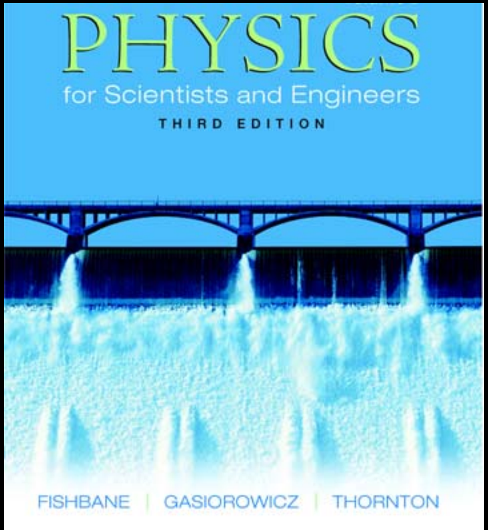


Lecture PowerPoint

Physics for Scientists and Engineers, 3rd edition

Fishbane
Gasiorowicz
Thornton

Chapter 17

Temperature and Ideal Gases

Main Points of Chapter 17

- Temperature, thermal equilibrium, the zeroth law of thermodynamics
- Ideal gases, absolute temperature
- Thermal expansion
- Equation of state for gases
- Blackbody radiation

17-1 Temperature and Thermal Equilibrium

The zeroth law of thermodynamics:

If two thermal systems are in thermal equilibrium with one another, then *they have the same temperature*.

If two systems are each in thermal equilibrium with a third, then they are in thermal equilibrium with one another.

17-1 Temperature and Thermal Equilibrium

The zeroth law of thermodynamics (cont):

Thermal reservoir: system so large that its temperature doesn’t change when interacting with other systems

Thermal contact can occur through conduction, convection, and radiation

Thermometer: a device that measures temperature quantitatively

- Minimal effect on system being measured
- Good contact with system being measured
- Reproducible

17-2 Ideal Gases and Absolute Temperature

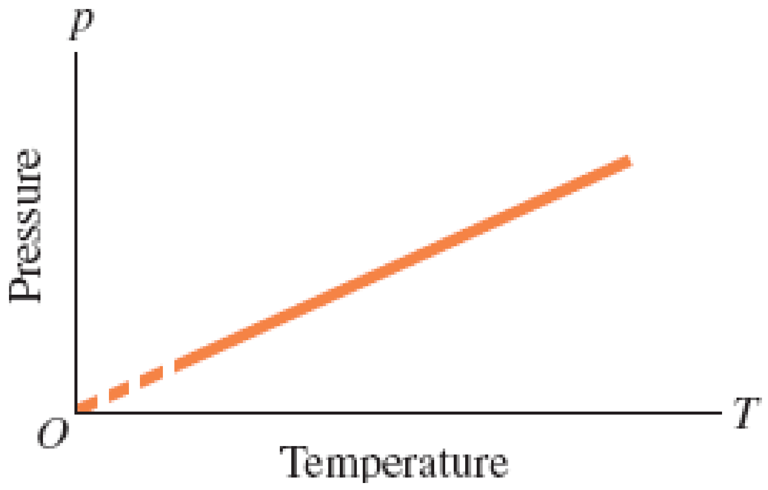
Product of pressure and volume, divided by amount of gas, increases if thermal reservoir is hotter and decreases if it is colder.

Therefore, define temperature:

$$T \propto pV/n$$

For an ideal gas at constant volume,

$$p = (\text{a constant}) \times T \qquad (17\text{-}1)$$



17-2 Ideal Gases and Absolute Temperature

To set temperature scale:

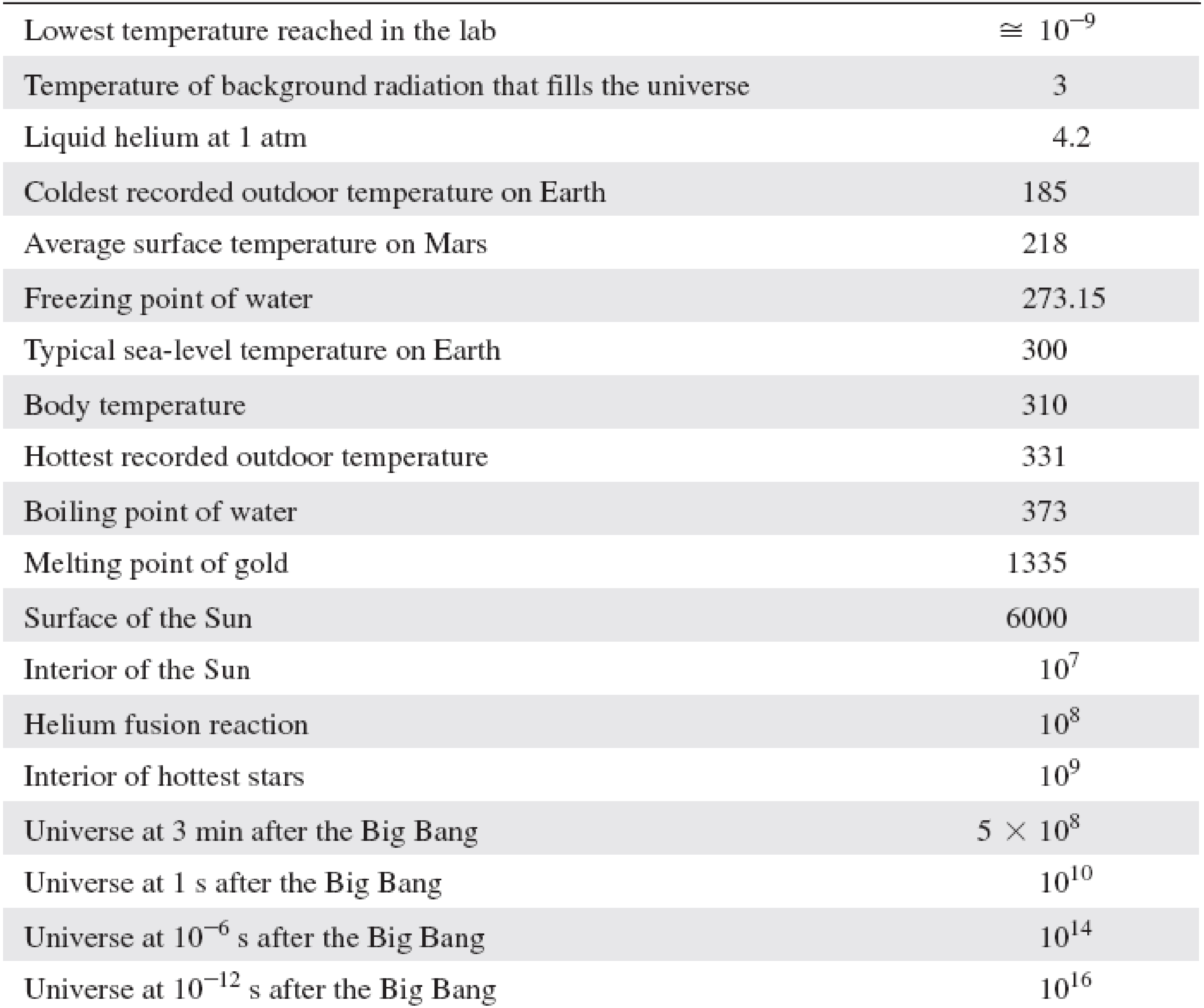
Define $T = 0$ as point where pressure would become zero – absolute zero

Then use triple point of water – where water vapor, liquid water, and ice coexist – to define scale

Defined as $T = 273.16\text{K}$ (Kelvin)

Next slide shows some temperatures occurring in nature, in K

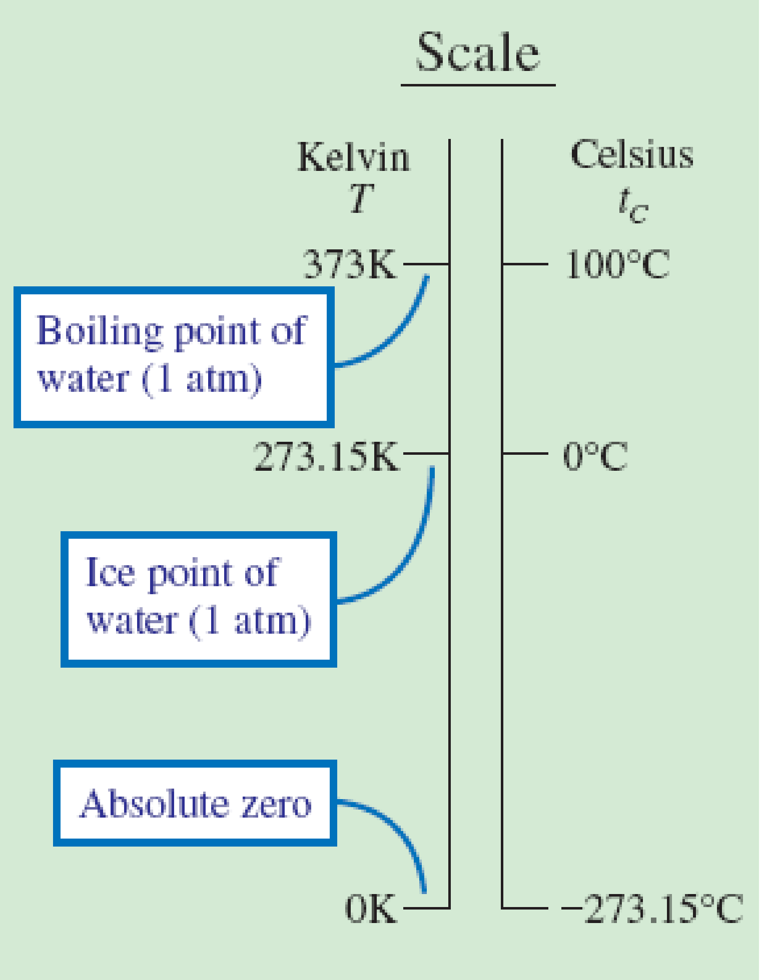
17-2 Ideal Gases and Absolute Temperature

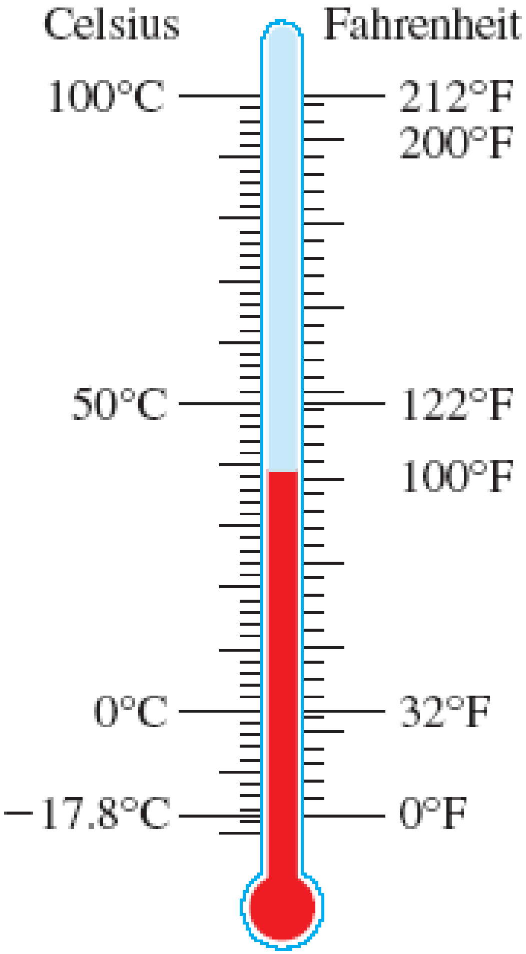


Lowest temperature reached in the lab	$\cong 10^{-9}$
Temperature of background radiation that fills the universe	3
Liquid helium at 1 atm	4.2
Coldest recorded outdoor temperature on Earth	185
Average surface temperature on Mars	218
Freezing point of water	273.15
Typical sea-level temperature on Earth	300
Body temperature	310
Hottest recorded outdoor temperature	331
Boiling point of water	373
Melting point of gold	1335
Surface of the Sun	6000
Interior of the Sun	10^7
Helium fusion reaction	10^8
Interior of hottest stars	10^9
Universe at 3 min after the Big Bang	5×10^8
Universe at 1 s after the Big Bang	10^{10}
Universe at 10^{-6} s after the Big Bang	10^{14}
Universe at 10^{-12} s after the Big Bang	10^{16}

17-2 Ideal Gases and Absolute Temperature

Comparison of Temperature Scales

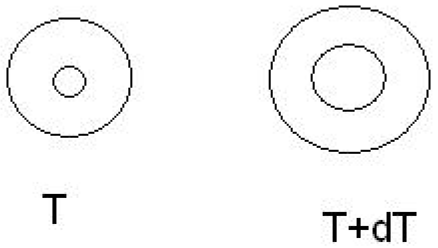




17-3 Thermal Expansion

Solids expand when temperature increases; describe by coefficient of thermal expansion:

$$\alpha \equiv \frac{1}{L}\frac{dL}{dT} \qquad (17\text{-}5)$$



For fluids, use coefficient of volume expansion instead (as length is not well-defined)

$$\beta \equiv \frac{1}{V}\frac{dV}{dT} \qquad (17\text{-}6)$$

17-4 The Equation of State of Gases

One mole of gas has a mass in grams equal to the atomic or molecular weight of the gas.

Example: The atomic weight of helium is 4; one mole of helium has a mass of 4 grams.

17-4 The Equation of State of Gases

One mole always has the same number of atoms or molecules, called Avogadro's number:

$$N_A = 6.022 \times 10^{23}$$

The number of atoms or molecules in a sample of gas can then be written in terms of N_A and n, the number of moles:

$$N = nN_A \qquad (17\text{-}8)$$

17-4 The Equation of State of Gases

For constant temperature, ideal gases obey Boyle's law:

$$\frac{pV}{n} = \text{a constant.} \qquad (17\text{-}9)$$

Combine that with earlier result for constant volume:

$$p = (\text{a constant}) \times T \qquad (17\text{-}1)$$

to get the ideal gas law: $pV = nRT.$ (17-10)

where:

$$R \cong 8.314 \frac{\text{N} \cdot \text{m}}{\text{mol} \cdot \text{K}} = 8.314 \text{ J/mol} \cdot \text{K} \qquad (17\text{-}11)$$

17-4 The Equation of State of Gases

Alternatively, can write:

$$pV = NkT \qquad (17\text{-}12)$$

where N is the number of atoms or molecules, and:

$$k = \frac{R}{N_A} \cong 1.381 \times 10^{-23}\ \mathrm{J/K} \qquad (17\text{-}13)$$

k is called Boltzmann’s constant.

17-4 The Equation of State of Gases

The state of an ideal gas is described by its temperature, volume, pressure, and number of atoms or molecules (which is usually assumed to stay the same). Changing any one, or more, of these results in a change of the state.

Several types of changes are commonly used:

- isothermal: temperature is constant
- isobaric: pressure is constant

17-4 The Equation of State of Gases

How Close do Real Gases Come to Being Ideal?

Better equation for real gases: van der Walls

$$\left[p + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT. \quad (17\text{-}15)$$

The constants *a* and *b* depend on the specific gas.

17-5 Blackbody Radiation

Objects that become sufficiently hot will glow visibly; as they get hotter they go from red, to yellow, to a bluish white.

This is electromagnetic radiation; objects at any temperature will emit it at various frequencies, from radio waves all the way to gamma rays.

This radiation from a body in thermal equilibrium is called blackbody radiation, as it is purely thermal and doesn’t depend on any properties of the body other than its temperature and area.

17-5 Blackbody Radiation

Deriving the energy density as a function of frequency and temperature required introducing some new concepts:

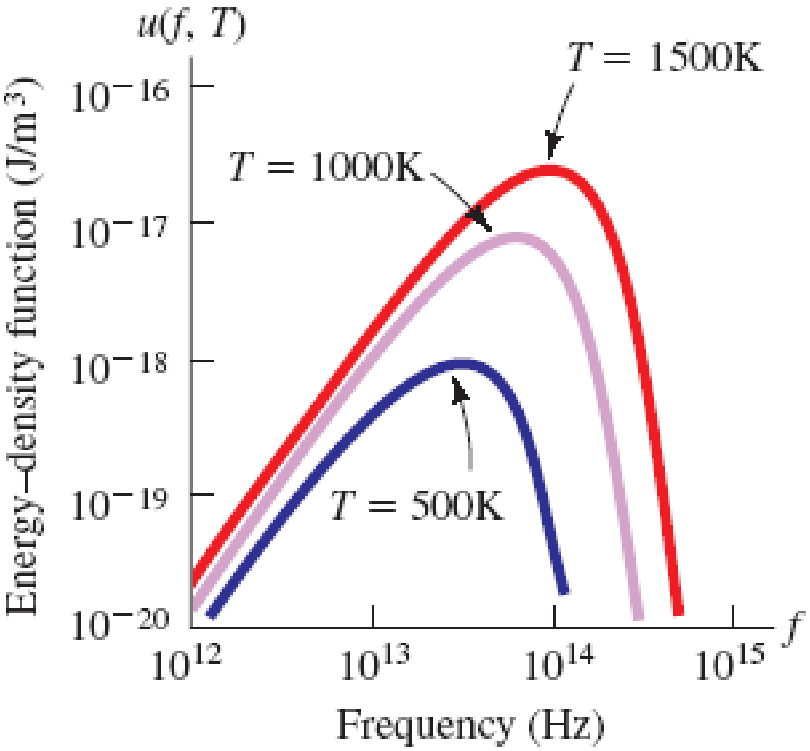
$$u(f, T) = \frac{8\pi h}{c^3} \frac{f^3}{e^{hf/kT} - 1} \qquad (17\text{-}16)$$

Here, c is the speed of light:

$$c = 3 \times 10^8 \text{ m/s}$$

And h is Planck's constant:

$$h = 6.625 \times 10^{-34} \text{ J} \cdot \text{s}$$



17-5 Blackbody Radiation

This formula for blackbody radiation was one of the first hints of the necessity of quantum theory to describe matter and radiation.

Stefan-Boltzmann formula gives power radiated as a function of temperature:

$$E(T) = \sigma T^4 \tag{17-17}$$

All bodies emit (or absorb) energy under the form of radiation (E&M wave).

17-5 Blackbody Radiation

The Discovery and Measurement of the Background Radiation of the Universe

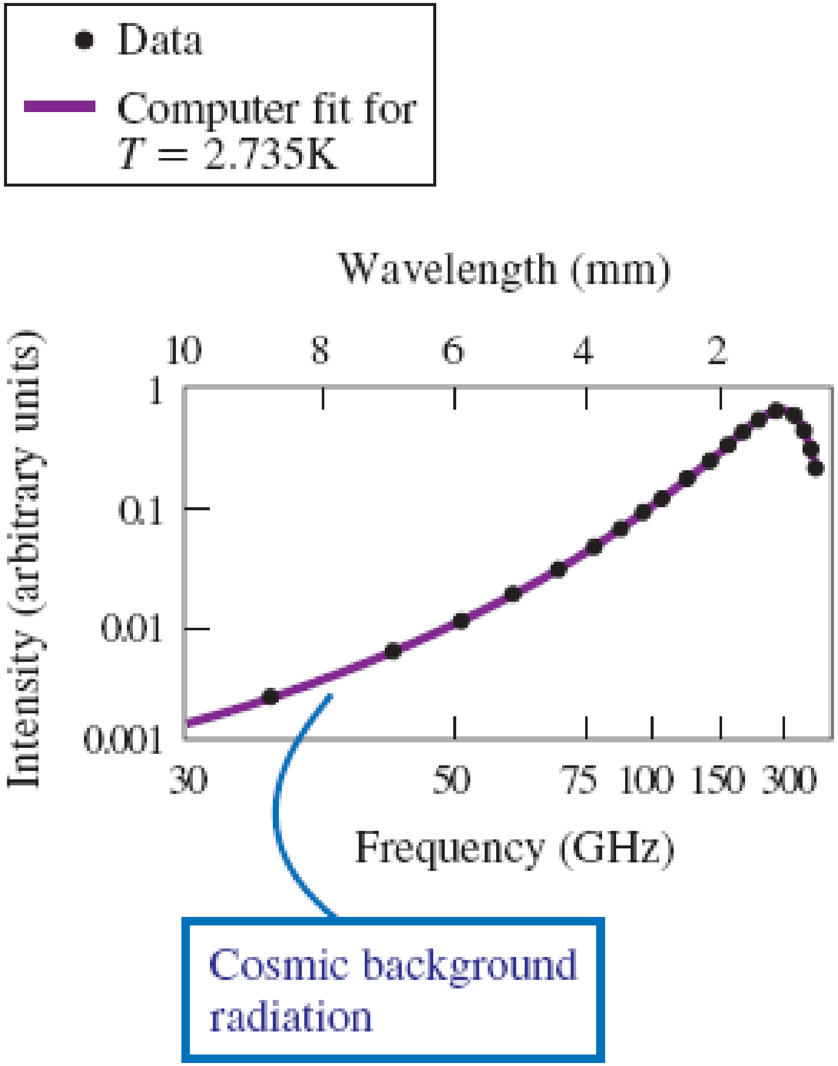
In 1964, background radiation was discovered, coming from no particular source but having a blackbody frequency distribution corresponding to a temperature of about 3K.

This radiation is left over from the early days of the universe.

At first, matter and radiation were in thermal equilibrium; as the universe cooled this was no longer true. The blackbody radiation is the remnant of the frozen-out radiation, cooled to near absolute zero by the expansion of the universe.

17-5 Blackbody Radiation

This is the observed blackbody radiation data as well as the distribution for T = 2.735K. The error bars on the data points are smaller than the points themselves.



Cosmic background radiation

Chapter 18

Heat Flow and the First Law of Thermodynamics

Main Points of Chapter 18

- Changes in thermal systems – isothermal, adiabatic
- Reversible and irreversible processes
- Heat flow
- Phase changes
- Thermal resistance
- Mechanical equivalent of heat
- Work done by thermal systems
- Internal energy of ideal gases
- First law of thermodynamics

18-1 Changes in Thermal Systems

Change where system is always in thermal equilibrium: reversible process

Change where system is not always in thermal equilibrium: irreversible process

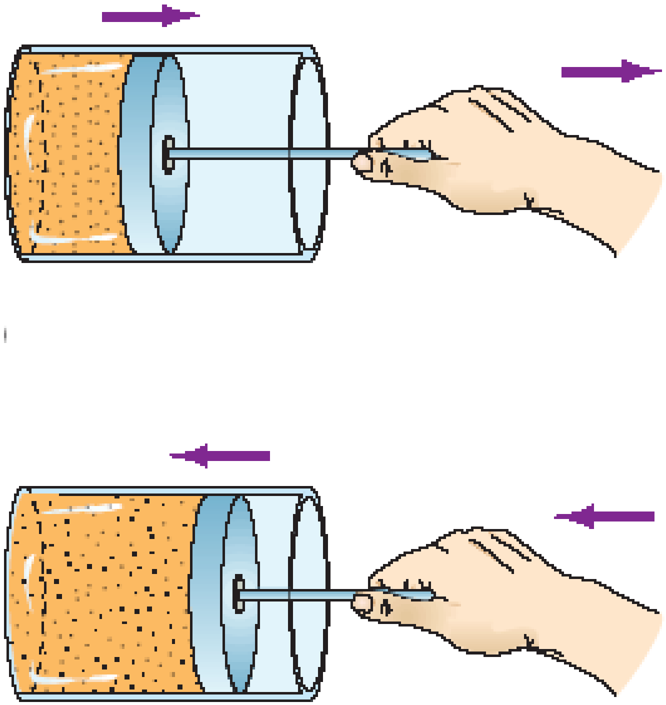
Examples of irreversible processes:

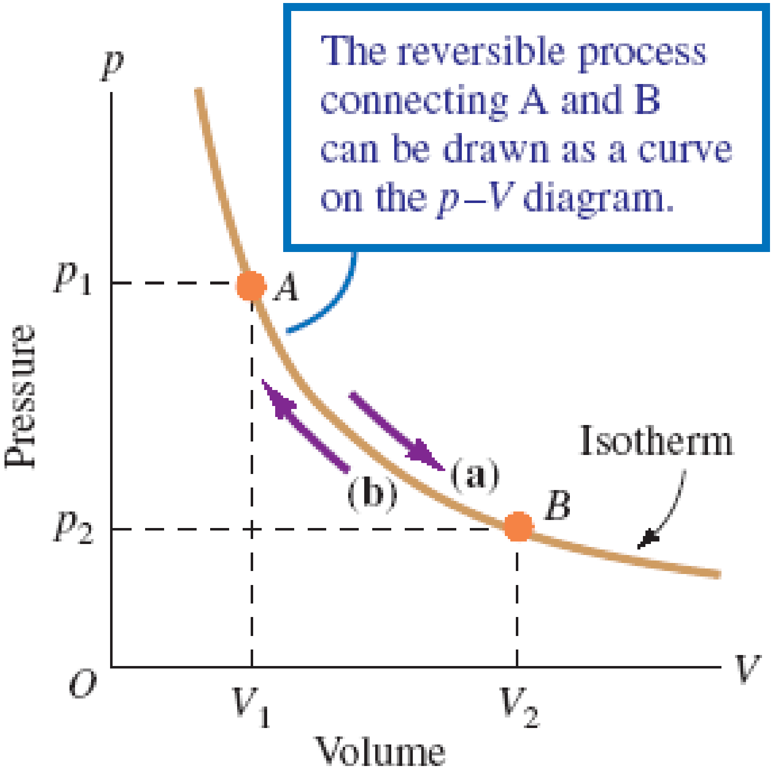
- Free expansion
- melting of ice in warmer liquid
- frictional heating

18-1 Changes in Thermal Systems

Example of a Reversible Process:

Cylinder must be pulled or pushed slowly enough that the system remains in thermal equilibrium



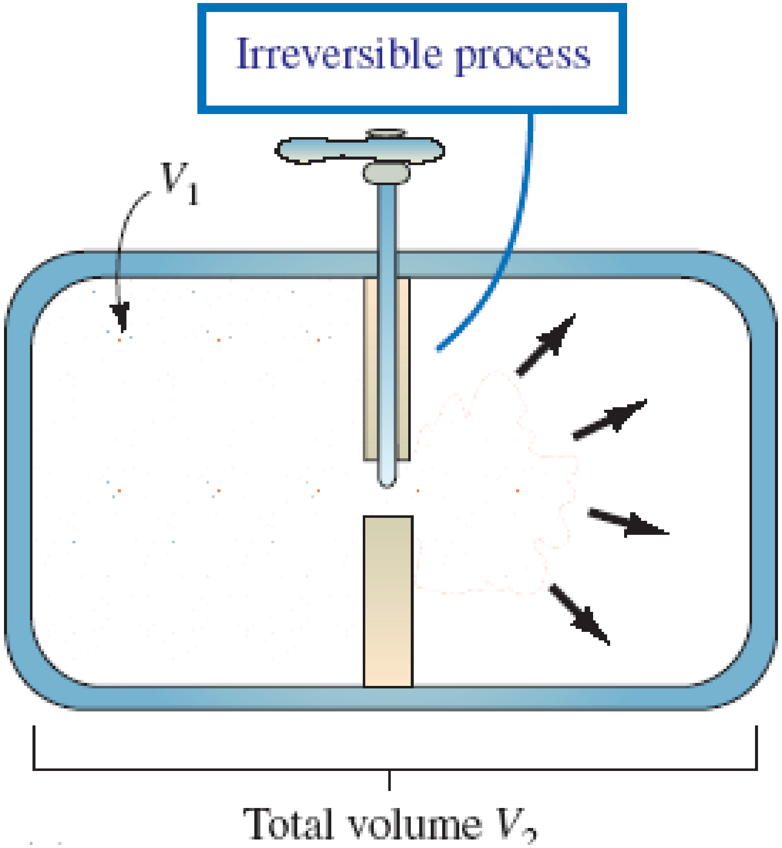


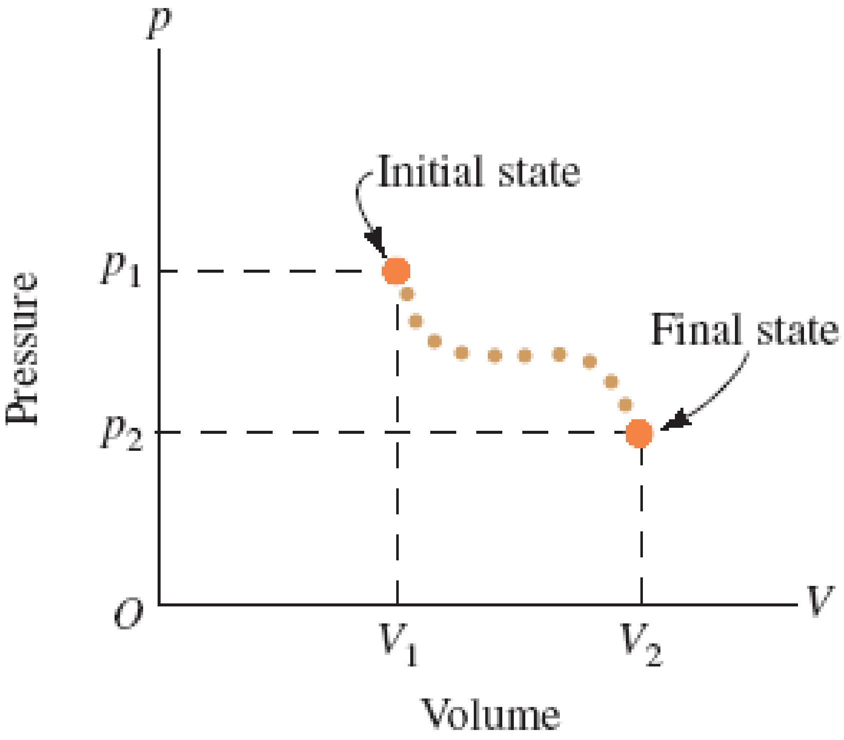
The reversible process connecting A and B can be drawn as a curve on the p–V diagram.

18-1 Changes in Thermal Systems

Example of an Irreversible Process:

The gas expands freely when the valve is opened.





18-2 Heat Flow

Temperature of a system is closely related to its internal (thermal) energy

System can transfer energy by changing temperature or phase, by doing work, or both

When temperature of system changes, there has been heat flow *Q*

Heat capacity C (quantity of energy required to raise the temperature of a body by one degree Celsius) connects heat flow to temperature change:

$$dQ = C\, dT \qquad (18\text{-}1a)$$

18-2 Heat Flow

Heat capacity depends on material, and also on the quantity of material present.

Eliminate quantity dependence by introducing specific heat *c* and molar heat capacity *c*′:

$$C = mc = nc'$$

Here, *m* is the mass in grams, and *n* the number of moles.

Units of heat flow: calories; 1 cal is heat needed to raise 1g of water from 14.5°C to 15.5°C.

18-2 Heat Flow

- A phase change occurs when a solid melts to a liquid, a liquid boils to a gas, a gas condenses to a liquid, and a liquid freezes to a solid.

- Each of these phase changes requires a certain amount of heat, although the temperature does not change.

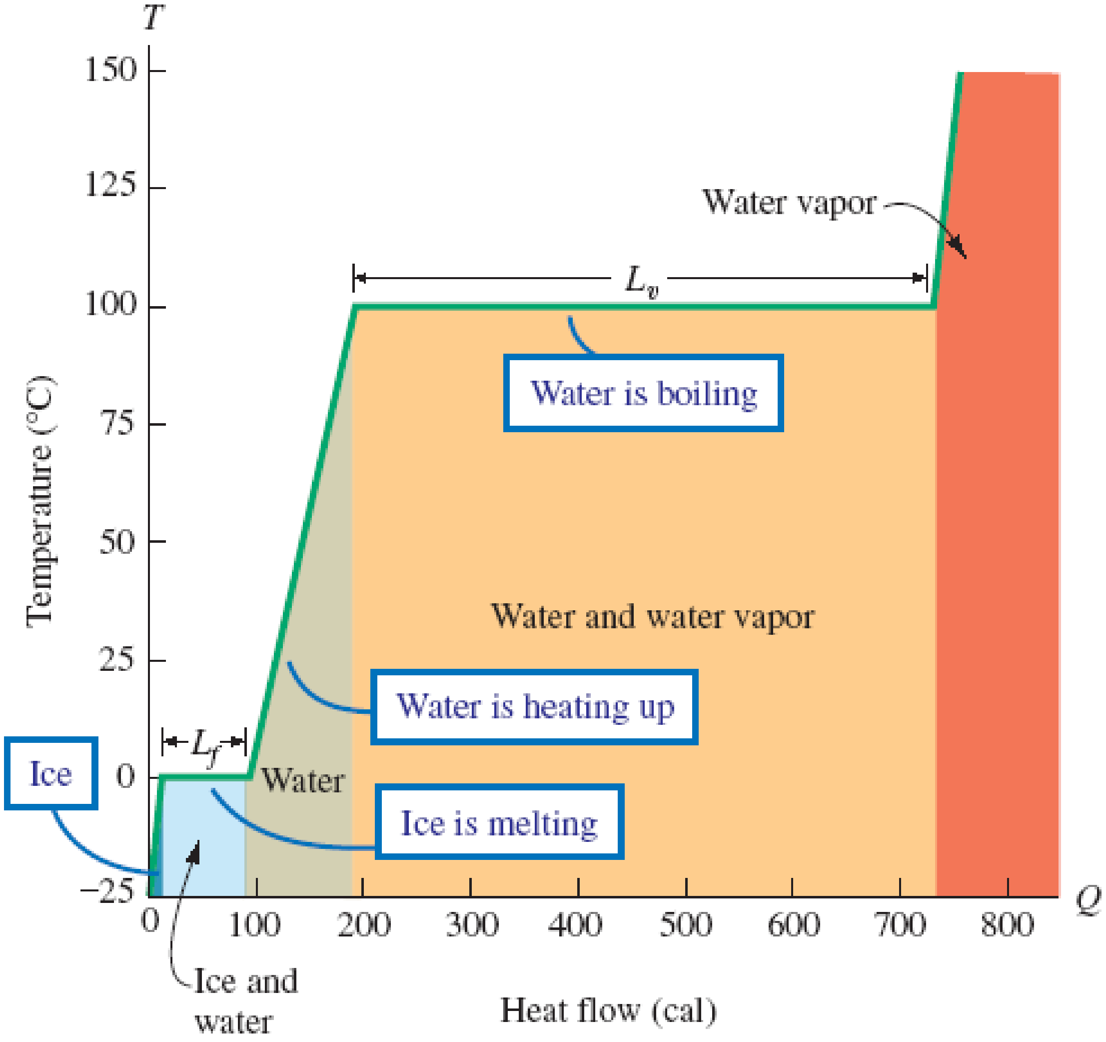
18-2 Heat Flow

- If a solid becomes liquid, or vice versa, the amount of heat per gram is the latent heat of fusion.

- If a liquid becomes gas, or vice versa, the amount of heat per gram is the latent heat of vaporization.

18-2 Heat Flow

This diagram shows how water (in the form of ice) behaves as heat is steadily added to it:



18-3 Heat Flow in Materials

If one end of a solid of length *L* is maintained at a temperature T_1 and the other at a lower temperature T_2, the rate of heat flow depends on the temperature difference, the cross-sectional area of the solid, and its length:

$$\frac{\Delta Q}{\Delta t} \propto A\frac{\Delta T}{L} \qquad (18\text{-}7)$$

18-3 Heat Flow in Materials

As long as ΔT is small enough to keep the relationship linear, we can write:

$$\frac{dQ}{dt} = -\kappa A \frac{dT}{dx} \qquad (18\text{-}8)$$

where κ is the thermal conductivity.

18-3 Heat Flow in Materials

Thermal resistance, also known as R value, is inversely proportional to conductivity and depends on the thickness of the material:

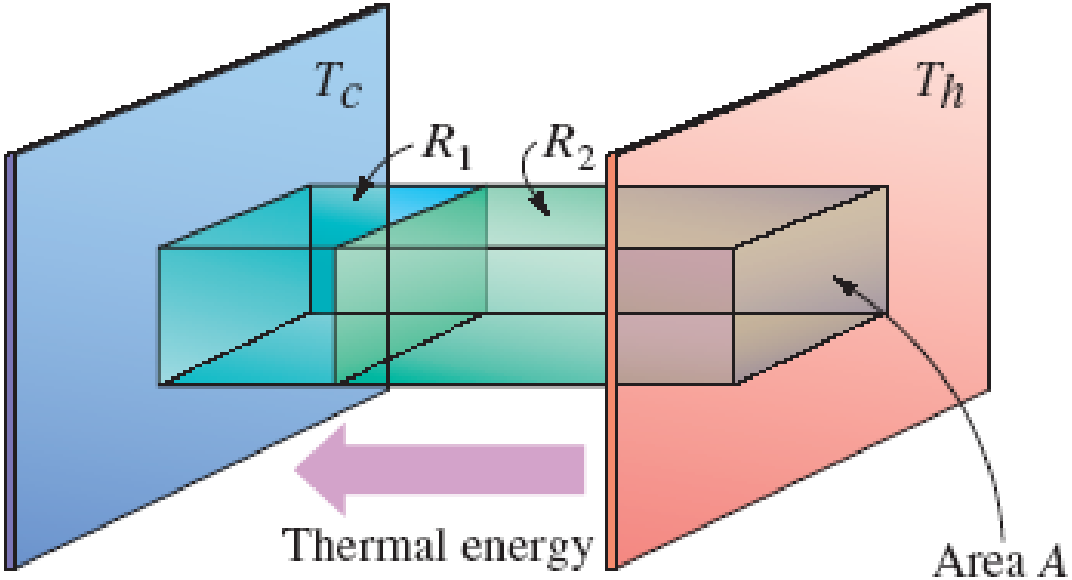
$$R \equiv \frac{L}{\kappa} \qquad (18\text{-}9)$$

If the R value is high, the material is a good insulator; if it is low, the material is a poor insulator.

18-3 Heat Flow in Materials

Two different materials can be connected in series (so the heat flows first through one and then the other) or parallel (so they are next to each other and heat flows through both simultaneously.

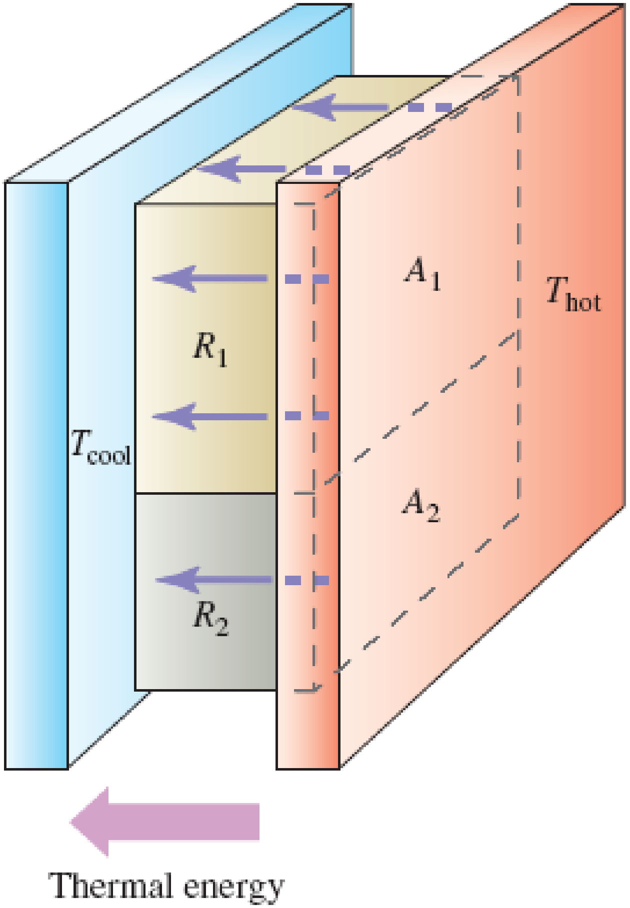
In series: $R_{\mathrm{eff}} = R_1 + R_2$ (18-11)



18-3 Heat Flow in Materials

In parallel:

$$\frac{1}{R_{\text{eff}}} = \frac{1}{A_1 + A_2}\left(\frac{A_1}{R_1} + \frac{A_2}{R_2}\right) \qquad (18\text{-}12)$$



18-4 The Mechanical Equivalent of Heat

Temperature of a system can also be raised by performing mechanical work on it.

No experiment can detect whether a change in temperature was due to mechanical work or to heat flow: heat flow must be an energy transfer!

18-4 The Mechanical Equivalent of Heat

Therefore, can relate units of heat flow to units of work:

$$1 \text{ cal} = 4.185 \text{ J} \qquad (18\text{-}13)$$

This is now the numerical definition of the calorie.

18-5 Work Done by Thermal Systems

Work can be done by, instead of on, thermal systems, as in the expansion of a gas.

Using the definitions of work and pressure:

$$dW = \vec{F} \cdot d\vec{x} = pA\,dx \qquad (18\text{-}14)$$

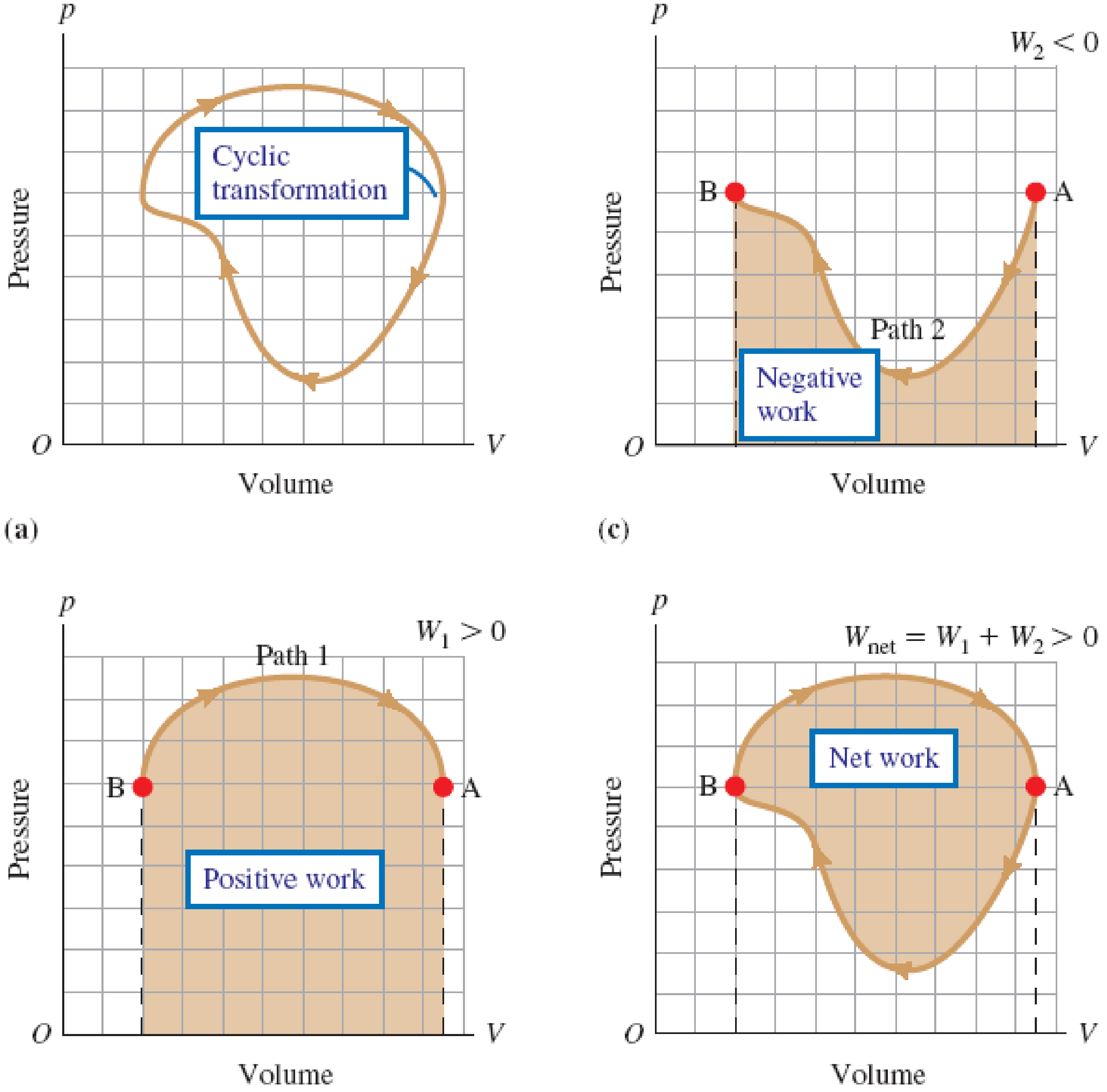
$$= p\,dV \qquad (18\text{-}15)$$

Then:

$$W = \int_{V_1}^{V_2} p\,dV. \qquad (18\text{-}16)$$

The next slide shows that the work done by a cyclic transformation is the area enclosed by the *p-V* curve.

18-5 Work Done by Thermal Systems



18-5 Work Done by Thermal Systems

Types of transformations

- Isobaric (constant pressure): $W = p\Delta V$ (18-18)

- Isochoric (constant volume): no work is done, as there is no movement

- Adiabatic (no heat flow in or out of system): temperature can change only if work is done.

18-5 Work Done by Thermal Systems

Types of transformations (cont)

- Internal (or thermal) energy U in adiabatic transformations:

- Infinitesimal: $dU = -dW$ (18-21)

- Finite: $U_B - U_A = -W_{A \to B}$ (18-22)

18-5 Work Done by Thermal Systems

A finite change in internal energy is independent of the path between *A* and *B*; therefore:

$$\int_A^B dU = U_B - U_A \qquad (18\text{-}23)$$

18-6 The First Law of Thermodynamics

First law is a statement of conservation of energy:

Change in internal energy of system equals is work done on system plus heat flow into system.

$$\Delta U = U_B - U_A = -W_{A\to B} + Q_{A\to B} \qquad (18\text{-}24)$$

In differential form,

$$dU = -dW + dQ \qquad (18\text{-}25b)$$

18-6 The First Law of Thermodynamics

In a closed cycle:

$$Q_{\text{cycle}} = W_{\text{cycle}} \tag{18-26}$$

If the volume is constant:

$$dU = dQ_V = C_V\, dT \tag{18-27}$$

If pressure is constant:

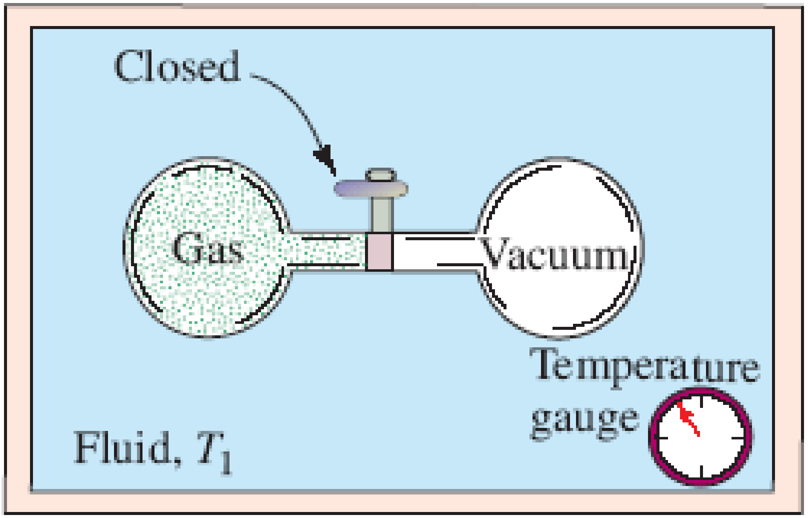
$$dU = -dW_p + dQ_p = -pdV + C_p\, dT \tag{18-28}$$

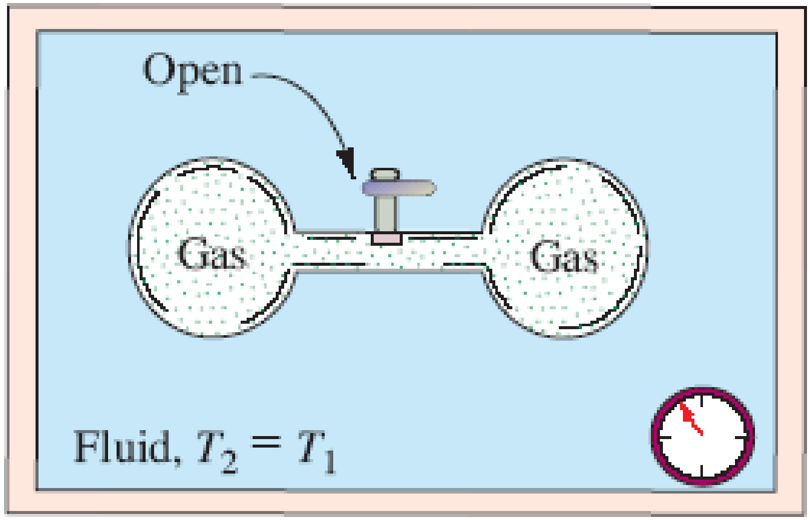
18-7 Internal Energy of Ideal Gases

Joule experiment: on left, have a container filled with a dilute (ideal) gas.

Open stopcock; gas expands, doing no work – find that its temperature does not change (on right)

- **The temperature of an ideal gas undergoing free expansion remains constant.**





18-7 Internal Energy of Ideal Gases

Therefore, for an ideal gas, U is a function only of temperature.

Combining this with the energy changes in in constant-volume transformations:

$$U(T) = \int_0^T C_V\, dT + \text{a constant} \qquad (18\text{-}31)$$

C_V is independent of temperature over a large range; when it is:

$$U(T) = C_V T \qquad (18\text{-}32)$$

18-7 Internal Energy of Ideal Gases

Can also express C_p in terms of C_V:

$$C_V\,dT = -nR\,dT + C_p\,dT.$$

so that:

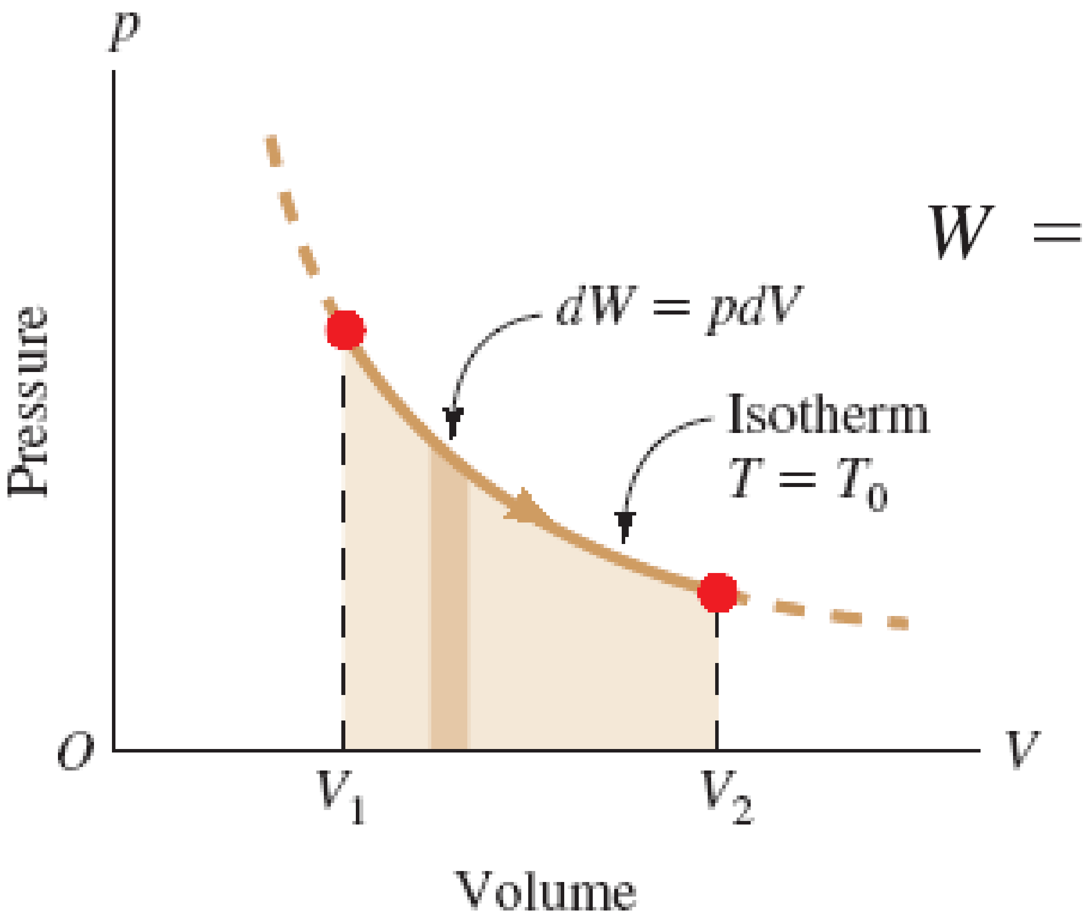
$$C_p = C_V + nR \qquad (18\text{-}33)$$

18-8 More Applications for Ideal Gases

Work done during isothermal transformation

$$W = \int_{V_1}^{V_2} p\,dV \qquad (18\text{-}34)$$

$$W = nRT_0 \ln\left(\frac{V_2}{V_1}\right) \qquad (18\text{-}35)$$



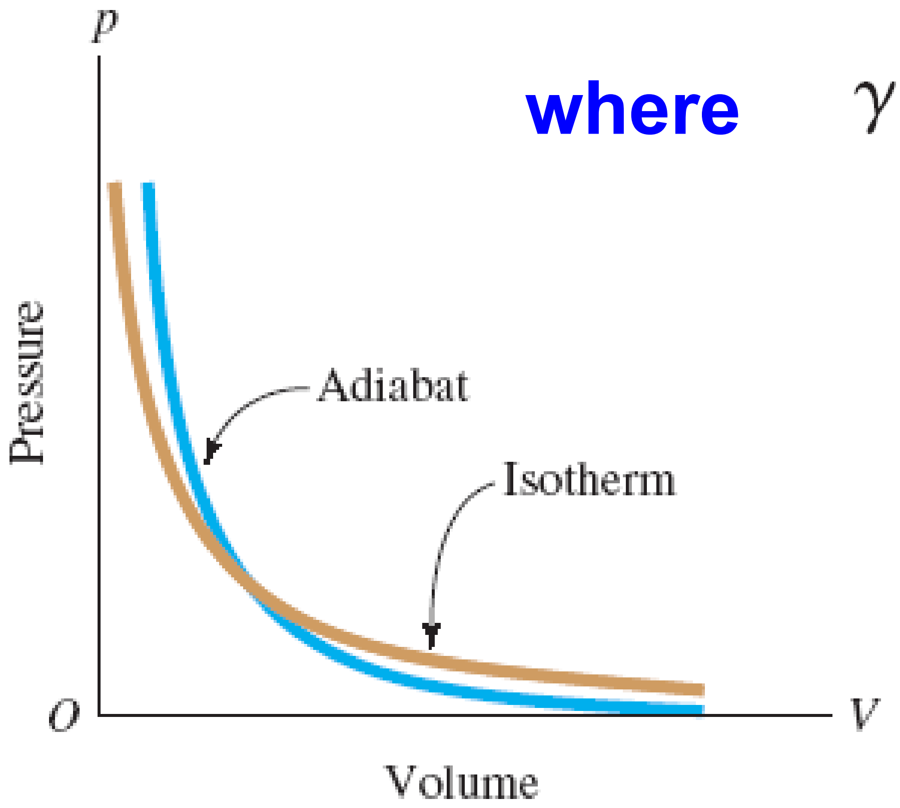
18-8 More Applications for Ideal Gases

In an adiabatic transformation, $dU = -dW$.

The *p-V* curve has the form:

$$pV^{\gamma} = p_0 V_0^{\gamma} = \text{a constant}, \qquad (18\text{-}36)$$

where $$\gamma \equiv \frac{C_p}{C_V} \qquad (18\text{-}37)$$



18-8 More Applications for Ideal Gases

Earth's atmosphere is cooler the higher one goes. When the air rises, it expands, and its temperature decreases.

Assuming the air is an ideal gas, the temperature is found to decrease linearly with altitude:

$$T = T_0 - \left(\frac{mgh}{R}\right)\left(\frac{\gamma - 1}{\gamma}\right) \qquad (18\text{-}43)$$

Chapter 19

The Molecular Basis of Thermal Physics

Main Points of Chapter 19

- Microscopic view of gases
- Pressure
- Temperature
- Probability distributions
- Maxwell-Boltzmann velocity distribution
- Collisions and transport

19-1 A Microscopic View of Gases

Knowing:

- The mass and volume of a certain amount of air at room temperature and pressure
- The mass of a typical air molecule
- The size of a typical air molecule

We can calculate the average separation between molecules:

- On average, molecules are separated by about 20 times their radii

19-1 A Microscopic View of Gases

A balloon-sized volume of air contains about 10^{23} molecules – even though individual molecular actions are random, we can understand air very well through its bulk properties.

19-2 Pressure and Molecular Motion

Have box containing dilute gas, volume *V*, temperature *T*.

Average velocity in any direction is zero – there is no net movement of the gas:

$$\langle v_x \rangle = \langle v_y \rangle = \langle v_z \rangle \quad \text{so that} \quad \langle \vec{v} \rangle = 0 \qquad (19\text{-}1)$$

The brackets are used to indicate average value.

19-2 Pressure and Molecular Motion

Average speed is not zero, though; we take the square of the speeds (which is positive), average it, and then take the square root. This is the rms (root mean square) value, and is never negative:

$$\sqrt{\langle v^2 \rangle}$$

19-2 Pressure and Molecular Motion

Internal energy *U* comes mostly from the kinetic energies of the molecules:

$$U = N\langle K\rangle = N\left(\frac{1}{2}m\langle v^2\rangle\right) \tag{19-2}$$

The average squares of velocities in all three directions are the same:

$$\langle v^2\rangle = 3\langle v_x^2\rangle$$

$$\langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle = \frac{2}{3}\frac{U}{mN} \tag{19-5}$$

19-2 Pressure and Molecular Motion

Now, relate $\langle v_x^2 \rangle$ to the pressure of the gas:

Pressure comes from the collisions of molecules with the walls of the container.

If we look at a wall in the *y-z* plane, only the *x*-component of the molecules' momentum transfers momentum to it:

$$\Delta \vec{P} = 2mv_x \hat{i}. \qquad (19\text{-}6)$$

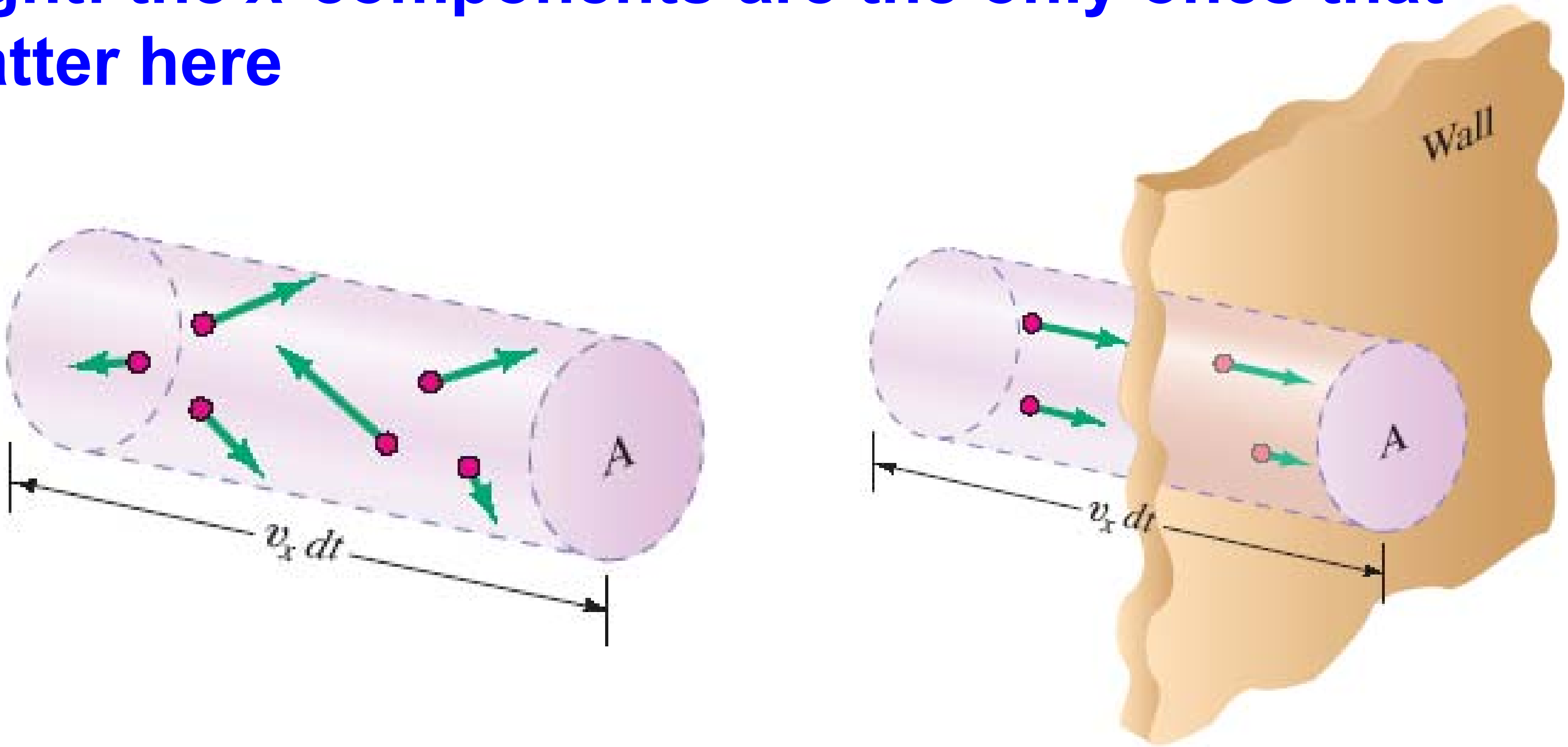
Next: look at the number of collisions per unit time.

19-2 Pressure and Molecular Motion

Take imaginary cylindrical volume that abuts the wall.

Left: the volume

Right: the *x*-components are the only ones that matter here



19-2 Pressure and Molecular Motion

If the number density of molecules (same in the cylinder as in the rest of the gas) is *N*/*V*, then the number of collisions in time *dt* is:

$$\#\text{ of collisions } = N_{\text{coll}} = \frac{1}{2}\frac{N}{V}(v_x\,dt)A \tag{19-7}$$

And the momentum transfer is:

$$dP_x = (2mv_x)\left(\frac{N}{2V}\right)(v_x\,dt)A = mv_x^2\frac{N}{V}A\,dt$$

19-2 Pressure and Molecular Motion

The force is the momentum transfer per unit time:

$$\frac{dP_x}{dt} = F_x = mv_x^2 \frac{N}{V} A \qquad (19\text{-}8)$$

and the pressure is the force per unit area:

$$p = \frac{F_x}{A} = mv_x^2 \frac{N}{V} \qquad (19\text{-}9)$$

19-2 Pressure and Molecular Motion

Finally, using the rms value of the velocity”

$$p = m\langle v_x^2 \rangle \frac{N}{V} = m\left(\frac{2}{3}\frac{U}{mN}\right)\frac{N}{V} = \frac{2}{3}\frac{U}{V} \qquad (19\text{-}10)$$

$$pV = \frac{2}{3}U \qquad (19\text{-}11)$$

This is important!

Microscopic properties have been used to find a relation between macroscopic thermodynamic variables.

19-3 The Meaning of Temperature

Since internal energy is related to pressure and volume, it is also related to temperature:

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT. \qquad (19\text{-}12)$$

and to the average kinetic energy of the molecules:

$$kT = \frac{2}{3}\frac{U}{N} = \frac{2}{3}\langle K\rangle \qquad (19\text{-}13)$$

19-3 The Meaning of Temperature

We can also understand the van der Waals equation better now.

It includes the effects of intermolecular forces, which act over distances larger than the size of the molecule, are repulsive at short range, and slightly attractive at longer distances.

$$\left[p + a\left(\frac{n}{V}\right)^2\right]\left(\frac{V}{n} - b\right) = RT \qquad (17\text{-}15)$$

19-4 Probability Distributions

Not all molecules have the average velocity, of course; for a more complete description we need a velocity distribution function, which tells us how many molecules have any particular velocity.

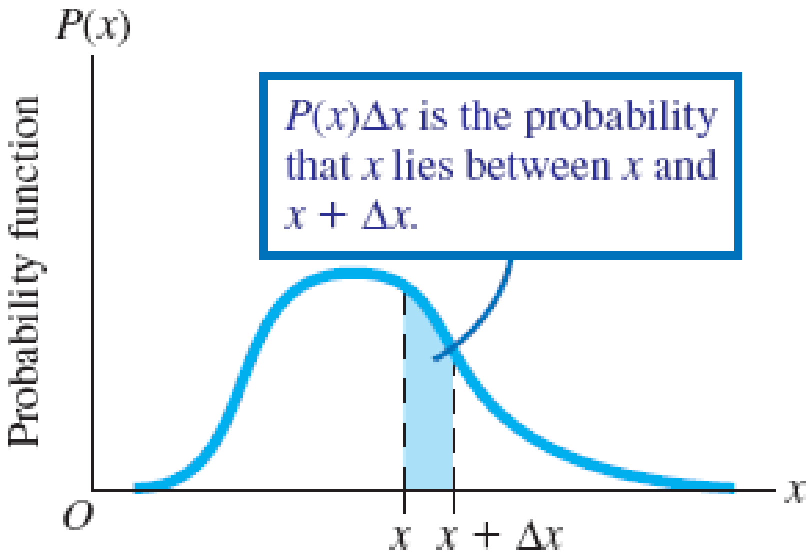
The position distribution function does the same thing for the molecules' location in space.

19-4 Probability Distributions

There are enough molecules in a macroscopic gas sample that the distributions can be considered to be continuous. We define the probability that a value lies within an interval Δ*x* around a value *x*:

The probabilities are normalized so that the total value is one – *x* must be *something*.

$$\int_{x_1}^{x_2} P(x)\,dx = 1 \qquad (19\text{-}22)$$



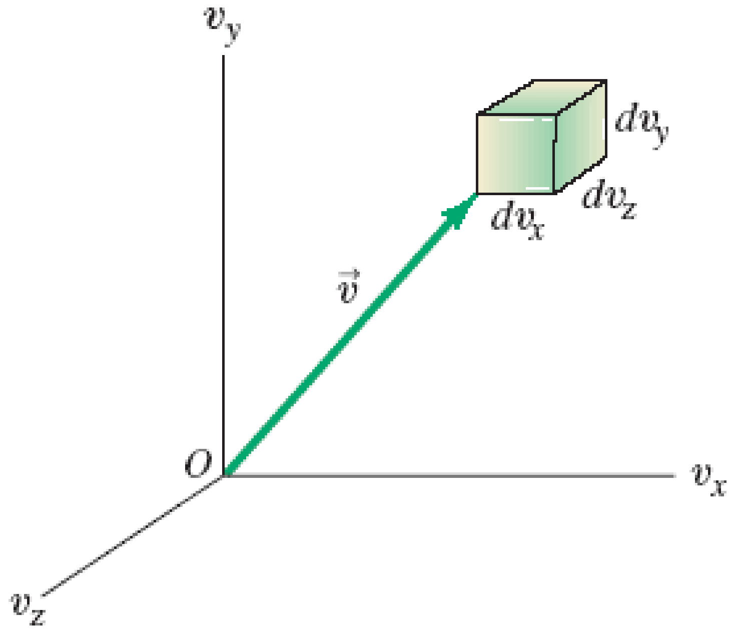
$$P(x)\,\Delta x$$

19-5 The Velocity Distribution of Gases

First, define a velocity probability function:

$$F(\vec{v})\, d^3v$$

This is the probability that the velocity lies between $\vec{v}$ and $\vec{v} + d\vec{v}$:



19-5 The Velocity Distribution of Gases

Assumption:

- **Any way in which a gas’s total energy and total momentum can be shared among the molecules is equally likely.**

19-5 The Velocity Distribution of Gases

Taking into account the individual and average kinetic energies, and how many ways different states of the gas can be created, the distribution function is found to be:

$$F(\vec{v}) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \qquad (19\text{-}28)$$

19-5 The Velocity Distribution of Gases

Now, can use this function to calculate the average of the square of the velocity:

$$\langle v^2 \rangle = \int v^2 F(\vec{v})\, d^3v = \left(\frac{m}{2\pi kT}\right)^{3/2} \int v^2 e^{-mv^2/2kT} d^3v \tag{19-29}$$

With some manipulation, this can be turned into an integral that can be looked up; finally:

$$v_{\text{rms}} = \sqrt{\langle v^2 \rangle} = \sqrt{\frac{3kT}{m}} \tag{19-33}$$

19-6 The Maxwell-Boltzmann Distribution

The velocity distribution for an ideal gas can be written:

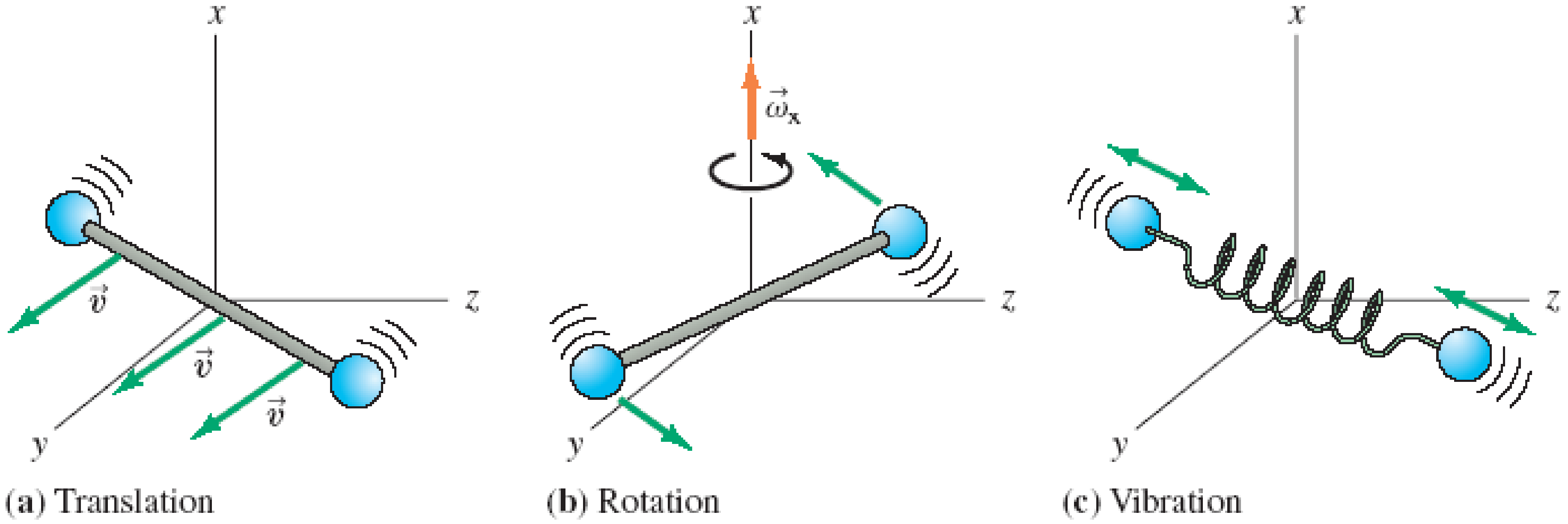
$$F = \frac{1}{Z} e^{-E/kT} \qquad (19\text{-}35)$$

Here, *E* is the total energy of a molecule, and *Z* is a factor that ensures proper normalization.

19-6 The Maxwell-Boltzmann Distribution

A diatomic molecule can do more than just move – it can rotate or vibrate, and both contribute to its total kinetic energy. Including just the rotation:

$$F = \frac{1}{Z} e^{-(mv^2/2kT) - (I\omega_x^2/2kT) - (I\omega_y^2/2kT)} \qquad (19\text{-}37)$$



19-6 The Maxwell-Boltzmann Distribution

Therefore, while the average kinetic energy of translation is

$$\langle E \rangle = \tfrac{3}{2} kT \qquad (19\text{-}12)$$

the addition of rotations about two axes adds two more factors of ½ *kT*:

$$\langle E \rangle = \frac{5}{2} kT \qquad (19\text{-}39)$$

19-6 The Maxwell-Boltzmann Distribution

Finally, the addition of vibration contributes two more factors of ½ *kT*, one for the motion of the atoms and one for the energy in the "spring":

$$\langle E \rangle = \frac{7}{2} kT$$

19-6 The Maxwell-Boltzmann Distribution

$$\langle E \rangle = \frac{7}{2} kT$$

So, each possible independent motion is seen to add ½ *kT* to the energy of the molecule; these are called degrees of freedom.

Contributing to the $^7/_2$ *kT* above, we have:

- velocity in *x*, *y*, and *z*
- rotation about two different axes
- vibration, which includes two contributions

19-6 The Maxwell-Boltzmann Distribution

Therefore, we have the equipartition theorem, which states that each degree of freedom contributes ½ *kT* to the average energy of a molecule. For *s* degrees of freedom:

$$\langle E \rangle = \frac{s}{2}kT \qquad (19\text{-}40)$$

19-6 The Maxwell-Boltzmann Distribution

We can now relate this to the internal energy :

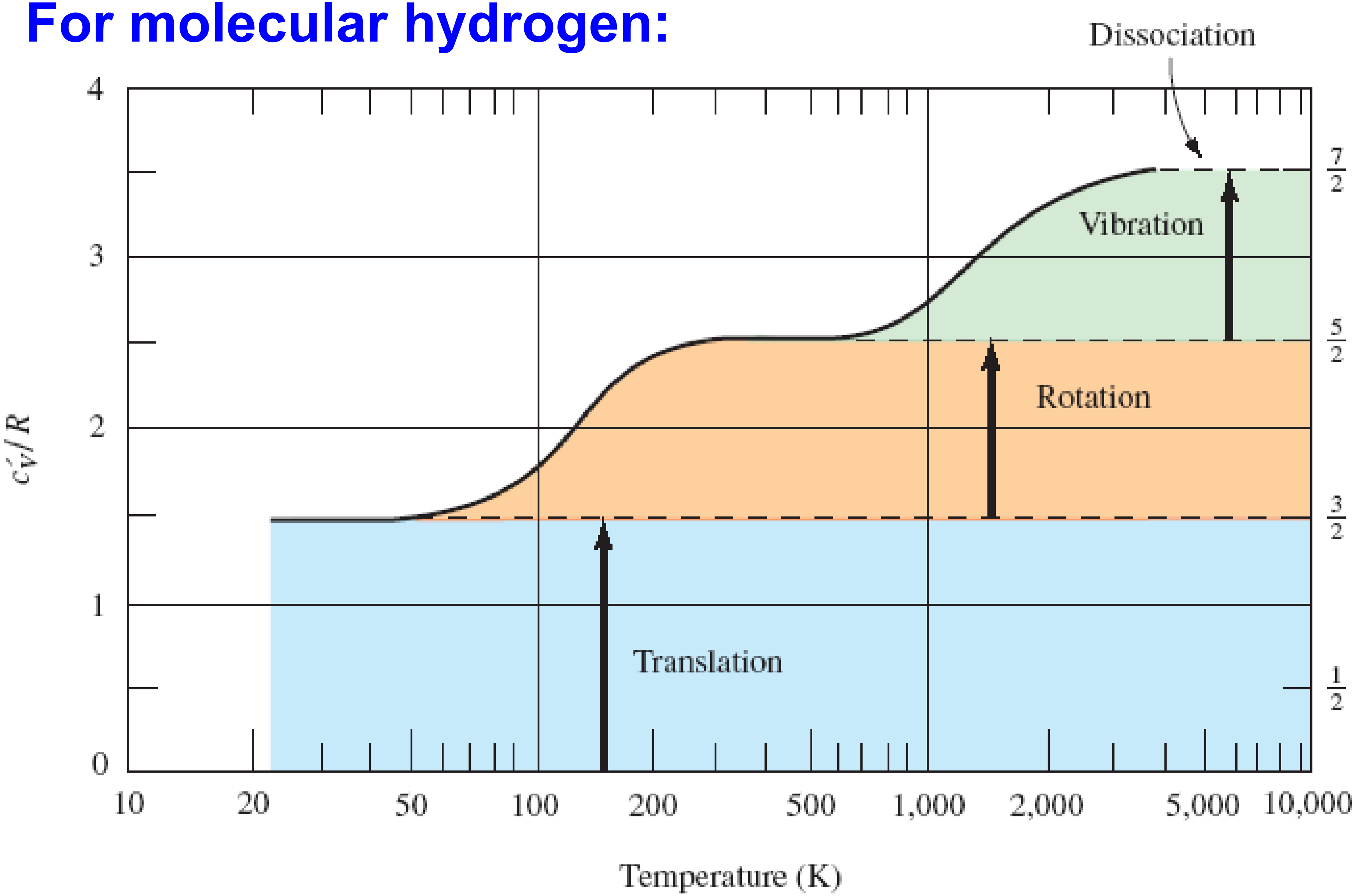
$$U = N\langle E\rangle = \frac{s}{2}NkT \qquad (19\text{-}41)$$

The constant multiplying the temperature is the constant-volume heat capacity of the gas:

$$C_V = \frac{s}{2}nR \qquad (19\text{-}42)$$

19-6 The Maxwell-Boltzmann Distribution

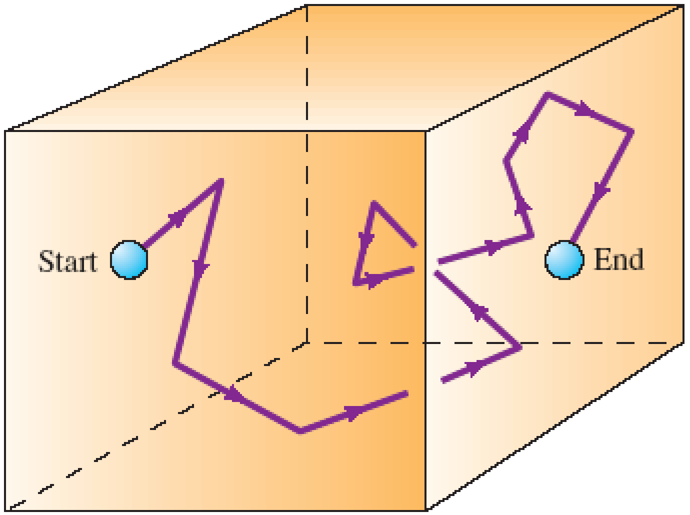
For molecular hydrogen:



19-7 Collisions and Transport Phenomena

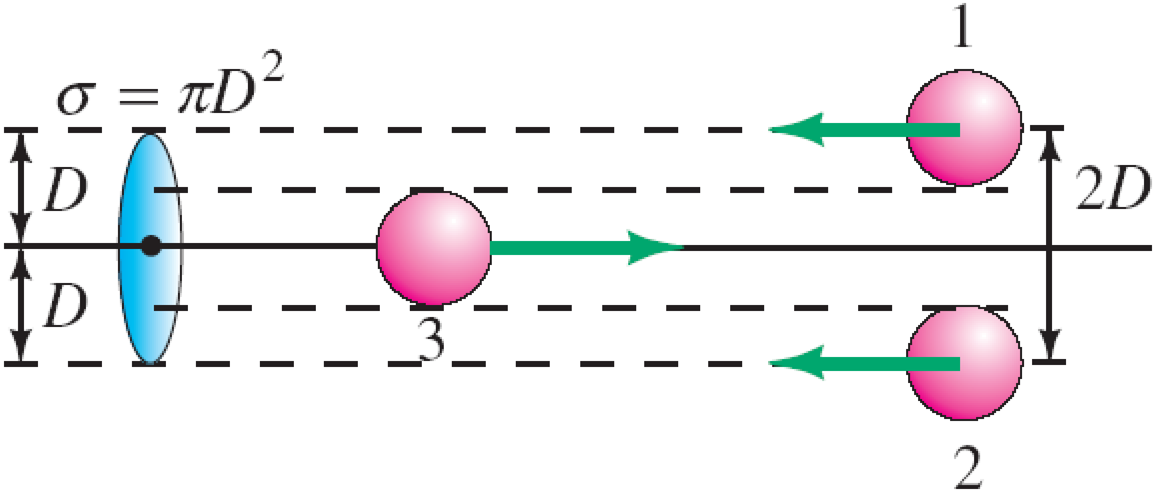
Molecules in ideal gases have many collisions per second – billions in the case of air at STP – but between collisions the molecules interact very little.

Therefore, the average distance the molecule travels between collisions, called the mean free path, can be calculated.



19-7 Collisions and Transport Phenomena

Molecules will collide when they overlap:



Here, σ is called the collision cross section.

A second collision will take place, on the average, after a mean collision time during which the molecule has traveled an average distance of the mean free path.

19-7 Collisions and Transport Phenomena

The collision time and mean free path are found to be:

$$\tau = \frac{1}{\sqrt{2}n\sigma v_{\mathrm{rms}}} \qquad (19\text{-}45)$$

$$\lambda = \tau v_{\mathrm{rms}} = \frac{1}{\sqrt{2}n\sigma} \qquad (19\text{-}46)$$

Chapter 20

The Second Law of Thermodynamics

Main Points of Chapter 20

- Second law of thermodynamics
- Engines and refrigerators
- Carnot cycle
- Other types of engines
- Entropy

20-1 Beyond Energy Conservation

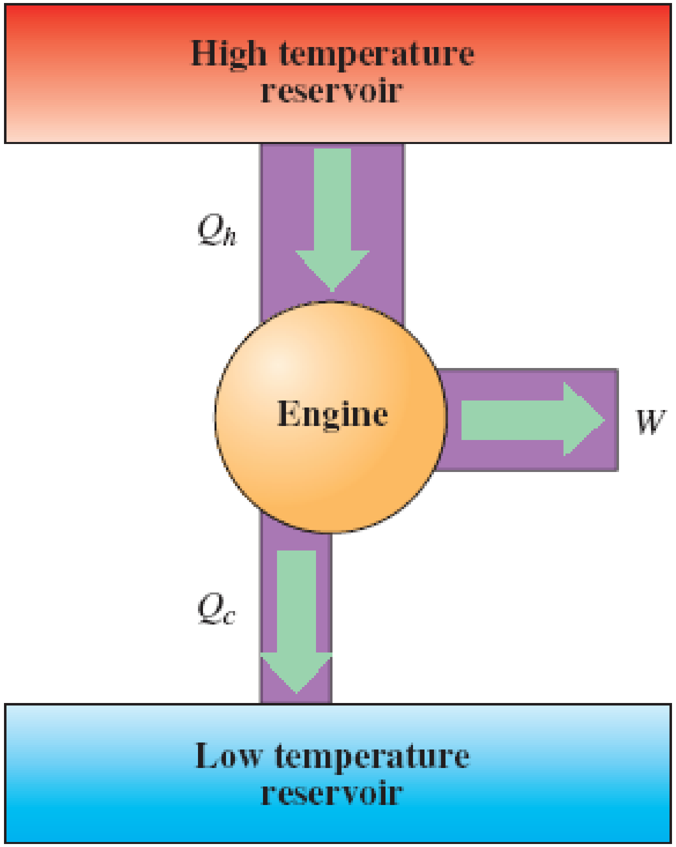
There are processes that do not occur spontaneously even though energy would be conserved, such as a lukewarm drink forming ice cubes and becoming hot.

The second law of thermodynamics is formulated to account for the absence of such processes:

1. Thermal energy cannot be entirely converted to work.
2. Spontaneous heat flow always goes from the higher-temperature body to the lower-temperature one.

20-1 Beyond Energy Conservation

- An engine is a device that cyclically transforms thermal energy into mechanical energy.



1. An engine must work in cycles if it is to be useful – otherwise, when one cycle does work the engine stops.
2. A cyclic engine must include more than one thermal reservoir.

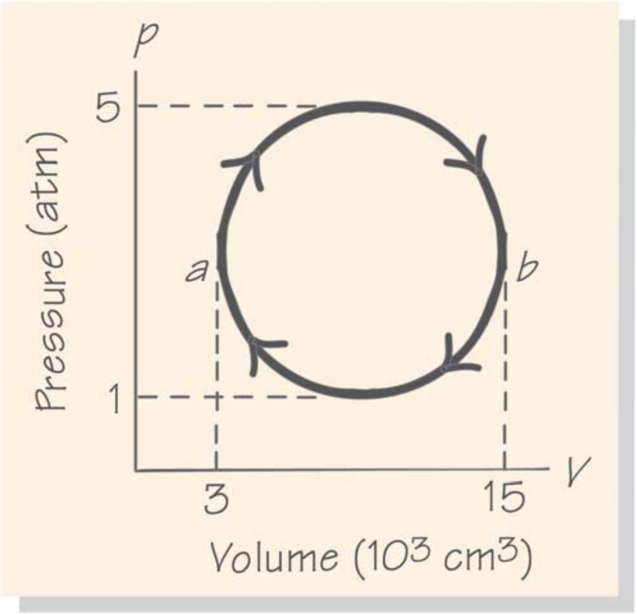
20-1 Beyond Energy Conservation: Efficiency

Every engine has an efficiency, which is a measure of what fraction of the heat flow becomes mechanical work:

$$\eta \equiv \frac{W}{Q_h} \qquad (20\text{-}1)$$

since $\Delta U=0$ and $W=Q_h-Q_c$

Machine based on cycle



20-1 Beyond Energy Conservation: Efficiency

Spontaneous processes: compressed gas in a bottle will expand when bottle is opened, but won’t spontaneously go back in – why not?

Answer: the fraction of all possible distributions that has the gas back in the bottle is impossibly small

20-2 The Second Law of Thermodynamics

There are many ways of expressing the second law of thermodynamics; here are two:

The Kelvin form: It is impossible to construct a cyclic engine that converts thermal energy from a body into an equivalent amount of mechanical work
without a further change in its surroundings.

The Clausius form: It is impossible to construct a cyclic engine whose only effect is to transfer thermal energy from a colder body to a hotter body.

20-3 The Carnot Cycle

Carnot French Engineer 1824

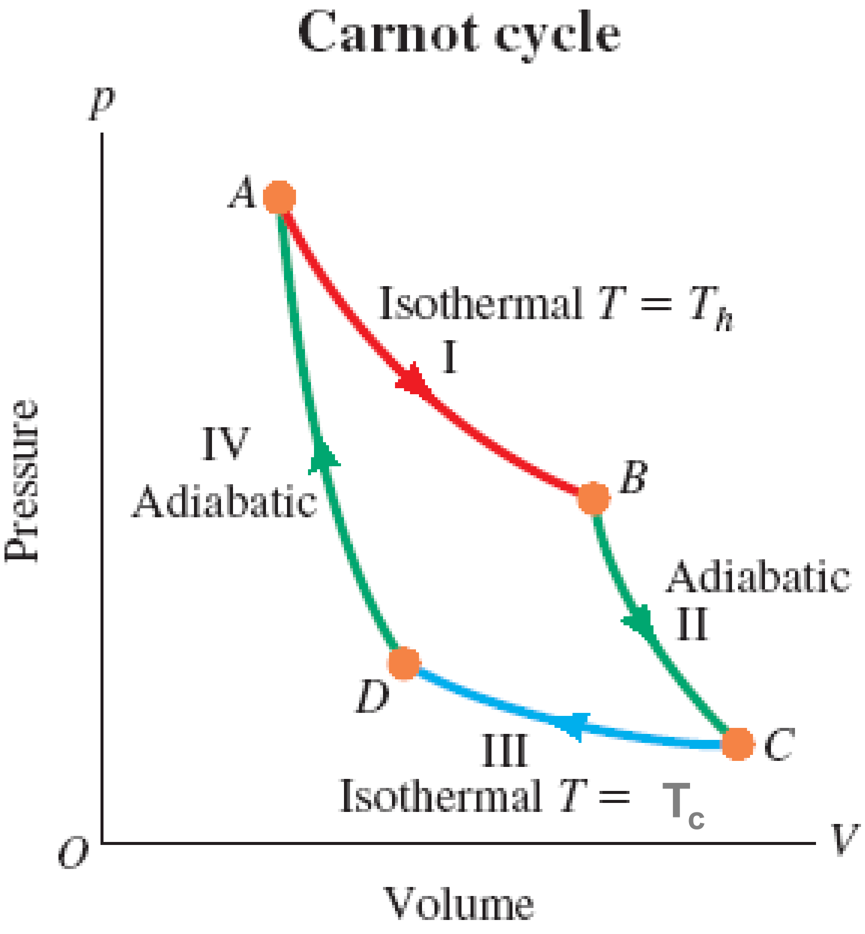
A minimal version of an engine has two reservoirs at different temperatures T_h and T_c, and follows a reversible cycle known as the Carnot cycle.

The Carnot cycle has four steps:

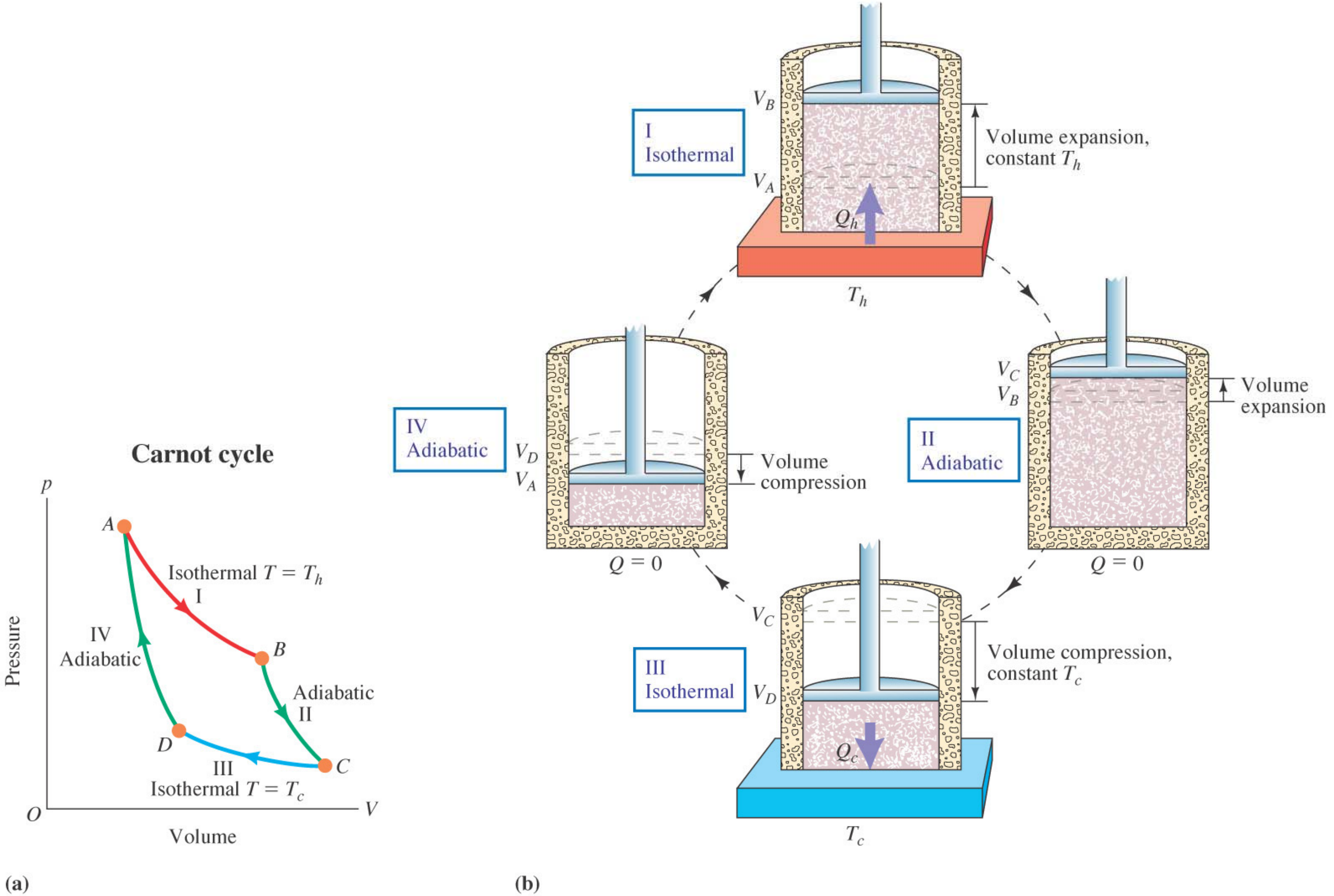
1. **Isothermal expansion**
2. **Adiabatic expansion**
3. **Isothermal compression**
4. **Adiabatic compression**

20-3 The Carnot Cycle

The work done during the Carnot cycle is the area enclosed by the curve in the *p*-*V* diagram:



20-3 The Carnot Cycle



20-3 The Carnot Cycle

Efficiency

The efficiency of the Carnot cycle, defined as

$$\eta_C = W/Q_h$$

is

$$\eta_C = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \qquad (20\text{-}3)$$

Through analysis, this can be related to the reservoir temperatures:

$$\eta_C = 1 - \frac{T_c}{T_h} \qquad (20\text{-}4)$$

20-3 The Carnot Cycle

The Importance of the Carnot Engine

1. All Carnot cycles that operate between the same two temperatures have the same efficiency.

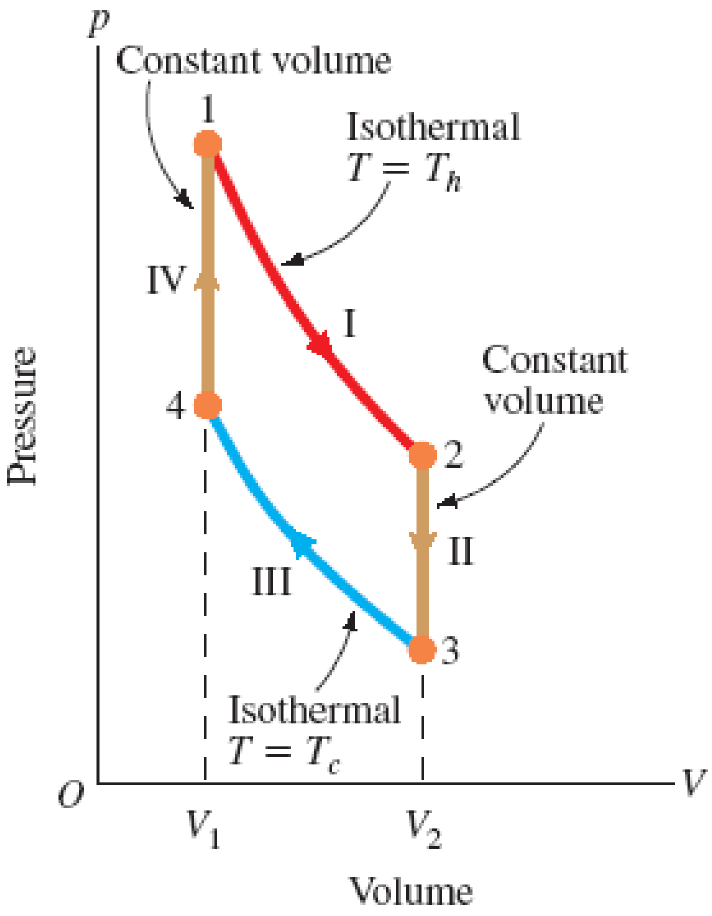
2. The Carnot engine is the most efficient engine possible that operates between any two given temperatures.

20-4 Other Types of Engines

The Stirling Engine

The Stirling cycle is also reversible:

1. Isothermal expansion
2. Cooling at constant volume
3. Isothermal compression
4. Heating at constant volume



20-4 Other Types of Engines

The efficiency of the Stirling cycle is less than that of the Carnot engine, as more heat is required in steps 2 and 4.

The efficiency can be shown to be:

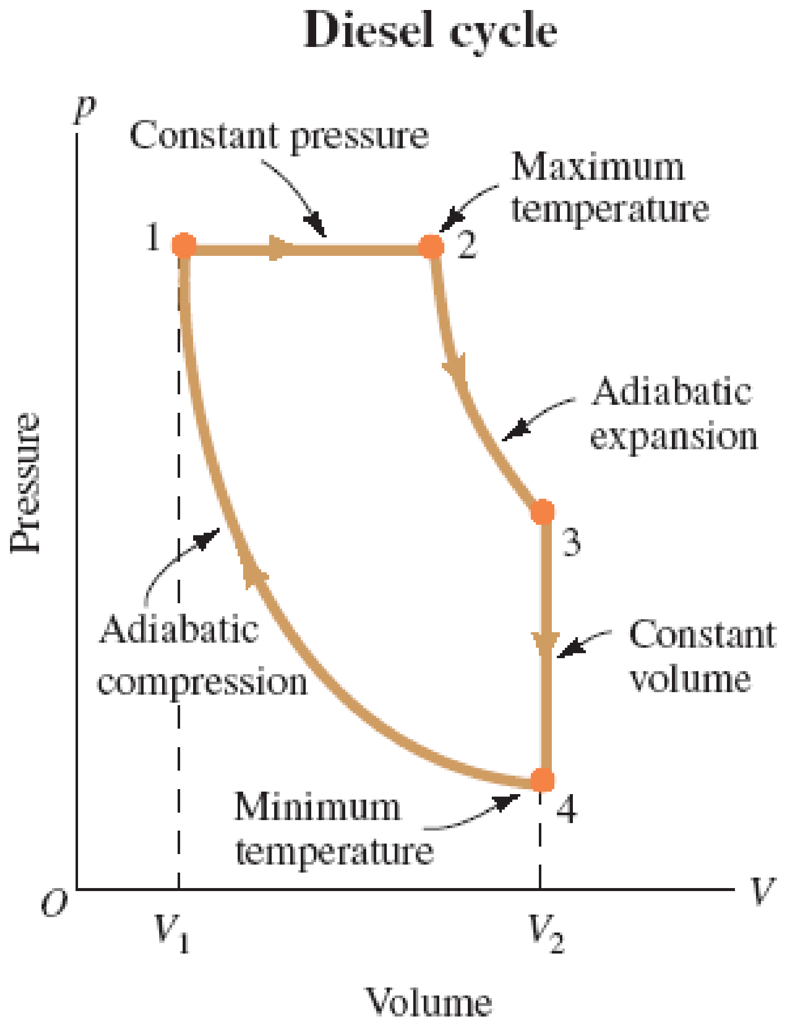
$$\eta_S = \frac{R(T_h - T_c)\ln(V_2/V_1)}{RT_h \ln(V_2/V_1) + C_V(T_h - T_c)} \qquad (20\text{-}8)$$

$W=W_1+W_2=R\ T_h\ \ln(V_2/V_1)+R\ T_c\ \ln(V_1/V_2)$
i.e. $W=R(T_h-T_c)\ln(V_2/V_1)$
And $Q_{pos}=Q_I+Q_{IV}=R\ T_h\ \ln(V_2/V_1) + C_V(T_h-T_c)$

$\eta_s=W/Q_{pos}$

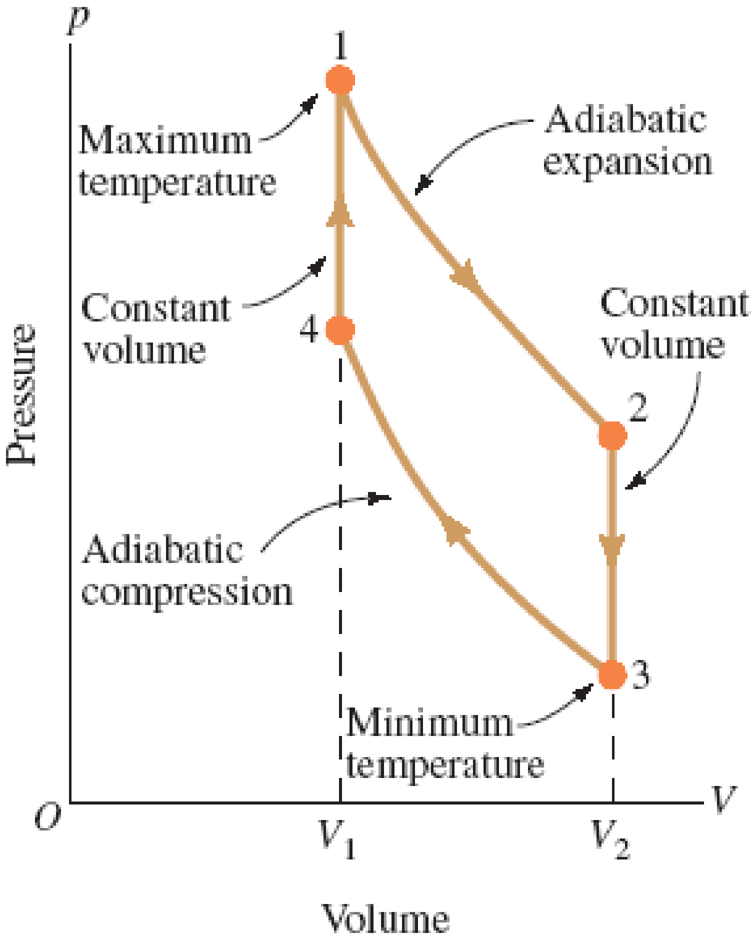
20-4 Other Types of Engines

There are other possible cycles; here are a few:

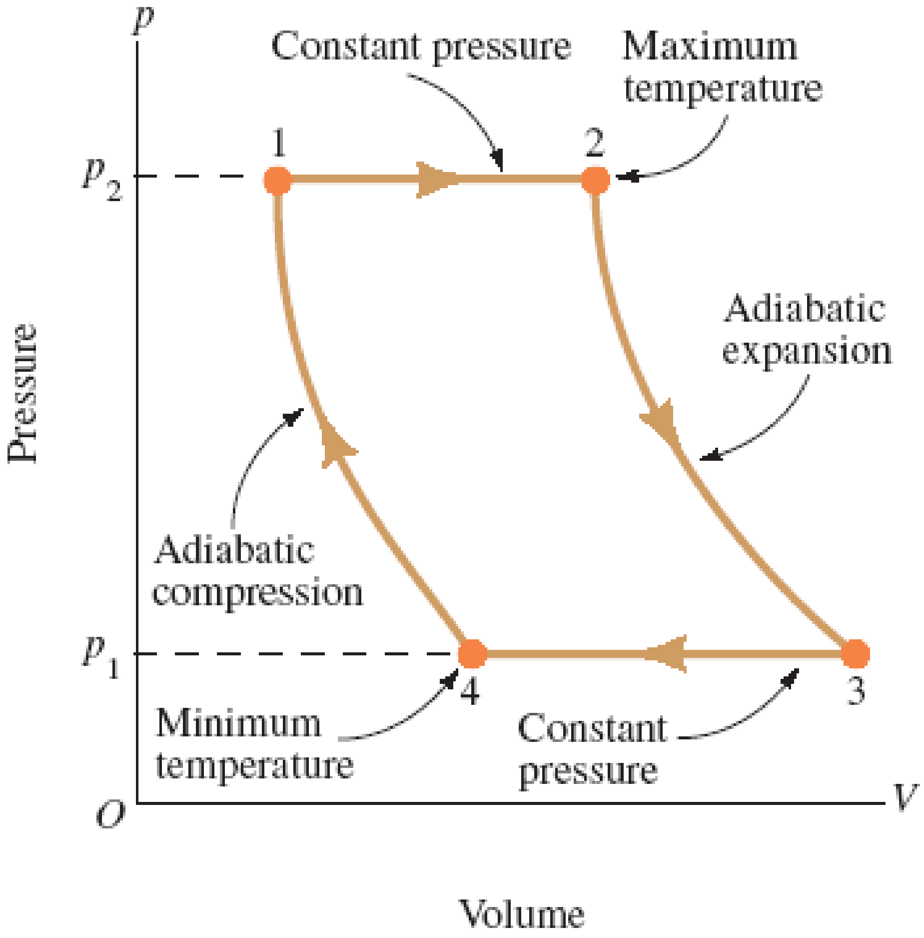


20-4 Other Types of Engines

Otto cycle



Brayton cycle



20-4 Other Types of Engines

Heat Pumps and Refrigerators

Heat pumps and refrigerators are engines run in reverse:

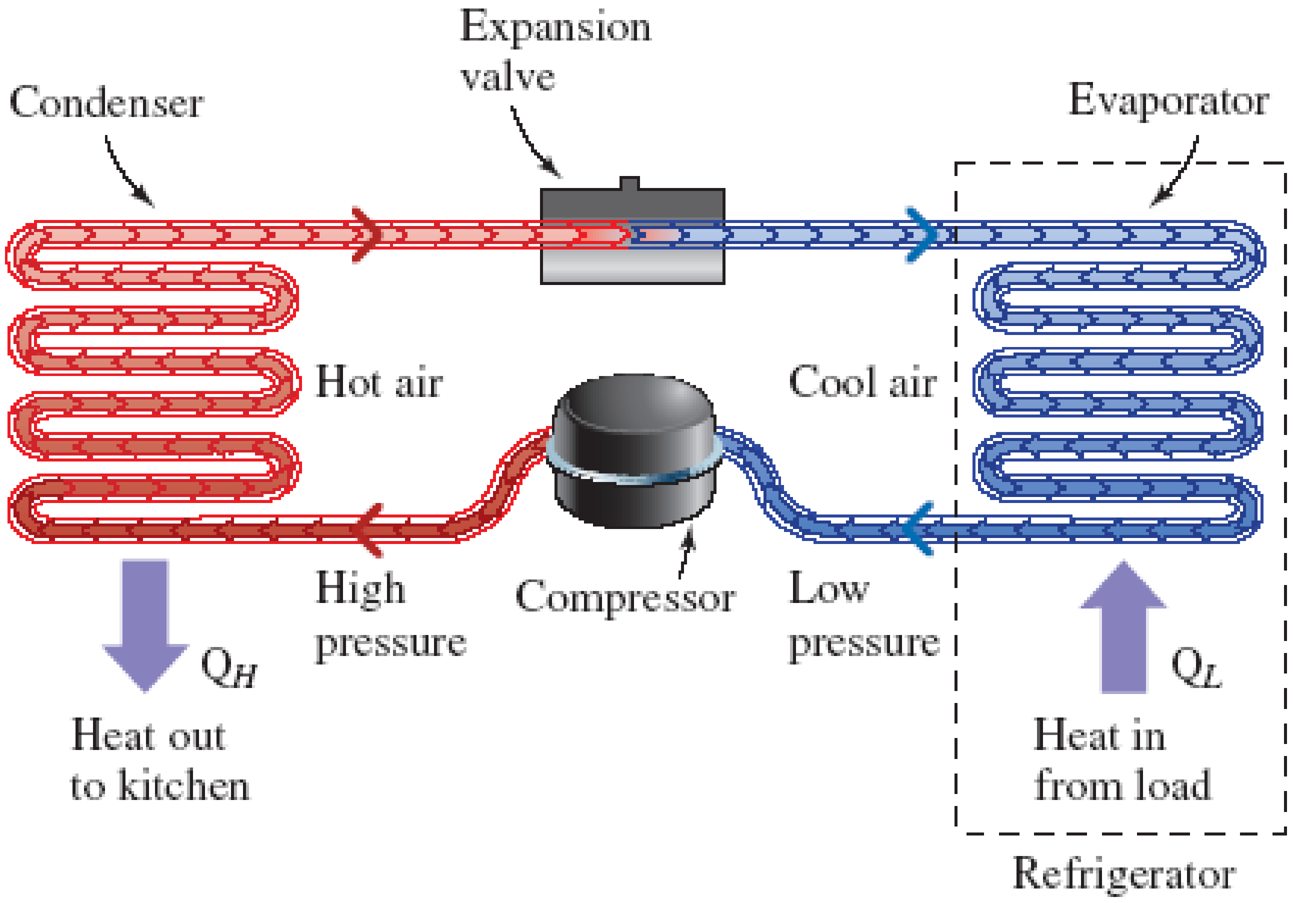
Refrigerator removes heat from cold reservoir, puts it into surroundings, keeping food in reservoir cold.

Heat pump takes energy from cold reservoir and puts it into a room or house, thereby warming it.

In either case, energy must be added!

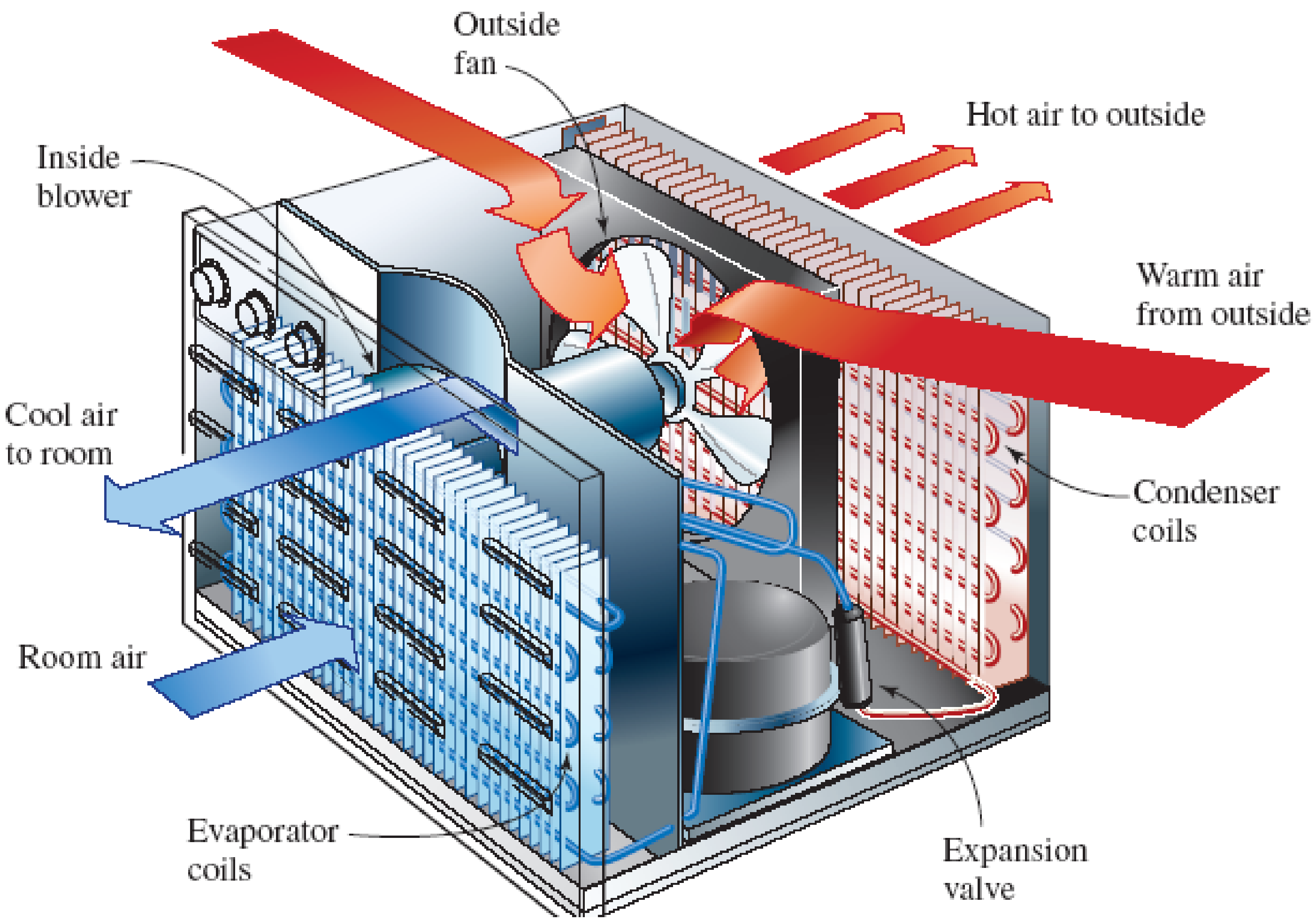
20-4 Other Types of Engines

Schematic diagram of a refrigerator:



20-4 Other Types of Engines

Diagram of a room air conditioner:



20-5 Entropy and the Second Law

Entropy is a measure of disorder, and of the energy unavailable to do work.

In the Carnot cycle:

$$\frac{-Q_c}{T_c} + \frac{Q_h}{T_h} = 0 \qquad (20\text{-}13)$$

Generalizing to multiple reservoirs:

$$\sum_i \frac{Q_i}{T_i} = 0 \qquad (20\text{-}14)$$

20-5 Entropy and the Second Law

Now, look at the integral $\int_A^B \frac{dQ}{T}$ between points *A* and *B*:

$$\int_A^B \frac{dQ}{T} = \int_A^B \frac{dU + pdV}{T} = \int_A^B \frac{C_V\,dT}{T} + \int_A^B R\frac{dV}{V}$$
$$= (C_V \ln T_B + R \ln V_B) - (C_V \ln T_A + R \ln V_A). \tag{20-15}$$

This integral depends only on the initial and final states, and not on the path

20-5 Entropy and the Second Law

There must be a function *S* that depends only on the state of the gas and not on how it got that way; this is called entropy.

Definition of Entropy:

$$S(B) - S(A) = \int_A^B \frac{dQ}{T} \qquad (20\text{-}16)$$

For a reversible cycle:

$$\oint \frac{dQ}{T} = 0 \qquad (20\text{-}17)$$

20-5 Entropy and the Second Law

For an irreversible cycle, there is less work done for the same amount of absorbed heat; therefore the entropy increases through the cycle:

$$\oint \frac{dQ}{T} < 0. \qquad (20\text{-}19)$$

20-5 Entropy and the Second Law

The entropy of an isolated system never decreases; spontaneous (irreversible) processes always increase entropy.

20-6 Entropy and Ideal Gases

The general form of the entropy, equation 20-15, can be generalized to *n* moles of an ideal gas:

$$S(B) - S(A) = C_V \ln \frac{T_B}{T_A} + nR \ln \frac{V_B}{V_A} \qquad (20\text{-}22)$$

20-6 Entropy and Ideal Gases

As a reminder:

$$\int_A^B \frac{dQ}{T} = \int_A^B \frac{dU + pdV}{T} = \int_A^B \frac{C_V\, dT}{T} + \int_A^B R\frac{dV}{V}$$
$$= (C_V \ln T_B + R \ln V_B) - (C_V \ln T_A + R \ln V_A).$$

(20-15)

20-6 The Meaning of Entropy

All the consequences of the second law of thermodynamics follow from the treatment of entropy as a measure of disorder.

20-6 The Meaning of Entropy

Making engines that would convert mechanical energy entirely to work would require entropy to decrease in isolated system – can’t happen.

20-6 The Meaning of Entropy

Many familiar processes increase entropy – shuffling cards, breaking eggs, and so on.

We never see these processes spontaneously happening in reverse – a movie played backwards looks silly. This directionality is referred to as the arrow of time.