Equations of state

When you boil water in a tea kettle, the increase in temperature produces steam that whistles out of the spout at high pressure. If you forget to poke holes in a potato before baking it, the high-pressure steam produced inside the potato can cause it to explode messily. Water vapor in the air can condense into liquid on the sides of a glass of ice water; if the glass is just out of the freezer, water vapor will solidify and form frost on its sides.

These examples show the relationships among the large-scale or *macroscopic* properties of a substance, such as pressure, volume, temperature, and mass. But we can also describe a substance by using a *microscopic* perspective. This means investigating small-scale quantities such as the masses, speeds, kinetic energies, and momenta of the individual molecules that make up a substance.

The macroscopic and microscopic descriptions are intimately related. For example, the (microscopic) forces that occur when air molecules strike a solid surface (such as your skin) cause (macroscopic) atmospheric pressure. To produce standard atmospheric pressure of 1.01×10^5 Pa, 10^{32} molecules strike your skin every day with an average speed of over 1700 km/h (1000 mi/h)!

In this section we'll begin by looking at some macroscopic aspects of matter in general. We'll pay special attention to the *ideal gas*, one of the simplest types of matter to understand. We'll relate the macroscopic properties of an ideal gas to the microscopic behavior of its molecules. We'll also use microscopic ideas to understand the heat capacities of gases and solids. Finally, we'll look at the various phases of matter – gas, liquid, and solid – and the conditions under which each occurs.

Quantities such as pressure, volume, temperature, and amount of substance describe the conditions, or *state*, in which a particular material exists. (For example, a tank of medical oxygen has a pressure gauge and a label stating the volume within the tank. We can add a thermometer and put the tank on a scale to measure the mass of oxygen.) These quantities are called **state variables**.

The volume V of a substance is usually determined by its pressure p, temperature T, and amount of substance, described by the mass m_{total} or number of moles n. (We are calling the total mass of a substance m_{total} because later in the chapter we will use m for the mass of one molecule.) Ordinarily, we can't change one of these variables without causing a change in another. When the tank of oxygen gets hotter, the pressure increases. If the tank gets too hot, it explodes.

In a few cases the relationship among p, V, T, and m_{total} (or n) is simple enough that we can express it as an equation called the **equation of state.** When it's too complicated for that, we can use graphs or numerical tables. Even then, the relationship among the variables still exists; we call it an equation of state even when we don't know the actual equation.

Here's a simple (though approximate) equation of state for a solid material. The temperature coefficient of volume expansion b is the fractional volume change $\Delta V/V_0$ per unit temperature change, and the compressibility k is the negative of the fractional volume change $\Delta V/V_0$ per unit pressure change. If a certain amount of material has volume V_0 when the pressure is p_0 and the temperature is T_0 , the volume V at slightly differing pressure p and temperature T is approximately $V = V_0[1 + \beta(T - T_0) - k(p - p_0)]$. (There is a negative sign in front of the term $k(p - p_0)$ because an *increase* in pressure causes a *decrease* in volume.)

The ideal-gas equation

Another simple equation of state is the one for an *ideal gas*. We can measure the pressure (p), volume (V), temperature (T), and amount of gas $(m_{total} \text{ or } n)$. It is usually easiest to describe the amount of gas in terms of the number of moles n, rather than the mass. The **molar mass** M of a compound (sometimes confusingly called *molecular weight*) is the mass per mole:



Hence if we know the number of moles of gas, we can determine the mass of gas from this Equation.

Measurements of the behavior of various gases lead to three conclusions:

1. The volume V is proportional to the number of moles n. If we double n, keeping pressure and temperature constant, the volume doubles.

2. The volume varies *inversely* with the absolute pressure p. If we double p while holding the temperature T and number of moles n constant, the gas compresses to one-half of its initial volume. In other words, pV = constant when n and T are constant.

3. The pressure is proportional to the *absolute* temperature *T*. If we double *T*, keeping the volume and number of moles constant, the pressure doubles. In other words, $p = (\text{constant}) \times T$ when *n* and *V* are constant.

We can combine these three relationships into a single **ideal-gas equation:**



An **ideal gas** is one for which the Equation holds precisely for *all* pressures and temperatures. This is an idealized model; it works best at very low pressures and high temperatures, when the gas molecules are far apart and in rapid motion. It is valid within a few percent at moderate pressures (such as a few atmospheres) and at temperatures well above those at which the gas liquefies.

We might expect that the proportionality constant *R* in the ideal-gas equation would have different values for different gases, but it turns out to have the same value for *all* gases, at least at sufficiently high temperature and low pressure. It is called the **gas constant** (or *ideal-gas constant*). In SI units, in which the unit of *p* is Pa (1 Pa = 1 N/m²) and the unit of *V* is m³, the current best numerical value of *R* is

 $R = 8.3144621(75) \text{ J/mol} \cdot \text{K}$

or R = 8.314 J/mol · K to four significant figures. Note that the units of pressure times volume are the same as the units of work or energy (for example, N/m² times m³); that's why *R* has units of energy per mole per unit of absolute temperature. In chemical calculations, volumes are often expressed in liters (L) and pressures in atmospheres (atm). In this system, to four significant figures,

$$R = 0.08206 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$$

We can express the ideal-gas equation, in terms of the mass m_{total} of gas, using expression $m_{total} = nM$:

 $pV = \frac{m_{\text{total}}}{M}RT$ From this we can get an expression for the density $\rho = m_{\text{total}}/V$ of the gas: $\rho = \frac{pM}{RT}$

For a *constant mass* (or constant number of moles) of an ideal gas the product nR is constant, so the quantity pV/T is also constant. If the subscripts 1 and 2 refer to any two states of the same mass of a gas, then

$$\frac{p_1 v_1}{T_1} = \frac{p_2 v_2}{T_2} = \text{constant} \quad \text{(ideal gas, constant mass)}$$

Notice that you don't need the value of *R* to use this equation.

We used the proportionality of pressure to absolute temperature earlier to define a temperature scale in terms of pressure in a constant-volume gas thermometer. That may make it seem that the pressure–temperature relationship in the ideal-gas equation, is just a result of the way we define temperature. But the ideal-gas equation also tells us what happens when we change the volume or the amount of substance. Also, it can be shown that the gas-thermometer scale corresponds closely to a temperature scale that does *not* depend on the properties of any particular material. For now, consider Eq. as being based on this genuinely material-independent temperature scale.



Example: respiration and the ideal-gas equation

To breathe, you rely on the ideal-gas equation pV = nRT. Contraction of the dome-shaped diaphragm muscle increases the volume *V* of the thoracic cavity (which encloses the lungs), decreasing its pressure *p*. The lowered pressure causes the lungs to expand and fill with air. (The temperature *T* is kept constant.) When you exhale, the diaphragm relaxes, allowing the lungs to contract and expel the air.

The van der Waals equation

In the kinetic-molecular theory, we can obtain the ideal-gas equation from a simple molecular model that ignores the volumes of the molecules themselves and the attractive forces between them (see the Figure a). Another equation of state, the **van der Waals equation**, makes approximate corrections for these two omissions (Fig. b). This equation was developed by the 19th-century Dutch physicist J. D. van der Waals; the interaction between atoms that we discussed earlier is named the *van der Waals interaction*. The van der Waals equation is

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

(a) An idealized model of a gas



(b) A more realistic model of a gas



... and they exert forces on the container's walls.

A gas as modeled by (a) the ideal gas equation and (b) the van der Waals equation.

The constants *a* and *b* are different for different gases. Roughly speaking, *b* represents the volume of a mole of molecules; the total volume of the molecules is *nb*, and the volume remaining in which the molecules can move is V - nb. The constant *a* depends on the attractive intermolecular forces, which reduce the pressure of the gas by *pulling* the molecules together as they *push* on the walls of the container. The decrease in pressure is proportional to the number of molecules per unit volume in a layer near the wall (which are exerting the pressure on the wall) and is also proportional to the number per unit volume in the next layer beyond the wall (which are doing the attracting). Hence the decrease in pressure due to intermolecular forces is proportional to n^2/V^2 .

When n/V is small (that is, when the gas is *dilute*), the average distance between molecules is large, the corrections in the van der Waals equation become insignificant, and the equation of state reduces to the ideal-gas equation. As an example, for carbon dioxide gas (CO₂) the constants in the van der Waals equation are $a = 0.364 \text{ J} \cdot \text{m}^3/\text{mol}^2$ and $b = 4.27 \times 10^{-5} \text{ m}^3/\text{mol}$. 1 mole of an ideal gas at $T = 0^{\circ}\text{C} = 273.15 \text{ K}$ and $p = 1 \text{ atm} = 1.013 \times 10^{5} \text{ Pa}$ occupies a volume $V = 0.0224 \text{ m}^3$; according to van der Waals equation, 1 mole of CO₂ occupying this volume at this temperature would be at a pressure 532 Pa less than 1 atm, a difference of only 0.5% from the ideal-gas value.



For each curve, pV is constant and is directly proportional to T(Boyle's law).



Isotherms, or constant-temperature curves, for a constant amount of an ideal gas. The highest temperature is T_4 ; the lowest is T_1 . This is a graphical representation of the ideal-gas equation of state.

pV-Diagrams

We could in principle represent the p-V-T relationship graphically as a *surface* in a three-dimensional space with coordinates p, V, and T. This representation is useful, but ordinary two-dimensional graphs are usually more convenient. One of the most useful of these is a set of graphs of pressure as a function of volume, each for a particular constant temperature. Such a diagram is called a *pV*-diagram. Each curve, representing behavior at a specific temperature, is called an **isotherm**, or a pVisotherm.

The Figure shows pV-isotherms for a constant amount of an ideal gas. Since p = nRT/V from ideal-gas equation of state, along an isotherm (constant *T*) the pressure *p* is inversely proportional to the volume *V* and the isotherms are hyperbolic curves. $T_4 > T_3 > T_c > T_2 > T_1$

p Above the critical temperature T_c , there is no liquid–vapor phase transition. Below T_c , the material condenses to liquid as it is compressed. Liquid *D* Liquid–vapor phase equilibrium region

A *pV*-diagram for a nonideal gas, showing isotherms for temperatures above and below the critical temperature T_c . The liquid–vapor equilibrium region is shown as a green shaded area. At still lower temperatures the material might undergo phase transitions from liquid to solid or from gas to solid; these are not shown here. The Figure shows a *pV*-diagram for a material that *does not* obey the ideal gas equation. At temperatures below T_c the isotherms develop flat regions in which we can compress the material (that is, reduce the volume *V*) without increasing the pressure *p*. Observation shows that the gas is *condensing* from the vapor (gas) to the liquid phase. The flat parts of the isotherms in the shaded area of the Figure represent conditions of liquid-vapor *phase equilibrium*. As the volume decreases, more and more material goes from vapor to liquid, but the pressure does not change. (To keep the temperature constant during condensation, we have to remove the heat of vaporization, discussed before.)

When we compress such a gas at a constant temperature T_2 in Figure, it is vapor until point *a* is reached. Then it begins to liquefy; as the volume decreases further, more material liquefies, and *both* the pressure and the temperature remain constant. At point *b*, all the material is in the liquid state. After this, any further compression requires a very rapid rise of pressure, because liquids are in general much less compressible than gases. At a lower constant temperature T_1 , similar behavior occurs, but the condensation begins at lower pressure and greater volume than at the constant temperature T_2 . At temperatures greater than T_c , *no* phase transition occurs as the material is compressed; at the highest temperatures, such as T_4 , the curves resemble the ideal-gas curves of the previous Figure. We call T_c the *critical temperature* for this material. a little later we'll discuss what happens to the phase of the gas above the critical temperature.

It is possible to show that the *area* under a *pV*-curve (whether or not it is an isotherm) represents the *work* done by the system during a volume change. This work, in turn, is directly related to heat transfer and changes in the *internal energy* of the system.

Moles and Avogadro's number

We have used the mole as a measure of quantity of substance. One **mole** of any pure chemical element or compound contains a definite number of molecules, the same number for all elements and compounds. The **old** official SI definition was:

One mole is the amount of substance that contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12.

In our discussion, the "elementary entities" are molecules. (In a monatomic substance such as carbon or helium, each molecule is a single atom.) Atoms of a given element may occur in any of several isotopes, which are chemically identical but have different atomic masses; "carbon-12" is a specific isotope of carbon.

The number of molecules in a mole is called **Avogadro's number**, denoted by N_A . The recent best numerical value of N_A was

 $N_{\rm A} = 6.02214129(27) \times 10^{23}$ molecules/mol (Avogadro's number).

On 16 November 2018, after a meeting of scientists from more than 60 countries at the CGPM in Versailles, France, all SI base units were defined in terms of physical constants. This meant that each SI unit, including the mole, would not be defined in terms of any physical objects but rather they would be defined by constants that are, in their nature, exact.

Such changes officially came into effect on 20 May 2019. Following such changes, "one mole" of a substance was redefined as "exactly 6.02214076×10²³ elementary entities" of that substance.

So, the **new** numerical value of N_A is **exactly**

 $N_{\rm A} = 6.02214076 \times 10^{23}$ molecules/mol (Avogadro's number).

The *molar mass* M of a compound is the mass of 1 mole. It is equal to the mass m of a single molecule multiplied by Avogadro's number:

Molar mass
of a substance $M = N_A m$ Avogadro's number
Mass of a molecule of substance

When the molecule consists of a single atom, the term *atomic mass* is often used instead of molar mass.

Heat capacities of gases

In the simple kinetic-molecular theory it is possible to obtain the formula for the average translational kinetic energy K_{tr} of a single molecule:

Average translational
kinetic energy of an
ideal gasNumber of moles of gas
$$K_{tr} = \frac{3}{2}nRT$$
Absolute temperature of gasGas constant

The average translational kinetic energy of a single molecule is the total translational kinetic energy K_{tr} of all molecules divided by the number of molecules, N:

$$\frac{K_{\rm tr}}{N} = \frac{1}{2}m(v^2)_{\rm av} = \frac{3nRT}{2N}$$

Also, the total number of molecules N is the number of moles n multiplied by Avogadro's number N_A , so $N = nN_A$ and $n/N = 1/N_A$. Thus the above equation becomes

$$\frac{K_{\rm tr}}{N} = \frac{1}{2}m(v^2)_{\rm av} = \frac{3}{2}\left(\frac{R}{N_{\rm A}}\right)T$$

The ratio R/N_A is called the **Boltzmann constant**, *k*:

$$k = \frac{R}{N_{\rm A}} = \frac{8.314 \text{ J/mol} \cdot \text{K}}{6.022 \times 10^{23} \text{ molecules/mol}} = 1.381 \times 10^{-23} \text{ J/molecule} \cdot \text{K}$$

(The current numerical value of k is exactly 1.380649×10^{-23} J/molecule • K). In terms of k we can rewrite the last Equation as



This shows that the average translational kinetic energy *per molecule* depends only on the temperature, not on the pressure, volume, or kind of molecule. We can obtain the average translational kinetic energy *per mole* by multiplying this Equation by Avogadro's number and using the relation $M = N_A m$:

$$N_{\rm A}\frac{1}{2}m(v^2)_{\rm av} = \frac{1}{2}M(v^2)_{\rm av} = \frac{3}{2}RT$$

(average translational kinetic energy per mole of gas)

The translational kinetic energy of a mole of an ideal gas depends only on *T*.

When we introduced the concept of heat capacity earlier, we talked about ways to *measure* the specific heat or molar heat capacity of a particular material. Now we'll see how to *predict* these on theoretical grounds.

The basis of our analysis is that heat is *energy* in transit. When we add heat to a substance, we are increasing its molecular energy. We'll assume that the volume of the gas remains constant; if we were to let the gas expand, it would do work by pushing on the moving walls of its container, and this additional energy transfer would have to be included in our calculations.

In the simple kinetic-molecular model as we say, the molecular energy consists of only the translational kinetic energy K_{tr} of the pointlike molecules. This energy is directly proportional to the absolute temperature *T*, $K_{tr} = 3/2 nRT$. When the temperature changes by a small amount *dT*, the corresponding change in kinetic energy is

$$dK_{\rm tr} = \frac{3}{2}nR \ dT$$

From the definition of molar heat capacity at constant volume, C_V , we also have

$$dQ = nC_V dT,$$

where dQ is the heat input needed for a temperature change dT. Now if K_{tr} represents the total molecular energy, as we have assumed, then dQ and dK_{tr} must be *equal*. From the last Equations, this says

$$nC_V dT = \frac{3}{2}nR dT$$

So, we obtain the formula for C_V , the molar heat capacity *at constant volume* of the pointlike molecules:

Type of Gas	Gas	$C_V(\mathbf{J}/\mathrm{mol}\cdot\mathbf{K})$
Monatomic	He	12.47
	Ar	12.47
Diatomic	H_2	20.42
	N_2	20.76
	O ₂	20.85
	CO	20.85
Polyatomic	CO_2	28.46
	SO_2	31.39
	H_2S	25.95

Molar heat capacities of gases

Molar heat capacity $C_V = \frac{3}{2}R^{4}$ Gas constant ideal gas of point particles

This surprisingly simple result says that the molar heat capacity at constant volume is 3R/2 for *any* gas whose molecules can be represented as points. Does this Equation agree with experiment? In SI units, the Eq. gives

 $C_V = 3/2(8.314 \text{ J/mol} \cdot \text{K}) = 12.47 \text{ J/mol} \cdot \text{K}$

For comparison, the Table gives measured values of C_V for several gases. We see that for *monatomic* gases our prediction is right on the money, but that it is way off for diatomic and polyatomic gases.

(a) Translational motion. The molecule moves as a whole; its velocity may be described as the x-, y-, and z-velocity components of its center of mass.



(b) Rotational motion. The molecule rotates about its center of mass. This molecule has two independent axes of rotation.

(c) Vibrational motion. The molecule oscillates as though the nuclei were connected by a spring.



Motions of a diatomic molecule.

This comparison tells us that our point-molecule model is good enough for monatomic gases but that for diatomic and polyatomic molecules we need something more sophisticated. For example, we can picture a diatomic molecule as *two* point masses, like a little elastic dumbbell (see the Figure), with an interaction force between the atoms of the kind shown in the Fig. Such a molecule can have additional kinetic energy associated with *rotation* about axes through its center of mass. The atoms may also *vibrate* along the line joining them, with additional kinetic and potential energies.

When heat flows into a *monatomic* gas at constant volume, *all* of the added energy goes into an increase in random *translational* molecular kinetic energy. This leads to an increase in temperature.

But when the temperature is increased by the same amount in a *diatomic* or *polyatomic* gas, additional heat is needed to supply the increased rotational and vibrational energies. Thus polyatomic gases have *larger* molar heat capacities than monatomic gases, as the Table shows.

But how do we know how much energy is associated with each additional kind of motion of a complex molecule, compared to the translational kinetic energy? The new principle that we need is called the principle of **equipartition of energy.** It can be derived from sophisticated statistical-mechanics considerations; that derivation is beyond our scope, and we will treat the principle as an axiom.

The principle of equipartition of energy states that each velocity component (either linear or angular) has, on average, an associated kinetic energy per molecule of 1/2kT, or one-half the product of the Boltzmann constant and the absolute temperature. The number of velocity components needed to describe the motion of a molecule completely is called the number of **degrees of freedom.** For a monatomic gas, there are three degrees of freedom (for the velocity components v_x , v_y , and v_z); this gives a total average kinetic energy per molecule of 3(1/2kT).

For a *diatomic* molecule there are two possible axes of rotation, perpendicular to each other and to the molecule's axis. (We don't include rotation about the molecule's own axis because in ordinary collisions there is no way for this rotational motion to change.) If we add two rotational degrees of freedom for a diatomic molecule, the average total kinetic energy per molecule is 5/2kT instead of 3/2kT. The total kinetic energy of *n* moles is $K_{\text{total}} = nN_A(5/2kT) = 5/2n(kN_A)T = 5/2nRT$, and the molar heat capacity (at constant volume) is

Molar heat capacity at constant volume, $C_V = \frac{5}{2}R^{4}$ Gas constant ideal diatomic gas

In SI units,

$$C_V = \frac{5}{2}(8.314 \text{ J/mol} \cdot \text{K}) = 20.79 \text{ J/mol} \cdot \text{K}$$

This value is close to the measured values for diatomic gases in the last Table.

Vibrational motion can also contribute to the heat capacities of gases. Molecular bonds can stretch and bend, and the resulting vibrations lead to additional degrees of freedom and additional energies. For most diatomic gases, however, vibration does not contribute appreciably to heat capacity. The reason for this involves some concepts of quantum mechanics. Briefly, vibrational energy can change only in finite steps. If the energy change of the first step is much larger than the energy possessed by most molecules, then nearly all the molecules remain in the minimum-energy state of motion. Changing the temperature does not change their average vibrational energy appreciably, and the vibrational degrees of freedom are said to be "frozen out." In more complex molecules the gaps between permitted energy levels can be much smaller, and then vibration *does* contribute to heat capacity. The rotational energy of a molecule also changes by finite steps, but they are usually much smaller; the "freezing out" of rotational degrees of freedom occurs only in rare instances.

In the Table the large values of C_V for polyatomic molecules show the effects of vibrational energy. In addition, a molecule with three or more atoms that are not in a straight line has *three* rotational degrees of freedom.

From this discussion we expect heat capacities to be temperature-dependent, generally increasing with increasing temperature. The Figure is a graph of the temperature dependence of C_V for hydrogen gas (H₂), showing the temperatures at which the rotational and vibrational energies begin to contribute.



Experimental values of C_V , the molar heat capacity at constant volume, for hydrogen gas (H₂). The temperature is plotted on a logarithmic scale.

Heat capacities of solids

We can carry out a similar heat-capacity analysis for a crystalline solid. Consider a crystal consisting of N identical atoms (a *monatomic solid*). Each atom is bound to an equilibrium position by interatomic forces. Solid materials are elastic, so forces must permit stretching and bending of the bonds. We can think of a crystal as an array of atoms connected by little springs (see the Figure).

Each atom can *vibrate* around its equilibrium position and has three degrees of freedom, corresponding to its three components of velocity. According to the equipartition principle, each atom has an average kinetic energy of $1/2 \ kT$ for each degree of freedom. In addition, there is *potential* energy associated with the elastic deformation. For a simple harmonic oscillator (discussed earlier) it is not hard to show that the average kinetic energy is *equal* to the average potential energy. In our model of a crystal, each atom is a three-dimensional harmonic oscillator; it can be shown that the equality of average kinetic and potential energies also holds here, provided that the "spring" forces obey Hooke's law.



To visualize the forces between neighboring atoms in a crystal, envision every atom as being attached to its neighbors by springs. Thus we expect each atom to have an average kinetic energy 3/2 kT and an average potential energy 3/2 kT, or an average total energy 3kT per atom. If the crystal contains N atoms or n moles, its total energy is $E_{\text{total}} = 3NkT = 3nRT$. From this we conclude that the molar heat capacity of a crystal should be

Molar heat capacity of an ideal monatomic solid (rule of Dulong and Petit) $C_V = 3R^{4}$ Gas constant

In SI units,

$$C_V = (3)(8.314 \text{ J/mol} \cdot \text{K}) = 24.9 \text{ J/mol} \cdot \text{K}$$

We have *derived* the **rule of Dulong and Petit**, which we encountered as an *empirical* finding in previously made review: Monatomic solids all have molar heat capacities of about 25 J/mol • K. The agreement is only approximate, but given the very simple nature of our model, it is quite significant.

At low temperatures, the heat capacities of most solids *decrease* with decreasing temperature (see the Figure) for the same reason that vibrational degrees of freedom of molecules are frozen out at low temperatures. At very low temperatures the quantity kT is much *smaller* than the smallest energy step the vibrating atoms can take. Hence most of the atoms remain in their lowest energy states because the next higher energy level is out of reach.



The average vibrational energy per atom is then *less* than 3kT, and the heat capacity per molecule is *less* than 3k. At higher temperatures when kT is *large* in comparison to the minimum energy step, the equipartition principle holds, and the total heat capacity is 3k per molecule or 3R per mole as the rule of Dulong and Petit predicts. Quantitative understanding of the temperature variation of heat capacities was one of the triumphs of quantum mechanics during its initial development in the 1920s.

Experimental values of C_V for lead, aluminum, silicon, and diamond. At high temperatures, C_V for each solid approaches about 3R, in agreement with the rule of Dulong and Petit. At low temperatures, C_V is much less than 3R.

Phases of matter

An ideal gas is the simplest system to analyze from a molecular viewpoint because we ignore the interactions between molecules. But those interactions are the very thing that makes matter condense into the liquid and solid phases under some conditions. So it's not surprising that theoretical analysis of liquid and solid structure and behavior is a lot more complicated than that for gases. We won't try to go far here with a microscopic picture, but we can talk in general about phases of matter, phase equilibrium, and phase transitions.



Each phase is stable in only certain ranges of temperature and pressure. A transition from one phase another ordinarily to equilibrium requires phase between the two phases, and for a given pressure this occurs at only one specific temperature. We represent these can conditions on a graph with axes p and T, called a **phase diagram**; The Figure shows an example. Each point on the diagram represents a pair of values of p and *T*.

Triple-point data

Substance	Temperature (K)	Pressure (Pa)
Hydrogen	13.80	0.0704×10^{5}
Deuterium	18.63	0.171×10^{5}
Neon	24.56	0.432×10^{5}
Nitrogen	63.18	0.125×10^{5}
Oxygen	54.36	0.00152×10^{5}
Ammonia	195.40	0.0607×10^{5}
Carbon dioxide	216.55	5.17×10^{5}
Sulfur dioxide	197.68	0.00167×10^{5}
Water	273.16	0.00610×10^{5}

Only a single phase can exist at each point in the Figure, except for points on the solid lines, where two phases can coexist in phase equilibrium. The fusion curve separates the solid and liquid areas and represents possible conditions of solid-liquid phase equilibrium. The vaporization curve separates the liquid and vapor areas, and the sublimation curve separates the solid and vapor areas. All three curves meet at the **triple point**, the only condition under which all three phases can coexist. Earlier we used the triplepoint temperature of water to define the Kelvin temperature scale. The Table gives triple-point data for several substances.

If we heat a substance at a constant pressure p_a , it goes through a series of states represented by the horizontal line (a) in previous Figure.

The melting and boiling temperatures at this pressure are the temperatures at which the line intersects the fusion and vaporization curves, respectively. When the pressure is p_s , constantpressure heating transforms a substance from solid directly to vapor. This process is called *sublimation;* the intersection of line (s) with the sublimation curve gives the temperature T_s at which it occurs for a pressure p_s . At any pressure less than the triple-point pressure, no liquid phase is possible. The triple-point pressure for carbon dioxide (CO₂) is 5.1 atm. At normal atmospheric pressure, solid CO₂ ("dry ice") undergoes sublimation; there is no liquid phase.

Line (b) in the Fig. represents compression at a constant temperature T_b . The material passes from vapor to liquid and then to solid at the points where line (b) crosses the vaporization curve and fusion curve, respectively. Line (d) shows constant-temperature compression at a lower temperature T_d ; the material passes from vapor to solid at the point where line (d) crosses the sublimation curve.

We saw in the *pV*-diagram for a nonideal gas (van der Waals isotherms) that a liquidvapor phase transition occurs only when the temperature and pressure are less than those at the point at the top of the green shaded area labeled "Liquid-vapor phase equilibrium" region." This point corresponds to the endpoint at the top of the vaporization curve in our last Fig. It is called the **critical point**, and the corresponding values of p and T are called the critical pressure and temperature, p_c and T_c . A gas at a pressure *above* the critical pressure does not separate into two phases when it is cooled at constant pressure (along a horizontal line above the critical point in the Fig.). Instead, its properties change gradually and continuously from those we ordinarily associate with a gas (low density, large compressibility) to those of a liquid (high density, small compressibility) without a phase transition.

You can understand this by thinking about liquid-phase transitions at successively higher points on the vaporization curve. As we approach the critical point, the *differences* in physical properties (such as density and compressibility) between the liquid and vapor phases become smaller. Exactly *at* the critical point they all become zero, and at this point the distinction between liquid and vapor disappears. The heat of vaporization also grows smaller as we approach the critical point, and it too becomes zero at the critical point.

For nearly all familiar materials the critical pressures are much greater than atmospheric pressure, so we don't observe this behavior in everyday life. For example, the critical point for water is at 647.4 K and 221.2×10^5 Pa (about 218 atm or 3210 psi). But high-pressure steam boilers in electric generating plants regularly run at pressures and temperatures well above the critical point.

Many substances can exist in more than one solid phase. A familiar example is carbon, which exists as noncrystalline soot and crystalline graphite and diamond. Water is another example; more than a dozen types of ice, differing in crystal structure and physical properties, have been observed at very high pressures.

pVT-surfaces

We remarked earlier that for any material, it can be useful to represent the equation of state as a surface in a three-dimensional space with coordinates p, V, and T. The Figure shows a typical pVT-surface. The light lines represent pV-isotherms; projecting them onto the pV-plane gives a diagram similar to van der Waals isotherms. The pV-isotherms represent contour lines on the pVT-surface, just as contour lines on a topographic map represent the elevation (the third dimension) at each point. The projections of the edges of the surface onto the pT-plane give the pT phase diagram of previous Fig.

Line *abcdef* in our present Fig. represents constant-pressure heating, with melting along *bc* and vaporization along *de*. Note the volume changes that occur as *T* increases along this line.

Line *ghjklm* corresponds to an isothermal (constant temperature) compression, with liquefaction along hj and solidification along kl. Between these, segments gh and jk represent isothermal compression with increase in pressure; the pressure increases are much greater in the liquid region jk and the solid region lm than in the vapor region gh.

Finally, line *nopq* represents isothermal solidification directly from vapor, as in the formation of snowflakes or frost.



A *pVT*-surface for a substance that expands on melting. Projections of the boundaries on the surface onto the *pT*- and *pV*-planes are also shown.



A *pVT*-surface for an ideal gas. At the left, each orange line corresponds to a certain constant volume; at the right, each green line corresponds to a certain constant temperature.

The Figure shows the much simpler *pVT*-surface for a substance that obeys the idealgas equation of state under all conditions. The projections of the constant-temperature curves onto the pV-plane correspond to the *isotherms* for an ideal gas, and the projections of the constant-volume curves onto the pT-plane show that pressure is directly proportional to absolute temperature. The Figure also shows the *isobars* (curves of constant pressure) and *isochors* (curves of constant volume) for an ideal gas.

Thermodynamic systems

We can study energy transfer through mechanical work and through heat transfer. Now we are ready to combine and generalize these principles.

We always talk about energy transfer to or from some specific *system*. The system might be a mechanical device, a biological organism, or a specified quantity of material, such as the refrigerant in an air conditioner or steam expanding in a turbine. In general, a **thermodynamic system** is any collection of objects that is convenient to regard as a unit, and that may have the potential to exchange energy with its surroundings.

A familiar example is a quantity of popcorn kernels in a pot with a lid. When the pot is placed on a stove, energy is added to the popcorn by conduction of heat. As the popcorn pops and expands, it does work as it exerts an upward force on the lid and moves it through a displacement (see the Figure). The *state* of the popcorn – its volume, temperature, and pressure – changes as it pops. A process such as this one, in which there are changes in the state of a thermodynamic system, is called a **thermodynamic process.**



The popcorn in the pot is a thermodynamic system. In the thermodynamic process shown here, heat is added to the system, and the system does work on its surroundings to lift the lid of the pot.

In mechanics we used the concept of *system* with free-body diagrams and with conservation of energy and momentum. For *thermodynamic* systems, as for all others, it is essential to define clearly at the start exactly what is and is not included in the system. Only then can we describe unambiguously the energy transfers into and out of that system. For instance, in our popcorn example we defined the system to include the popcorn but not the pot, lid, or stove.

Thermodynamics has its roots in many practical problems other than popping popcorn. The gasoline engine in an automobile, the jet engines in an airplane, and the rocket engines in a launch vehicle use the heat of combustion of their fuel to perform mechanical work in propelling the vehicle. Muscle tissue in living organisms metabolizes chemical energy in food and performs mechanical work on the organism's surroundings. A steam engine or steam turbine uses the heat of combustion of coal or other fuel to perform mechanical work such as driving an electric generator or pulling a train.



(a) A rocket engine uses the heat of combustion of its fuel to do work propelling the launch vehicle. (b) Humans and other biological organisms are more complicated systems than we can analyze fully in this book, but the same basic principles of thermodynamics apply to them.

Signs for heat and work in thermodynamics

We describe the energy relationships in any thermodynamic process in terms of the quantity of heat Q added to the system and the work W done by the system. Both Q and W may be positive, negative, or zero (see the Figure). A positive value of Q represents heat flow *into* the system, with a corresponding input of energy to it; negative Q represents heat flow out of the system. A positive value of Wrepresents work done by the system against its surroundings, such as work done by an expanding gas, and hence corresponds to energy *leaving* the system. Negative W, such as work done during compression of a gas in which work is done on the gas by its surroundings, represents energy *entering* the system.

Be careful with the sign of work *W*! Note that our sign rule for work is *opposite* to the one we used in mechanics, in which we always spoke of the work done by the forces acting *on* a body. In thermodynamics it is usually more convenient to call *W* the work done *by* the system so that when a system expands, the pressure, volume change, and work are all positive. Use the sign rules for work and heat consistently!



A thermodynamic system may exchange energy with its surroundings (environment) by means of heat, work, or both. Note the sign conventions for Qand W.

Work done during volume changes

A simple example of a thermodynamic system is a quantity of gas enclosed in a cylinder with a movable piston. Internal-combustion engines, steam engines, and compressors in refrigerators and air conditioners all use some version of such a system. In the next several sections we will use the gas-in-cylinder system to explore several kinds of thermodynamic processes.

We'll use a microscopic viewpoint, based on the kinetic and potential energies of individual molecules in a material, to develop intuition about thermodynamic quantities. But it is important to understand that the central principles of thermodynamics can be treated in a completely *macroscopic* way, without reference to microscopic models. Indeed, part of the great power and generality of thermodynamics is that it does *not* depend on details of the structure of matter.

First we consider the *work* done by the system during a volume change. When a gas expands, it pushes outward on its boundary surfaces as they move outward. Hence an expanding gas always does positive work. The same thing is true of any material that expands under pressure, such as the popcorn in the Figure above.



^{*}Molecule gains kinetic energy, does negative work on piston. We can understand the work done by a gas in a volume change by considering the molecules that make up the gas. When one such molecule collides with a stationary surface, it exerts a momentary force on the wall but does no work because the wall does not move. But if the surface is moving, like a piston in a gasoline engine, the molecule *does* do work on the surface during the collision. If the piston in the Figure a moves to the right, so the volume of the gas increases, the molecules that strike the piston exert a force through a distance and do *positive* work on the piston. If the piston moves toward the left as in Fig. b, so the volume of the gas decreases, positive work is done *on* the molecule during the collision. Hence the gas molecules do *negative* work on the piston.

A molecule striking a piston (a) does positive work if the piston is moving away from the molecule and (b) does negative work if the piston is moving toward the molecule. Hence a gas does positive work when it expands as in (a) but does negative work when it compresses as in (b).



The next Figure shows a system whose volume can change (a gas, liquid, or solid) in a cylinder with a movable piston. Suppose that the cylinder has cross-sectional area A and that the pressure exerted by the system at the piston face is p. The total force F exerted by the system on the piston is F = pA. When the piston moves out an infinitesimal distance dx, the work dW done by this force is

dW = F dx = pA dx

The infinitesimal work done by the system during the small expansion dx is But dW = pAdx.

A dx = dV

where dV is the infinitesimal change of volume of the system. Thus we can express the work done by the system in this infinitesimal volume change as $dW = p \, dV$ In a finite change of volume from V_1 to V_2 ,

Work done in a
$$W = \int_{V_1}^{V_2} p \, dV$$
 Upper limit = final volume
volume change $W = \int_{V_1}^{V_2} p \, dV$ Integral of the pressure
with respect to volume
Lower limit = initial volume

In general, the pressure of the system may vary during the volume change.

For example, this is the case in the cylinders of an automobile engine as the pistons move back and forth. To evaluate the integral in the Equation, we have to know how the pressure varies as a function of volume. We can represent this relationship as a graph of p as a function of V (a pV-diagram).

The Figure shows a simple example. In this figure, the last Equation is represented graphically as the *area* under the curve of p versus V between the limits V_1 and V_2 . (In mechanics we use a similar interpretation of the work done by a force F as the area under the curve of F versus x between the limits x_1 and x_2 .)



According to the rule we stated above, work is *positive* when a system *expands*. In an expansion from state 1 to state 2 in Fig. a, the area under the curve and the work are positive. A *compression* from 1 to 2 in Fig. b gives a *negative* area; when a system is compressed, its volume decreases and it does *negative* work on its surroundings.

Be careful with subscripts 1 and 2 in these notations, V_1 is the *initial* volume and V_2 is the *final* volume. That's why labels 1 and 2 are reversed in Fig. b compared to Fig. a, even though both processes move between the same two thermodynamic states.

If the pressure p remains constant while the volume changes from V_1 to V_2 (Fig. c), the work done by the system is

Work done in a work done in a work done in a work done in a work work with the second	$V = p(V_2 - V_1)$
constant pressure	Final volume Initial volume

If the volume is *constant*, there is no displacement and the system does no work.

Internal energy and the first law of thermodynamics

Internal energy is one of the most important concepts in thermodynamics. When we discussed energy changes for a body sliding with friction, we stated that warming a body increased its internal energy and that cooling the body decreased its internal energy. But what *is* internal energy? We can look at it in various ways; let's start with one based on the ideas of mechanics. Matter consists of atoms and molecules, and these are made up of particles having kinetic and potential energies. We *tentatively* define the **internal energy** of a system as the sum of the kinetic energies of all of its constituent particles, plus the sum of all the potential energies of interaction among these particles.

Internal energy does *not* include potential energy arising from the interaction between the system and its surroundings. If the system is a glass of water, placing it on a high shelf increases the gravitational potential energy arising from the interaction between the glass and the earth. But this has no effect on the interactions among the water molecules, and so the internal energy of the water does not change.

We use the symbol U for internal energy. (We used this symbol in our study of mechanics to represent potential energy. However, U has a different meaning in thermodynamics.) During a change of state of the system, the internal energy may change from an initial value U_1 to a final value U_2 . We denote the change in internal energy as $\Delta U = U_2 - U_1$.

When we add a quantity of heat Q to a system and the system does no work during the process (so W = 0), the internal energy increases by an amount equal to Q; that is, $\Delta U = Q$. When a system does work W by expanding against its surroundings and no heat is added during the process, energy leaves the system and the internal energy decreases: W is positive, Q is zero, and $\Delta U = -W$. When *both* heat transfer and work occur, the *total* change in internal energy is

First law of thermodynamics:	Internal energy change of thermodynamic system $\Delta U = Q - W$	nge of thermodynamic system
Heat ac	ded to system* Work done by system	*•••• Work done by system

We can rearrange this to the form $Q = \Delta U + W$ The message of this Equation is that when heat Q is added to a system, some of this added energy remains within the system, changing its internal energy by ΔU ; the remainder leaves the system as the system does work W on its surroundings. Because W and Q may be positive, negative, or zero, ΔU can be positive, negative, or zero for different processes (see the Figure below).

The last two Equations represents the **first law of thermodynamics.** It is a generalization of the principle of conservation of energy to include energy transfer through heat as well as mechanical work. As you will see in later chapters, this principle can be extended to ever-broader classes of phenomena by identifying additional forms of energy and energy transfer. In every situation in which it seems that the total energy in all known forms is not conserved, it has been possible to identify a new form of energy such that the total energy, including the new form, *is* conserved.

(a) More heat is added to system than system does work: Internal energy of system increases.

(b) More heat flows out of system than work is done: Internal energy of system decreases.

(c) Heat added to system equals work done by system: Internal energy of system unchanged.



In a thermodynamic process, the internal energy U of a system may (a) increase ($\Delta U > 0$), (b) decrease ($\Delta U < 0$), or (c) remain the same ($\Delta U = 0$).

Understanding the first law of thermodynamics

At the beginning of this discussion we tentatively defined internal energy in terms of microscopic kinetic and potential energies. But actually *calculating* internal energy in this way for any real system would be hopelessly complicated. Furthermore, this definition isn't an *operational* one: It doesn't describe how to determine internal energy from physical quantities that we can measure.

So let's look at internal energy in another way. Starting over, we define the *change* in internal energy ΔU during any change of a system as the quantity given by Eq. $\Delta U = Q - W$. This *is* an operational definition because we can measure Q and W. It does not define U itself, only ΔU . This is not a shortcoming because we can *define* the internal energy of a system to have a specified value in some reference state, and then use the Equation of the first law of thermodynamics to define the internal energy in any other state.

This is analogous to our previous treatment of potential energy, in which we arbitrarily defined the potential energy of a mechanical system to be zero at a certain position. This new definition trades one difficulty for another. If we define ΔU by the Eq., then when the system goes from state 1 to state 2 by two different paths, how do we know that ΔU is the same for the two paths? Q and W are, in general, *not* the same for different paths. If ΔU , which equals Q - W, is also path dependent, then ΔU is ambiguous. If so, the concept of internal energy of a system is subject to the same criticism as the erroneous concept of quantity of heat in a system.

The only way to answer this question is through *experiment*. For various materials we measure Q and W for various changes of state and various paths to learn whether ΔU is or is not path dependent. The results of many such investigations are clear and unambiguous: While Q and W depend on the path, $\Delta U = Q - W$ is independent of path. The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the path leading from one to the other.

Experiment, then, is the ultimate justification for believing that a thermodynamic system in a specific state has a unique internal energy that depends only on that state. An equivalent statement is that the internal energy U of a system is a function of the state coordinates p, V, and T (actually, any two of these, since the three variables are related by the equation of state). To say that the first law of thermodynamics represents conservation of energy for thermodynamic processes is correct, as far as it goes.

But an important *additional* aspect of the first law is the fact that internal energy depends only on the state of a system (see the Figure). In changes of state, the change in internal energy is independent of the path. All this may seem a little abstract if you are satisfied to think of internal energy as microscopic mechanical energy. There's nothing wrong with that view, and we will make use of it at various times during our discussion. But as for heat, a precise *operational* definition of internal energy must be independent of the detailed microscopic structure of the material.

Your body is a thermodynamic system too. When you exercise, your body does work (such as the work done to lift your body as a whole in a push-up). Hence W > 0. Your body also warms up during exercise; by perspiration and other means the body rids itself of this heat, so Q < 0. Since Q is negative and W is positive, $\Delta U = Q - W < 0$ and the body's internal energy decreases. That's why exercise helps you lose weight: It uses up some of the internal energy stored in your body in the form of fat.



The internal energy of a cup of coffee depends on just its thermodynamic state – how much water and ground coffee it contains, and what its temperature is. It does not depend on the history of how the coffee was prepared – that is, the thermodynamic path that led to its current state.

Cyclic processes and isolated systems

Two special cases of the first law of thermodynamics are worth mentioning. A process that eventually returns a system to its initial state is called a *cyclic process*. For such a process, the final state is the same as the initial state, and so the *total* internal energy change must be zero. Then

$$U_2 = U_1$$
 and $Q = W$

If a net quantity of work W is done by the system during this process, an equal amount of energy must have flowed into the system as heat Q. But there is no reason either Q or W individually has to be zero (see the Figure). Another special case occurs in an *isolated system*, one that does no work on its surroundings and has no heat flow to or from its surroundings. For any process taking place in an isolated system,

W = Q = 0 and therefore $U_2 = U_1 = \Delta U = 0$

In other words, the internal energy of an isolated system is constant



Every day, your body (a thermodynamic system) goes through a cyclic thermodynamic process like this one. Heat Q is added by metabolizing food, and your body does work W in breathing, walking, and other activities. If you return to the same state at the end of the day, Q = W and the net change in your internal energy is zero.

Infinitesimal changes of state

In the preceding examples the initial and final states differ by a finite amount. Later we will consider *infinitesimal* changes of state in which a small amount of heat dQ is added to the system, the system does a small amount of work dW, and its internal energy changes by an amount dU. For such a process,



For the systems we will discuss, the work dW is given by dW = p dV, so we can also state the first law as

 $dU = dQ - p \ dV$

Kinds of thermodynamic processes

In this section we describe four specific kinds of thermodynamic processes that occur often in practical situations. We can summarize these briefly as "no heat transfer" or *adiabatic*, "constant volume" or *isochoric*, "constant pressure" or *isobaric*, and "constant temperature" or *isothermal*. For some of these processes we can use a simplified form of the first law of thermodynamics.

Adiabatic process

An adiabatic process is defined as one with no heat transfer into or out of a system; Q = 0. We can prevent heat flow either by surrounding the system with thermally insulating material or by carrying out the process so quickly that there is not enough time for appreciable heat flow.

From the first law we find that for every adiabatic process,

 $U_2 - U_1 = \Delta U = -W$ (adiabatic process)

When a system expands adiabatically, W is positive (the system does work on its surroundings), so ΔU is negative and the internal energy decreases. When a system is *compressed* adiabatically, W is negative (work is done on the system by its surroundings) and U increases. In many (but not all) systems an increase of internal energy is accompanied by a rise in temperature, and a decrease in internal energy by a drop in temperature (see the Figure).

The compression stroke in an internal-combustion engine is an approximately adiabatic process. The temperature rises as the air–fuel mixture in the cylinder is compressed. The expansion of the burned fuel during the power stroke is also an approximately adiabatic expansion with a drop in temperature.

To learn other important things (details about an adiabatic, isochoric, isobaric and isothermal processes, internal energy, relating of molar heat capacities C_p and C_V for an ideal gas), **please see description of the lab** "The Clément-Desormes experiment" in our manual "General physics: Laboratory works"!



When the cork is popped on a bottle of champagne, the pressurized gases inside the bottle expand rapidly and do work on the outside air (W > 0). There is little time for the gases to exchange heat with their surroundings, so the expansion is nearly adiabatic (Q = 0). Hence the internal energy of the expanding gases decreases ($\Delta U = -W < 0$) and their temperature drops. This makes water vapor condense and form a miniature cloud.

Directions of thermodynamic processes

Many thermodynamic processes proceed naturally in one direction but not the opposite. For example, heat by itself always flows from a hot body to a cooler body, never the reverse. Heat flow from a cool body to a hot body would not violate the first law of thermodynamics; energy would be conserved. But it doesn't happen in nature. Why not? As another example, note that it is easy to convert mechanical energy completely into heat; this happens every time we use a car's brakes to stop it. In the reverse direction, there are plenty of devices that convert heat *partially* into mechanical energy. (An automobile engine is an example.) But no one has ever managed to build a machine that converts heat *completely* into mechanical energy. Again, why not?

The answer to both of these questions has to do with the *directions* of thermodynamic processes and is called the *second law of thermodynamics*. This law places fundamental limitations on the efficiency of an engine or a power plant. It also places limitations on the minimum energy input needed to operate a refrigerator. So the second law is directly relevant for many important practical problems.

Thermodynamic processes that occur in nature are all **irreversible processes.** These are processes that proceed spontaneously in one direction but not the other. The flow of heat from a hot body to a cooler body is irreversible, as is the free expansion of a gas. Sliding a book across a table converts mechanical energy into heat by friction; this process is irreversible, for no one has ever observed the reverse process (in which a book initially at rest on the table would spontaneously start moving and the table and book would cool down).

Despite this preferred direction for every natural process, we can think of a class of idealized processes that *would* be reversible. A system that undergoes such an idealized **reversible process** is always very close to being in thermodynamic equilibrium within itself and with its surroundings. Any change of state that takes place can then be reversed by making only an infinitesimal change in the conditions of the system. For example, we can reverse heat flow between two bodies whose temperatures differ only infinitesimally by making only a very small change in one temperature or the other.

Reversible processes are thus **equilibrium processes**, with the system always in thermodynamic equilibrium. Of course, if a system were *truly* in thermodynamic equilibrium, no change of state would take place. Heat would not flow into or out of a system with truly uniform temperature throughout, and a system that is truly in mechanical equilibrium would not expand and do work against its surroundings. A reversible process is an idealization that can never be precisely attained in the real world. But by making the temperature gradients and the pressure differences in the substance very small, we can keep the system very close to equilibrium states and make the process nearly reversible.

By contrast, heat flow with finite temperature difference, free expansion of a gas, and conversion of work to heat by friction are all *irreversible* processes; no small change in conditions could make any of them go the other way. They are also all *nonequilibrium* processes, in that the system is not in thermodynamic equilibrium at any point until the end of the process.

The second law of thermodynamics

Experimental evidence suggests strongly that it is *impossible* to build a heat engine that converts heat completely to work – that is, an engine with 100% thermal efficiency. This impossibility is the basis of one statement of the **second law of thermodynamics**, as follows:

It is impossible for any system to undergo a process in which it absorbs heat from a reservoir at a single temperature and converts the heat completely into mechanical work, with the system ending in the same state in which it began.

We will call this the "engine" statement of the second law. (It is also known to physicists as the *Kelvin–Planck statement* of this law.)

The basis of the second law of thermodynamics is the difference between the nature of internal energy and that of macroscopic mechanical energy. In a moving body the molecules have random motion, but superimposed on this is a coordinated motion of every molecule in the direction of the body's velocity. The kinetic energy associated with this *coordinated* macroscopic motion is what we call the kinetic energy of the moving body. The kinetic and potential energies associated with the *random* motion constitute the internal energy.

When a body sliding on a surface comes to rest as a result of friction, the organized motion of the body is converted to random motion of molecules in the body and in the surface. Since we cannot control the motions of individual molecules, we cannot convert this random motion completely back to organized motion. We can convert *part* of it, and this is what a heat engine does.

If the second law were *not* true, we could power an automobile or run a power plant by cooling the surrounding air. Neither of these impossibilities violates the *first* law of thermodynamics. The second law, therefore, is not a deduction from the first but stands by itself as a separate law of nature. The first law denies the possibility of creating or destroying energy; the second law limits the *availability* of energy and the ways in which it can be used and converted.

Restating the second law

An analysis of refrigerators forms the basis for an alternative statement of the second law of thermodynamics. Heat flows spontaneously from hotter to colder bodies, never the reverse. A refrigerator does take heat from a colder to a hotter body, but its operation requires an input of mechanical energy or work. We can generalize this observation:

It is impossible for any process to have as its sole result the transfer of heat from a cooler to a hotter body.

We'll call this the "refrigerator" statement of the second law. (It is also known as the *Clausius statement*.) It may not seem to be very closely related to the "engine" statement. In fact, though, the two statements are completely equivalent.

The conversion of work to heat and the heat flow from hot to cold across a finite temperature gradient are *irreversible* processes. The "engine" and "refrigerator" statements of the second law state that these processes can be only partially reversed.

We could cite other examples. Gases naturally flow from a region of high pressure to a region of low pressure; gases and miscible liquids left by themselves always tend to mix, not to unmix. The second law of thermodynamics is an expression of the inherent one-way aspect of these and many other irreversible processes. Energy conversion is an essential aspect of all plant and animal life and of human technology, so the second law of thermodynamics is of fundamental importance.

Entropy

The second law of thermodynamics, as we have stated it, is not an equation or a quantitative relationship but rather a statement of *impossibility*. However, the second law *can* be stated as a quantitative relationship with the concept of *entropy*, the subject of this section.

We have talked about several processes that proceed naturally in the direction of increasing randomness. Irreversible heat flow increases randomness: The molecules are initially sorted into hotter and cooler regions, but this sorting is lost when the system comes to thermal equilibrium. Adding heat to a body also increases average molecular speeds; therefore, molecular motion becomes more random. In the free expansion of a gas, the molecules have greater randomness of position after the expansion than before.

Entropy provides a *quantitative* measure of randomness. To introduce this concept, let's consider an infinitesimal isothermal expansion of an ideal gas. We add heat dQ and let the gas expand just enough to keep the temperature constant. Because the internal energy of an ideal gas depends on only its temperature, the internal energy is also constant; thus from the first law, the work dW done by the gas is equal to the heat dQ added. That is,

$$dQ = dW = p \, dV = \frac{nRT}{V} dV$$
 so $\frac{dV}{V} = \frac{dQ}{nRT}$

The gas is more disordered after the expansion than before: The molecules are moving in a larger volume and have more randomness of position. Thus the fractional volume change dV/V is a measure of the increase in randomness, and the above equation shows that it is proportional to the quantity dQ/T. We introduce the symbol S for the entropy of the system, and we define the infinitesimal entropy change dS during an infinitesimal reversible process at absolute temperature T as

$$dS = \frac{dQ}{T}$$
 (infinitesimal reversible process)

If a total amount of heat Q is added during a reversible isothermal process at absolute temperature T, the total entropy change $\Delta S = S_2 - S_1$ is given by

 $\Delta S = S_2 - S_1 = \frac{Q}{T}$ (reversible isothermal process)

Entropy has units of energy divided by temperature; the SI unit of entropy is 1 J/K.

We can see how the quotient Q/T is related to the increase in randomness. Higher temperature means greater randomness of motion. If the substance is initially cold, with little molecular motion, adding heat Q causes a substantial fractional increase in molecular motion and randomness. But if the substance is already hot, the same quantity of heat adds relatively little to the greater molecular motion already present. So Q/T is an appropriate characterization of the increase in randomness when heat flows into a system.

We can generalize the definition of entropy change to include *any* reversible process leading from one state to another, whether it is isothermal or not. We represent the process as a series of infinitesimal reversible steps. During a typical step, an infinitesimal quantity of heat dQ is added to the system at absolute temperature *T*. Then we sum (integrate) the quotients dQ/T for the entire process; that is,



Because entropy is a measure of the randomness of a system in any specific state, it must depend only on the current state of the system, not on its past history. (It is possible to verify this statement.) When a system proceeds from an initial state with entropy S_1 to a final state with entropy S_2 , the change in entropy $\Delta S = S_2 - S_1$ defined by the last Equation does not depend on the path leading from the initial to the final state but is the same for *all possible* processes leading from state 1 to state 2. Thus the entropy of a system must also have a definite value for any given state of the system. *Internal energy*, introduced earlier, also has this property, although entropy and internal energy are very different quantities.

Since entropy is a function only of the state of a system, we can also compute entropy changes in *irreversible* (nonequilibrium) processes for which these last Equations are not applicable. We simply invent a path connecting the given initial and final states that *does* consist entirely of reversible equilibrium processes and compute the total entropy change for that path. It is not the actual path, but the entropy change must be the same as for the actual path.

As with internal energy, the above discussion does not tell us how to calculate entropy itself, but only the change in entropy in any given process. Just as with internal energy, we may arbitrarily assign a value to the entropy of a system in a specified reference state and then calculate the entropy of any other state with reference to this.

In an idealized, reversible process involving only equilibrium states, the total entropy change of the system and its surroundings is zero. But all *irreversible* processes involve an increase in entropy. Unlike energy, *entropy is not a conserved quantity.* The entropy of an isolated system *can* change, but as we shall see, it can never decrease. The free expansion of a gas is an irreversible process in an isolated system in which there is an entropy increase.

The results of example about the flow of heat from a higher to a lower temperature are characteristic of *all* natural (that is, irreversible) processes. When we include the entropy changes of all the systems taking part in the process, the increases in entropy are always greater than the decreases. In the special case of a *reversible* process, the increases and decreases are equal. Hence we can state the general principle: When all systems taking part in a process are included, the entropy either remains constant or increases. In other words: No process is possible in which the total entropy decreases, when all systems taking part in the process are included. This is an alternative statement of the second law of thermodynamics in terms of entropy. Thus it is equivalent to the "engine" and "refrigerator" statements discussed earlier. The Figure below shows a specific example of this general principle.

The increase of entropy in every natural, irreversible process measures the increase of randomness in the universe associated with that process. Consider again the example of mixing hot and cold water. We *might* have used the hot and cold water as the high- and low-temperature reservoirs of a heat engine. While removing heat from the hot water and giving heat to the cold water, we could have obtained some mechanical work. But once the hot and cold water have been mixed and have come to a uniform temperature, this opportunity to convert heat to mechanical work is lost irretrievably. The lukewarm water will never *unmix* itself and separate into hotter and colder portions. No decrease in *energy* occurs when the hot and cold water are mixed. What has been lost is the *opportunity* to convert part of the heat from the hot water into mechanical work. Hence when entropy increases, energy becomes less *available*, and the universe becomes more random or "run down."



The mixing of colored ink and water starts from a state of low entropy in which each fluid is separate and distinct from the other. In the final state, both the ink and water molecules are spread randomly throughout the volume of liquid, so the entropy is greater. Spontaneous unmixing of the ink and water, a process in which there would be a net decrease in entropy, is never observed.