer: 2077J

(b) What is the change ΔU in the internal energy of the helium during the temperature increase?

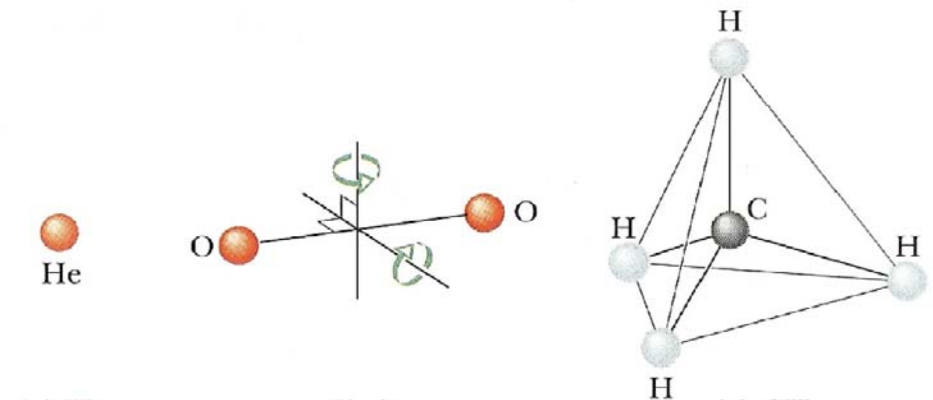
Answer: 1246.5 J

(c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

Answer: 831 J

Degrees of Freedom and molar specific heats

The equation for C_v for monatomic gases give the value 12.5 J / mol.K which agrees well with the experiment. However, for diatomic and polyatomic gases it does not. The reason is that molecules with more than one atom can store internal energy in forms other than translational motion.



(a) He (b) O_2 (c) CH_4

Figure shows kinetic theory models of helium (a monatomic gas), oxygen (diatomic), and methane (polyatomic). On the basis of their structure, it seems reasonable to assume that

- monatomic molecules-which are essentially point like and have only a very small rotational inertia about any axis-can store energy only in their translational motion.
- Diatomic and polyatomic molecules, however, should be able to store substantial additional amounts of energy by rotating or oscillating. To take these possibilities into account quantitatively, we use the **theorem of the equipartition of energy**, introduced by James Clerk Maxwell:

Every kind of molecule has a certain number ***f*** of *degrees of freedom*, which are independent ways in which the molecule can store energy. Each such degree of freedom has associated with it-on average -energy of $1/2kT$ per molecule (or $1/2RT$ per mole).

- For translational motion, there are three degrees of freedom, corresponding to the three perpendicular axes along which such motion can occur. For rotational motion, a monatomic molecule has no degrees of freedom.
- A diatomic molecule-the rigid dumbbell (see figure) has two rotational degrees of freedom, corresponding to the two perpendicular axes about which it can store rotational energy. Such a molecule cannot store rotational energy about the axis connecting the nuclei of its two constituent atoms because its rotational inertia about this axis is approximately zero.
- A molecule with more than two atoms has **six degrees of freedom**, three rotational and three translational.

Thus, for dia- and polyatomic gases, we replace

$$U = 3/2\ nRT \text{ with } U = (f/2)\ nRT$$

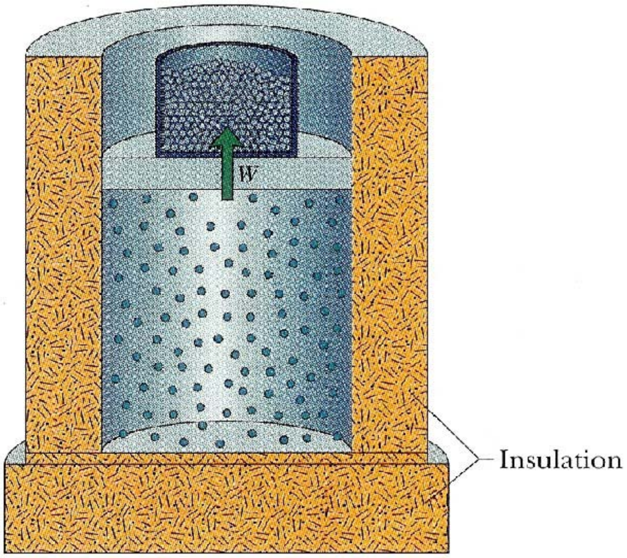
Doing so leads to the prediction

$$C_V = (f/2)\ R = 4.16 f\ J/mol.K \qquad 25$$

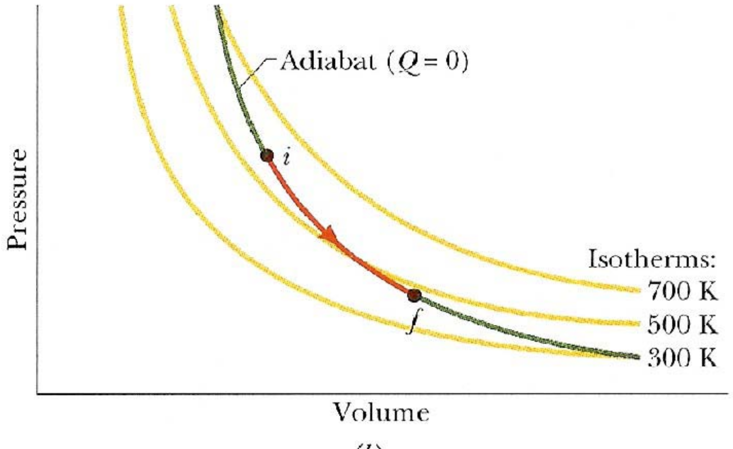
Note: This is OK for diatomic gases however is too low for polyatomic ones. More on this later.

Adiabatic expansion of an ideal gas

A process for which $Q = 0$ is an *adiabatic process*. We can ensure that $Q = 0$ either by carrying out the process very quickly (as in sound waves) or by doing it slowly in a well-insulated container.



(*a*)



(*b*)

Figure shows an insulated cylinder containing an ideal gas and resting on an insulating stand. By removing weight from the piston, we can allow the gas to expand adiabatically. As the volume increases, both the pressure and the temperature drop. The relation between the pressure and the volume during such an adiabatic process is

$$PV^{\gamma} = \text{a constant} \qquad 26$$

in which $\gamma = C_P / C_v$, the ratio of the molar specific heats for the gas.

On a *P*- *V* diagram the process occurs along a line (called an *adiabat*.

- When the gas goes from an initial state *i* to a final state *f*, Eq. *26* can be written as

$$P_i V^{\gamma}_i = P_f V^{\gamma}_f \qquad 27$$

- If we replace *P* from $PV = nRT$, Eq. *26* becomes

$$TV^{\gamma\text{-}1} = \text{a constant} \qquad 28$$

And Eq. 26 can be written as:

$$T_i V^{\gamma-1}_i = T_f V^{\gamma-1}_f \qquad 29$$

Note: Proof of Eq. 26

Suppose that you remove some lead shot from the piston in the above figure, allowing the ideal gas to push the piston and the remaining shot upward and thus to increase the volume by a differential amount *dV*. Since the volume change is tiny, we may assume that the pressure *P* of the gas on the piston is constant during the change. This assumption allows us to say that the work *dW* done by the gas during the volume increase is equal to *P dV*.
Eq. *23* tells us that:

$$Q = dU + PdV$$

where $Q = 0$, $dU = n\ C_V dT$.

Thus,

$$n\, C_V\, dT + P dV = 0$$

$$n\, dT = -\,(P / C_V)\, dV \qquad 30$$

From the ideal gas law $PV = nRT$, we get:

$$P\, dV + V\, dP = n\, R\, dT \qquad 31$$

But $C_P = C_V + R$,

Eq. 31 becomes:

$$ndT = \frac{PdV + VdP}{C_P - C_V} \qquad 32$$

30 and 32 become:

$$\frac{dP}{P} + \left(\frac{C_P}{C_V}\right)\frac{dV}{V} = 0$$

This becomes

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

and by integrating we get

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

or

$$\ln PV^{\gamma} = \text{a constant}$$

and by taking the antilog of both sides,

$$\boldsymbol{PV^{\gamma} = \textbf{a constant}}$$

Kinetic Theory for real gases

Recall that for real gases.

(i) The volume occupied by the molecules under ordinary conditions may not be negligible compared with the total volume of the gas.

(ii) The force exerted by the molecules on one another may not be negligible.

Let us now consider these assumptions in some detail.

(i) *Volume of molecules:* Under normal temperature and pressure, the volume of the molecules is less than 0.1 % of the total volume of the gas.

It has been found that at a pressure of about 10 MPa the molecules would occupy a volume which is only about 12 times their own volume. The effect of the finite size of the molecules will be to reduce the available free space for movement. As a result, the number of impacts on the walls of the container, and therefore the pressure on them, will be greater than that obtained by the use of the kinetic theory of gases.

(ii) *Force exerted by the molecules on one another*: Liquids possess the cohesive property. The fact that gases can be transformed into liquids implies that the molecules of a gas possess attractive force. The consequence of attractive forces among the molecules is to make the pressure less than that to be expected theoretically.

Note: The Joule-Thomson experiment provides direct experimental proof of molecular attraction. The general observation of this experiment is that a gas cools itself on passing through a porous plug. In passing from a high to a low pressure the gas does not perform any external work. Therefore, the cooling observed must be due to the work done in overcoming the mutual attraction of the molecules.

The Van der Waals Equation

In 1873, J. D. van der Waals made the first successful attempt to modify the ideal-gas equation in order to correct for the volume and molecular attraction. When gases at ordinary pressures and temperatures are compressed, the volume is reduced by reducing the intermolecular space. Because the molecules themselves are not compressible, at very high pressures the entire volume is not inversely proportional to the pressure.

- At comparatively low pressures, the molecules of a real gas do not exert any force on one another, because they are widely separated. Therefore, at relatively low pressures, real gases behave like ideal gases.

- At high pressures the molecules are brought closer together and consequently the attractive force between the molecules increases, which has the same effect as an increase in external pressure. It then follows that, if external pressure is applied to a volume of gas, particularly at low temperatures, the decrease in volume is slightly greater than would be obtained by pressure only. This effect is more pronounced at low temperatures for the simple reason that at such temperatures the molecules move more slowly and have less tendency to move apart on colliding with one another.

- To derive the ideal-gas equation $PV = nRT$ from the kinetic theory of gases, a number of assumptions were made. Van der Waals modified the ideal-gas equation to take into account that two of these assumptions may not be valid. The modified assumptions which are applicable to real gases are as follows.

(i) The volume of the molecules may not be negligible in relation to the volume V occupied by the gas.

(ii) The attractive forces between the molecules may not be negligible.

Pressure correction

Although there is no net force acting on a molecule inside a container from the rest of the molecules, when next to the wall, all the rest of the molecules reside on one side, thus producing a net (attractive) force and consequently the pressure on the wall will be diminished.

The measured pressure *P* is thus less than the ideal pressure given by the kinetic theory of gases.

It is, therefore, necessary to add a correction term *P'* to the measured pressure *P, so, the ideal pressure is P + P'*.

P' is proportional to the product of

- the number of molecules striking unit area of the wall per second at any instant and
- the number of molecules per unit volume behind them.

- For a given volume of gas, both these numbers are proportional to the density ρ of the gas. Therefore, the total attractive force which is related to the correction term P' is proportional to ρ^2.

$$\rho^2 \propto 1/V^2$$

Thus, the corrected pressure becomes:

$$P + P' = P + a/V^2 \qquad 1$$

where a is a constant depending on the gas.

The term a/V^2 is called the cohesion pressure.

Volume correction

The volume of a gas cannot be compressed indefinitely because of the final size of the molecules. A correction term *b,* known as the *co-volume,* must be subtracted from the measured volume *V,* so that the corrected volume is *V -b*. The term *b* is a factor depending on the actual volume of the molecules.

Note: *b* might be thought that as being equal to the volume of the molecules but this is not the case. According to van der Waals, the co-volume is equal to four times the actual volume of the molecules; other slightly different estimates have also been made.

The equation for the ideal gases becomes (for one mole of gas):

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad 2$$

When V is large, both b and a/V^2 become negligible and the van der Waals equation reduces to the ideal-gas equation $PV = RT$ (for $n = 1$).

Note: At low pressures, the correction *a* for intermolecular attraction is more important than the correction *b* for molecular volume. At high pressures and small volumes, the correction for the volume of the molecules becomes important, since the molecules are relatively incompressible and they form an appreciable part of the total volume.

Under ordinary conditions, the deviations from the gas laws are negligible.

A van der Waals gas can be liquefied and it possesses a critical point which is given by the conditions

$$\left(\frac{\partial P}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

The critical pressure, volume and temperature are given by:

$P_c = a / 27\, b^2$

$V_c = 3b$

$T_c = 8a / 27bR$

The van der Waals constants

- At very low pressures, both a and b may be neglected, and Eq. 2 becomes

$$PV = RT.$$

And under these conditions the gas obeys the ideal-gas law, which may be considered as representing the limiting behavior of gases at extremely low pressures.

- At slightly higher pressures, it is generally possible to ignore b relative to V. Then Eq. 2 becomes

$$\left(P + \frac{a}{V^2}\right)(V) = RT \qquad 3$$

or

$$PV = RT - a/V \qquad 4$$

Eq. 4 sho

- At moderately high pressures, V *becomes smaller, so* b *cannot be ignored.* However, a/V^2 is small compared with the high value of P. Thus Eq. 2 becomes

$$P\,(V - b) = RT$$

or

$$PV = RT + P\,b \qquad 6$$

Eq.6 shows that $PV > RT$ and increases with increasing pressure.

- It can be shown that when the product PV is plotted against P, it has a minimum (for $P = 0$) called Boyle Point T_B.

Rewriting van der Waals equation for P:

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

or

$$PV = RT\frac{V}{V-b} - \frac{a}{V}$$

Differentiating the equation with respect to P at constant temperature

Note: $\frac{\partial f}{\partial P} = \frac{\partial f}{\partial V}\frac{\partial V}{\partial P}$ where $f = RT\frac{V}{V-b} - \frac{a}{V}$

We get

$$\frac{\partial}{\partial P}(PV)_T = \left(\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial P}\right)_T \qquad 7$$

For a minimum, $\frac{\partial}{\partial P}(PV)_T = 0$

which gives

$$\left(\frac{RT}{V-b} - \frac{RTV}{(V-b)^2} + \frac{a}{V^2}\right) = 0$$

or,

$$RT = \frac{a}{b}\left(\frac{V-b}{V}\right)^2 \qquad 8$$

When $P=0$, $V>>0$,

$$RT_B = \frac{a}{b}$$

and

$$T_B = \frac{a}{Rb} \qquad 9$$

At all temperatures greater than the Boyle point the value of PV will always increase as pressure increases. Since the values of a for hydrogen and helium are very small, for these two gases, T_B will be relatively low. If we substitute the values of a and b for hydrogen ($a = 2.5 \times 10^{-2}$ Jm^3/mol; $b = 2.67 \times 10^{-5}$ m^3/mol and $R = 8.31$ J/mol.K), we obtain $T_B = 112$ K. The experimental value is found to be 106 K.

Conclusion: The Boyle point T_B is defined as the lowest temperature above which PV increases continuously with increasing P. It can be shown that if the pressure is not too large, van der Waals equation reduces to:

$$PV = RT_B \qquad 10$$

Virial Equation of State

If the pressure P and the volume V of n moles of a gas held at a constant temperature are measured over a wide range of values of the pressure, and the product $P\upsilon$, where $\upsilon = V / n$, is plotted as a function of $1/\upsilon$. The relation between $P\upsilon$ and $1/ \upsilon$ may be expressed by means of a power series or virial expansion of the form

$$P\upsilon = A'[1 + \frac{B'}{\upsilon} + \frac{C'}{\upsilon^2} + \frac{D'}{\upsilon^3} + \ldots] \qquad 11$$

where A', B', C', . . ., are called virial coefficients. A' is the first virial coefficient, B' the second virial coefficient, etc., and these coefficients all depend on the temperature and the nature of the gas. All the known forms of equation of state, can be expressed in the virial form if desired, the virial coefficients being determined by the constants of the various equations. Of all the virial coefficients, the second virial coefficient B' is the most important; it depends on molecular interaction.

In the pressure range 0-40 atms, the relation between $P\upsilon$ and $1/\upsilon$ is almost linear, so that only the first two terms in the expansion are significant. In general, the greater the pressure range, the greater are the number of terms in the virial expansion.

- Another form of the virial equation can be written as

$$PV = RT + BP = CP^2 + \ldots \qquad 12$$

where B, C,. .. are called the second, third,. . . virial coefficients. B', C',. .. in Equation 11 are related to B, C, in Eq. 12.

- The virial equation may be derived from some assumptions. For example, if we assume T and P to be independent variables, then PV is a function of T and P. Mathematically,

$$PV = f(T, P)$$

where f denotes some function. As $P \rightarrow 0$, $PV \rightarrow RT$ *with no appreciable deviation even at several atmospheres.*

Therefore, it is possible to expand $f(T, P)$ in a Maclaurin series about $P = 0$ at constant temperature. Thus,

$$f(T,P) = f(T,0) + \frac{\partial}{\partial P} f(T,P)_{P=0,T=T}\, P + \frac{1}{2!}\frac{\partial^2}{\partial P^2} f(T,P)_{P=0,T=T}\, P^2 + \ldots$$

where $f(T, 0) = RT$. If we take

$$\frac{\partial}{\partial P} f(T,P)_{P=0,T=T} P \equiv B$$

$$\frac{1}{2!}\frac{\partial^2}{\partial P^2} f(T,P)_{P=0,T=T} P^2 \equiv C$$

and so on, then the Maclaurin series becomes

$$PV = f(T,\, P) = f(T,\, 0) + BP + CP^2 + \ldots$$

$$PV = RT + BP + CP^2 + \ldots$$

This equation is identical with the virial Equation 12. If there are no attractive and repulsive intermolecular forces within a mass of gas, then it can be shown from statistical mechanics that the virial coefficients B, C, . .. identically vanish, and the virial equation reduces to $PV = RT$ (for 1 mol of gas), which is the ideal-gas law. Therefore, we can say that a gas which obeys $PV = RT$ at all pressures has no intermolecular forces acting between its molecules. However, it should be remembered that, in reality, null intermolecular forces never occur. Consequently some properties of real gases do not approach their ideal-gas values as pressure tends to zero.

Note: The Maclaurin series

A function f(x) expanded in the power series

$$f(x) = a_0 + a_1 x + a_2 x^2 + a_3 x^3 + \ldots$$

By differentiating the series term by term,

$$\frac{df}{dx} = f'(x) = a_1 + 2a_2 x + 3a_3 x^2 + \ldots$$

$$\frac{d^2 f}{dx^2} = f''(x) = 2a_2 + 6a_3 x + \ldots$$

By substituting $x = 0$ *in* $f(x), f'(x), f''(x),$ we get

$f(0) = a_0; f'(0) = a_1; f''(0) = 2!a_2; \ldots$

Thus, the above series becomes (in the range where it is convergent)

$$f(x) = f(0) + xf'(0) + \left(\frac{x^2}{2!}\right)f''(0) + \ldots + \left(\frac{x^n}{n!}\right)f^n(0) + \ldots$$

which is Maclaurin series.

Enthalpy – preliminary considerations

The quantity enthalpy was introduced into thermodynamics by the American physicist and physical chemist J. Willard Gibbs, who was one of the founders of modem chemical thermodynamics.

Chemical reactions are usually performed at constant pressure. In these situations usually the volume changes with work being done.

$$-\int_1^2 PdV = -P\Delta V \qquad 17$$

The net work being done can be separated into two terms, one at constant pressure and the rest:

$$W_{net} = W_{total} + P\Delta V$$

For isobaric processes, the function Enthalpy is:

$$H = U + PV \qquad 18$$

and is a state function.

- If we replace for ideal gases $PV = nRT$,

$$H = U + nRT \qquad 19$$