Chapter 19

Heat and the First Law of Thermodynamics

Units of Chapter 19

- **Heat as Energy Transfer**
- **Internal Energy**
- **Specific Heat**
- **Calorimetry—Solving Problems**
- **Latent Heat**
- **The First Law of Thermodynamics**
- **The First Law of Thermodynamics Applied; Calculating the Work**

Units of Chapter 19

- **Molar Specific Heats for Gases, and the Equipartition of Energy**
- **Adiabatic Expansion of a Gas**
- **Heat Transfer: Conduction, Convection, Radiation**

19-1 Heat as Energy Transfer

We often speak of **heat** as though it were a **material** that flows from one object to another; it is not. Rather, it is a form of **energy**.

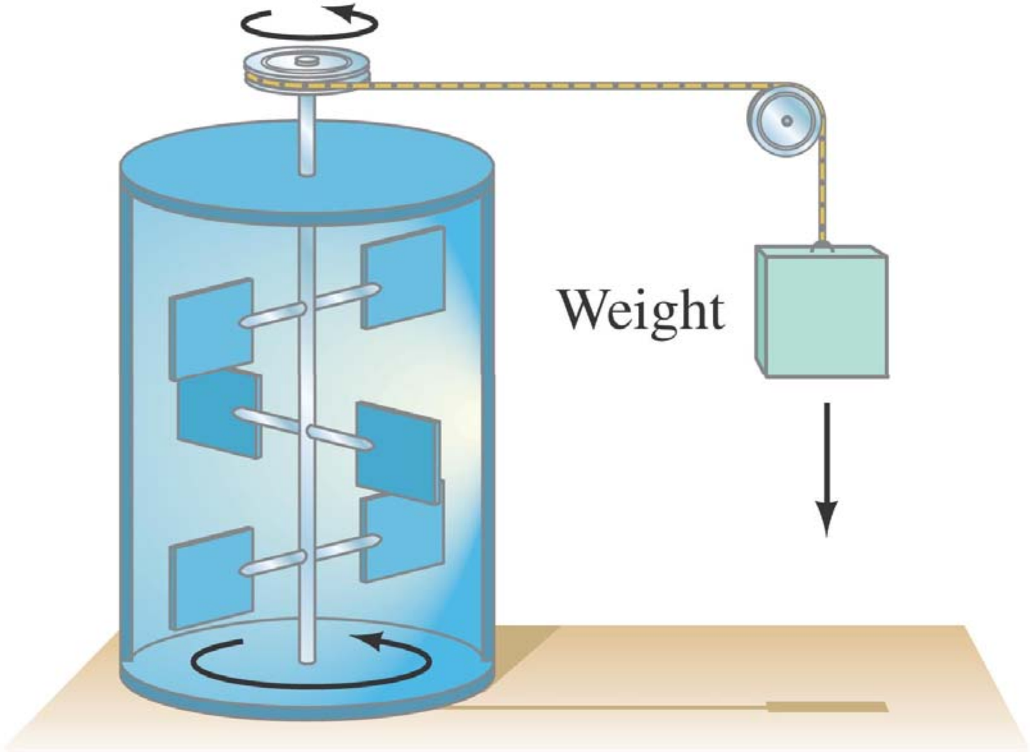
Unit of heat: **calorie** (cal)

1 **cal** is the amount of **heat** necessary to raise the **temperature** of 1 g of water by **1 Celsius degree**.

Don't be fooled—the calories on our food labels are really **kilocalories** (kcal or Calories), the heat necessary to raise 1 kg of water by 1 Celsius degree.

19-1 Heat as Energy Transfer

If **heat** is a form of **energy**, it ought to be possible to equate it to other forms. The experiment below found the **mechanical equivalent of heat** by using the falling weight to heat the water:



4.186 J = 1 cal

4.186 kJ = 1 kcal

19-1 Heat as Energy Transfer

Definition of **heat**:

Heat is energy transferred from one object to another because of a difference in temperature.

- **Remember that the temperature of a gas is a measure of the kinetic energy of its molecules.**

19-1 Heat as Energy Transfer

Example 19-1: Working off the extra calories.

Suppose you throw caution to the wind and eat too much ice cream and cake on the order of 500 Calories. To compensate, you want to do an equivalent amount of work climbing stairs or a mountain. How much total height must you climb?

19-2 Internal Energy

The **sum total** of all the energy of all the molecules in a substance is its **internal** (or thermal) **energy**.

Temperature: measures molecules’ average **kinetic energy**

Internal energy: **total** energy of all molecules

Heat: **transfer** of energy due to difference in temperature

19-2 Internal Energy

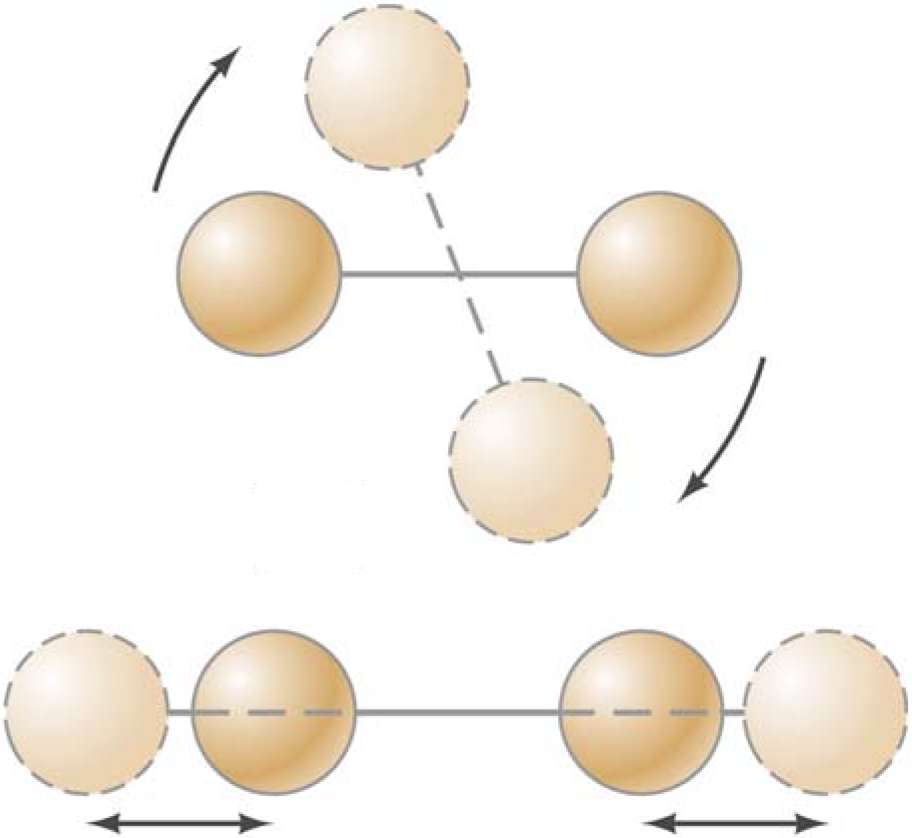
Internal energy of an **ideal** (atomic) gas:

$$E_{\text{int}} = N\left(\tfrac{1}{2}m\overline{v^2}\right).$$

But since we know the average kinetic energy in terms of the temperature, we can write:

$$E_{\text{int}} = \tfrac{3}{2}NkT.$$

19-2 Internal Energy



If the gas is **molecular** rather than **atomic**, **rotational** and **vibrational** kinetic energy need to be taken into account as well.

19-3 Specific Heat

TABLE 19–1 Specific Heats
(at 1 atm constant pressure and 20°C unless otherwise stated)

Substance	Specific Heat, *c* kcal/kg · C° (= cal/g · C°)	 J/kg · C°
Aluminum	0.22	900
Alcohol (ethyl)	0.58	2400
Copper	0.093	390
Glass	0.20	840
Iron or steel	0.11	450
Lead	0.031	130
Marble	0.21	860
Mercury	0.033	140
Silver	0.056	230
Wood	0.4	1700
Water		
Ice (−5°C)	0.50	2100
Liquid (15°C)	1.00	4186
Steam (110°C)	0.48	2010
Human body (average)	0.83	3470
Protein	0.4	1700

The amount of heat required to change the temperature of a material is proportional to the **mass** and to the **temperature change**:

$$Q = mc\,\Delta T.$$

The **specific heat**, c, is characteristic of the material. Some values are listed at left.

19-3 Specific Heat

Example 19-2: How heat transferred depends on specific heat.

(a) How much heat input is needed to raise the temperature of an empty 20-kg vat made of iron from 10°C to 90°C?

(b) What if the vat is filled with 20 kg of water?

19-4 Calorimetry—Solving Problems

Closed system: **no mass** enters or leaves, but energy may be exchanged

Open system: mass may transfer as well

Isolated system: closed system in which **no energy** in any form is transferred

For an isolated system,

energy out of one part = energy into another part,

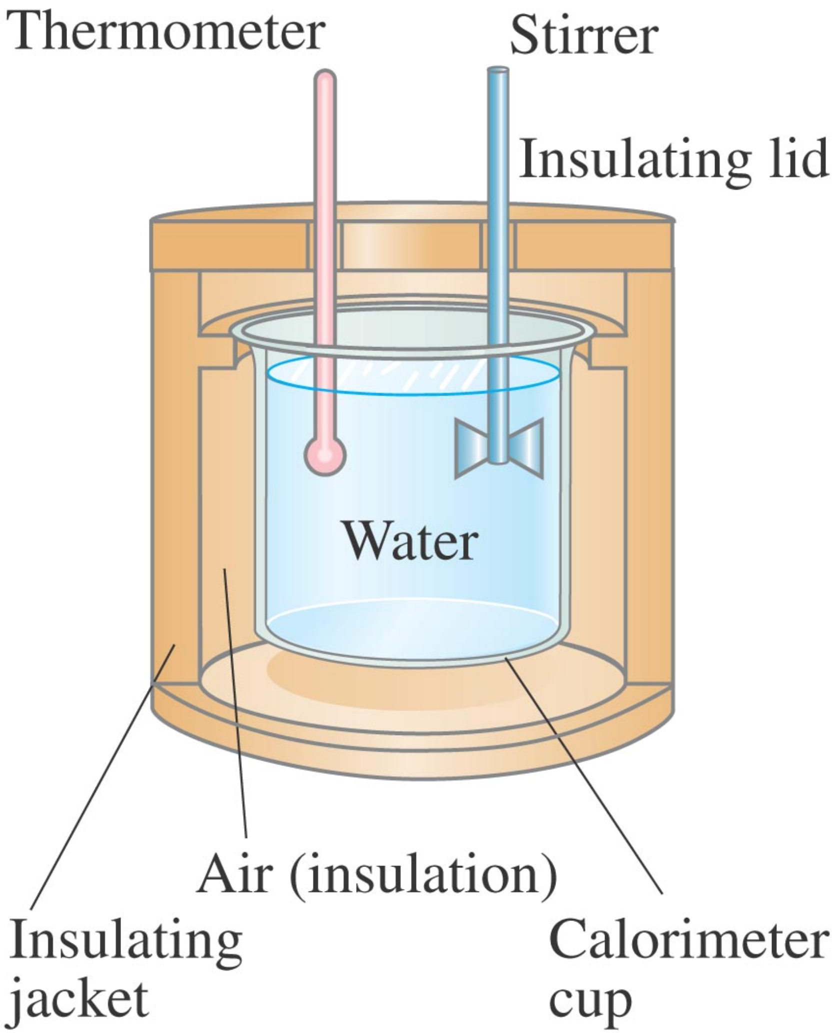
or: heat lost = heat gained.

19-4 Calorimetry—Solving Problems

Example 19-3: The cup cools the tea.

If 200 cm^3 of tea at 95°C is poured into a 150-g glass cup initially at 25°C, what will be the common final temperature *T* of the tea and cup when equilibrium is reached, assuming no heat flows to the surroundings?

19-4 Calorimetry—Solving Problems



The instrument to the left is a **calorimeter**, which makes **quantitative** measurements of heat exchange. A sample is heated to a well-measured high temperature and plunged into the water, and the **equilibrium** temperature is measured. This gives the **specific heat** of the sample.

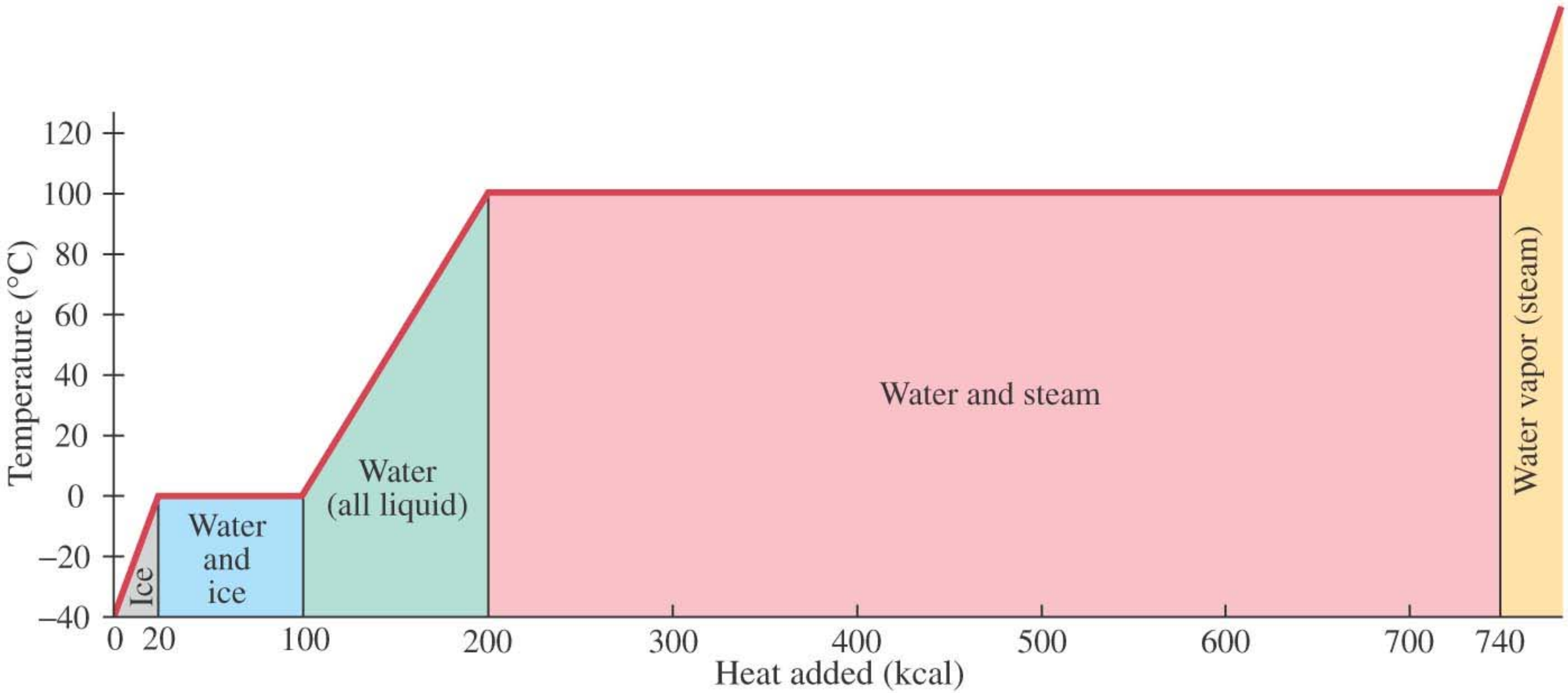
19-4 Calorimetry—Solving Problems

Example 19-4: Unknown specific heat determined by calorimetry.

An engineer wishes to determine the specific heat of a new metal alloy. A 0.150-kg sample of the alloy is heated to 540°C. It is then quickly placed in 0.400 kg of water at 10.0°C, which is contained in a 0.200-kg aluminum calorimeter cup. (We do not need to know the mass of the insulating jacket since we assume the air space between it and the cup insulates it well, so that its temperature does not change significantly.) The final temperature of the system is 30.5°C. Calculate the specific heat of the alloy.

19-5 Latent Heat

Energy is required for a material to change phase, even though its temperature is not changing.



19-5 Latent Heat

Heat of **fusion**, L_F: heat required to change 1.0 kg of material from solid to liquid

Heat of **vaporization**, L_V: heat required to change 1.0 kg of material from liquid to vapor

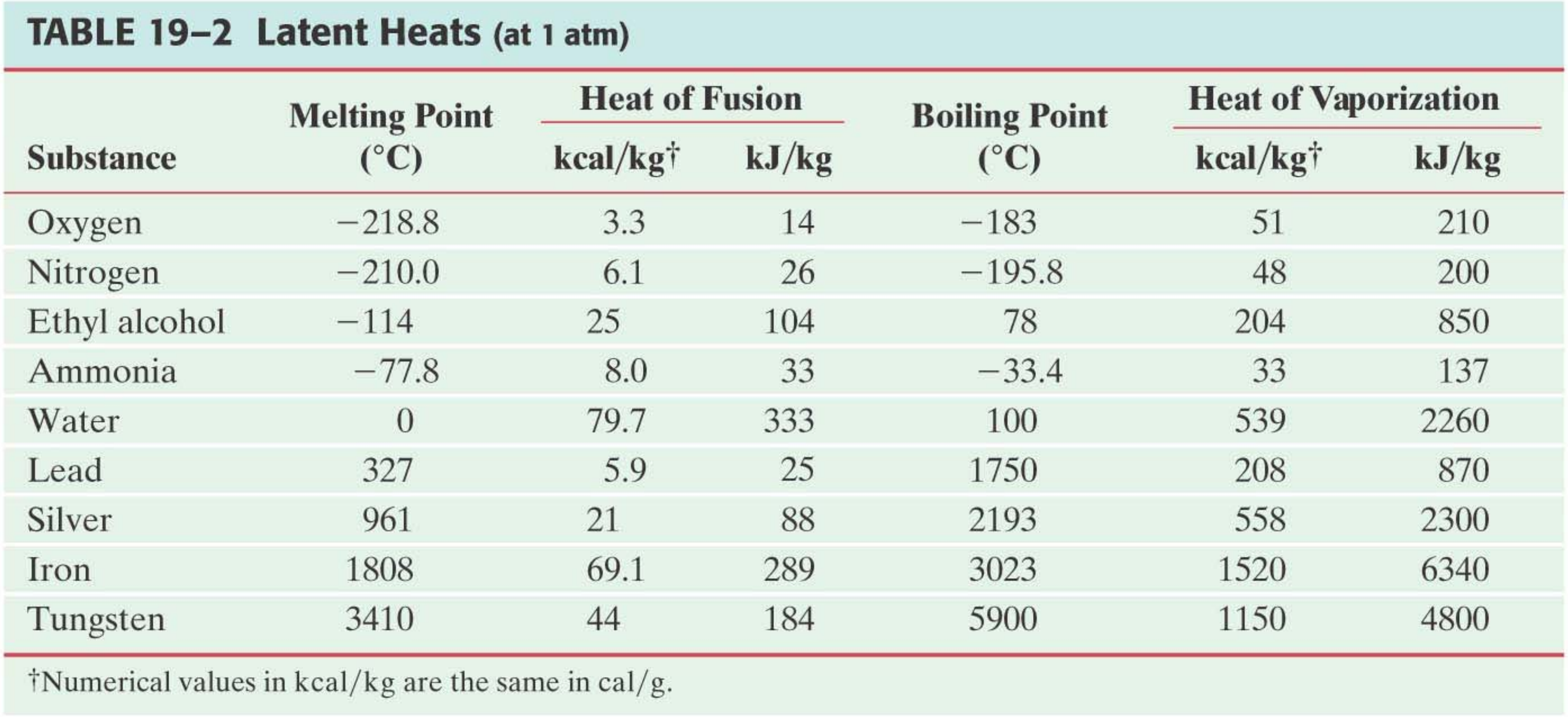


TABLE 19–2 Latent Heats (at 1 atm)

Substance	Melting Point (°C)	Heat of Fusion		Boiling Point (°C)	Heat of Vaporization	
		kcal/kg†	kJ/kg		kcal/kg†	kJ/kg
Oxygen	−218.8	3.3	14	−183	51	210
Nitrogen	−210.0	6.1	26	−195.8	48	200
Ethyl alcohol	−114	25	104	78	204	850
Ammonia	−77.8	8.0	33	−33.4	33	137
Water	0	79.7	333	100	539	2260
Lead	327	5.9	25	1750	208	870
Silver	961	21	88	2193	558	2300
Iron	1808	69.1	289	3023	1520	6340
Tungsten	3410	44	184	5900	1150	4800

†Numerical values in kcal/kg are the same in cal/g.

19-5 Latent Heat

The **total** heat required for a phase change depends on the total **mass** and the **latent heat**:

$$Q = mL.$$

Example 19-5: Will all the ice melt?

A 0.50-kg chunk of ice at -10°C is placed in 3.0 kg of "iced" tea at 20°C. At what temperature and in what phase will the final mixture be? The tea can be considered as water. Ignore any heat flow to the surroundings, including the container.

19-5 Latent Heat

Problem Solving: Calorimetry

1. Is the system isolated? Are all significant sources of energy transfer known or calculable?
2. Apply conservation of energy.
3. If no phase changes occur, the heat transferred will depend on the mass, specific heat, and temperature change.

(continued)

19-5 Latent Heat

4. If there are, or may be, phase changes, terms that depend on the mass and the latent heat may also be present. Determine or estimate what phase the final system will be in.

5. Make sure that each term is in the right place and that all the temperature changes are positive.

6. There is only one final temperature when the system reaches equilibrium.

7. Solve.

19-5 Latent Heat

Example 19-6: Determining a latent heat.

The specific heat of liquid mercury is 140 J/kg·°C. When 1.0 kg of solid mercury at its melting point of -39°C is placed in a 0.50-kg aluminum calorimeter filled with 1.2 kg of water at 20.0°C, the mercury melts and the final temperature of the combination is found to be 16.5°C. What is the heat of fusion of mercury in J/kg?

19-5 Latent Heat

The latent heat of vaporization is relevant for evaporation as well as boiling. The heat of vaporization of water rises slightly as the temperature decreases.

On a molecular level, the heat added during a change of state does not go to increasing the kinetic energy of individual molecules, but rather to breaking the close bonds between them so the next phase can occur.

19-6 The First Law of Thermodynamics

The change in internal energy of a closed system will be equal to the energy added to the system minus the work done by the system on its surroundings.

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

This is the law of conservation of energy, written in a form useful to systems involving heat transfer.

19-6 The First Law of Thermodynamics

Example 19-7: Using the first law.

2500 J of heat is added to a system, and 1800 J of work is done on the system. What is the change in internal energy of the system?

19-6 The First Law of Thermodynamics

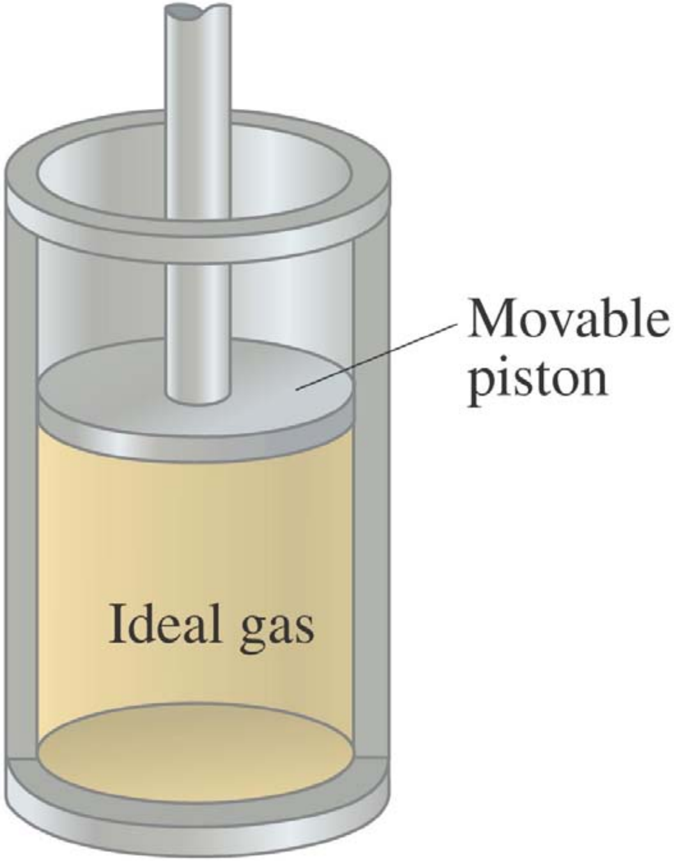
The first law can be extended to include changes in mechanical energy—kinetic energy and potential energy:

$$\Delta K + \Delta U + \Delta E_{\text{int}} = Q - W.$$

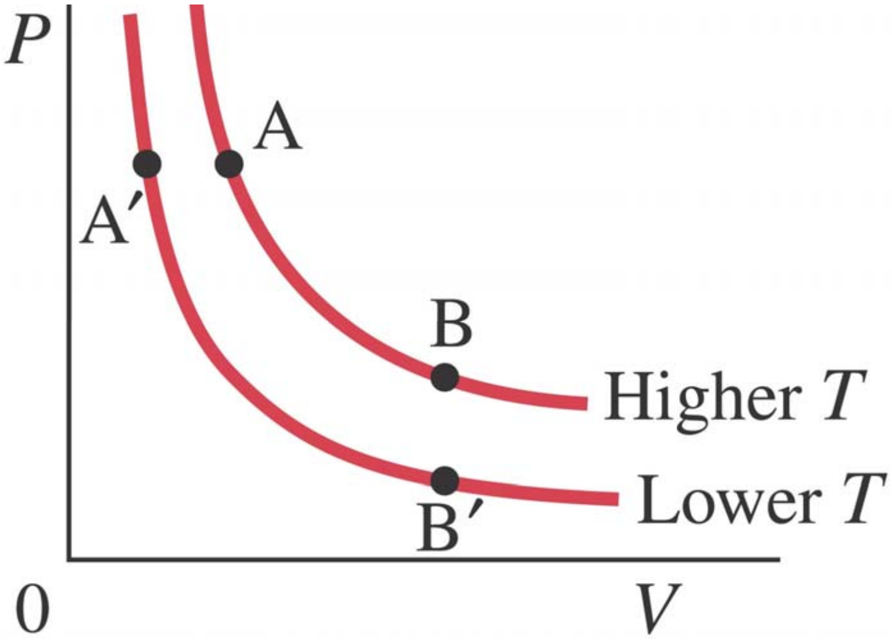
Example 19-8: Kinetic energy transformed to thermal energy.

A 3.0-g bullet traveling at a speed of 400 m/s enters a tree and exits the other side with a speed of 200 m/s. Where did the bullet's lost kinetic energy go, and what was the energy transferred?

19-7 The First Law of Thermodynamics Applied; Calculating the Work



An isothermal process is one in which the temperature does not change.



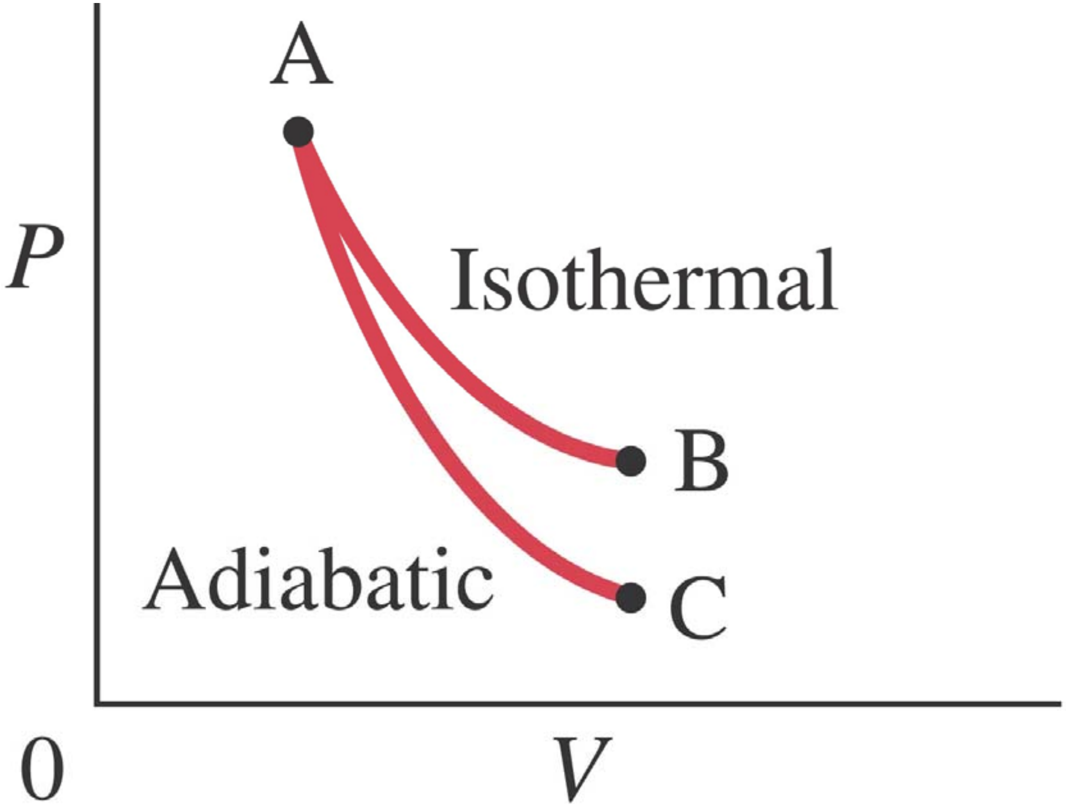
19-7 The First Law of Thermodynamics Applied; Calculating the Work

In order for an isothermal process to take place, we assume the system is in contact with a heat reservoir.

In general, we assume that the system remains in equilibrium throughout all processes.

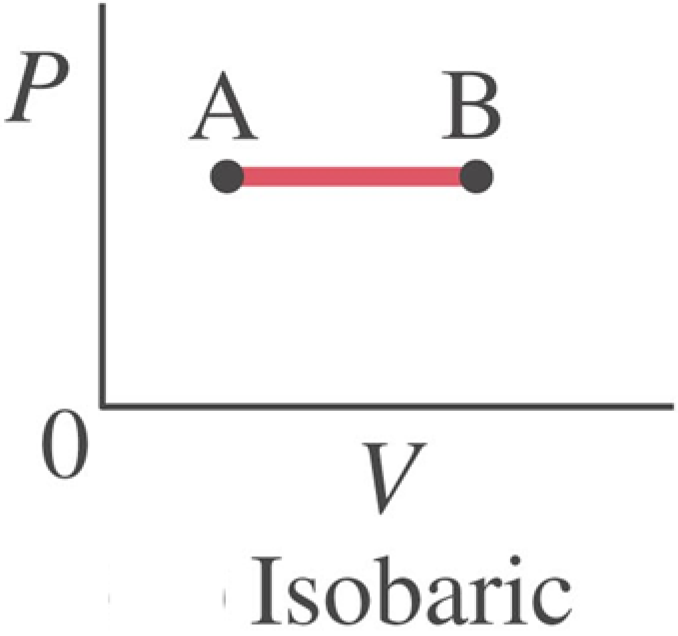
19-7 The First Law of Thermodynamics Applied; Calculating the Work

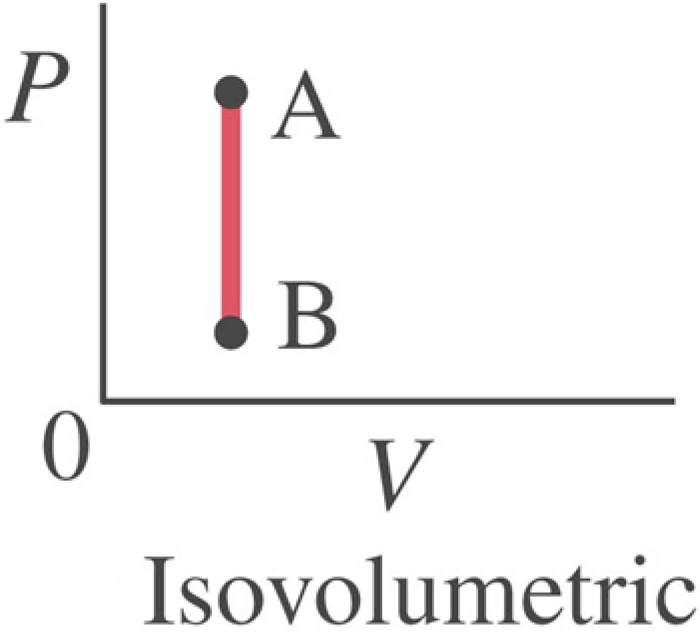
An adiabatic process is one in which there is no heat flow into or out of the system.



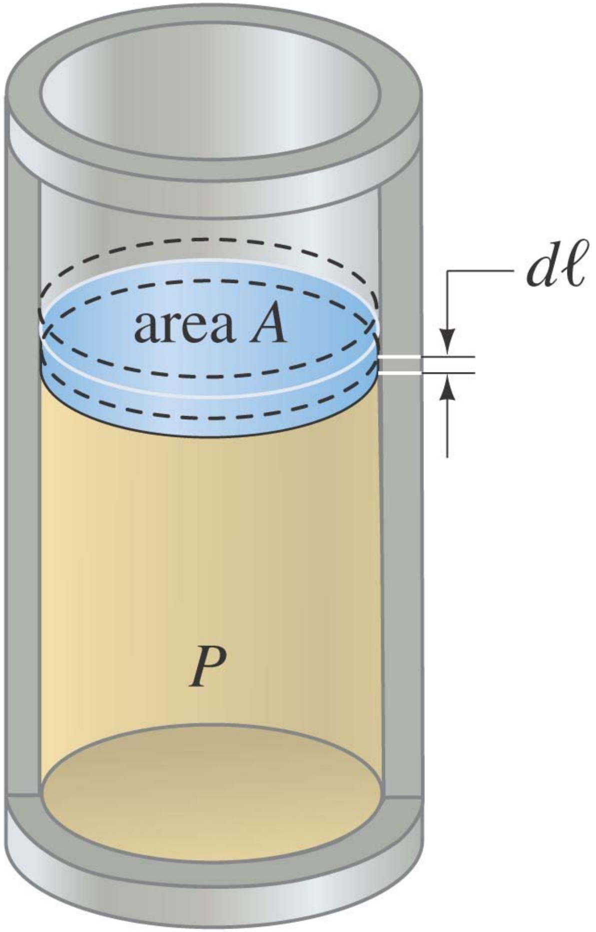
19-7 The First Law of Thermodynamics Applied; Calculating the Work

An isobaric process (a) occurs at constant pressure; an isovolumetric one (b) occurs at constant volume.





19-7 The First Law of Thermodynamics Applied; Calculating the Work



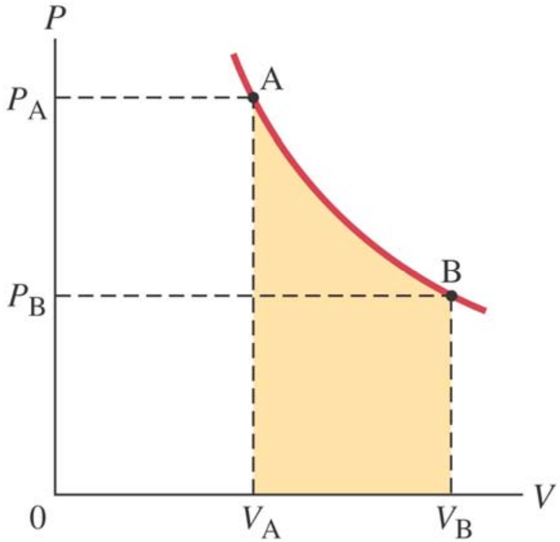
The work done in moving a piston by an infinitesimal displacement is:

$$dW = \vec{\mathbf{F}} \cdot d\vec{\boldsymbol{\ell}} = PA\,d\ell = P\,dV.$$

19-7 The First Law of Thermodynamics Applied; Calculating the Work

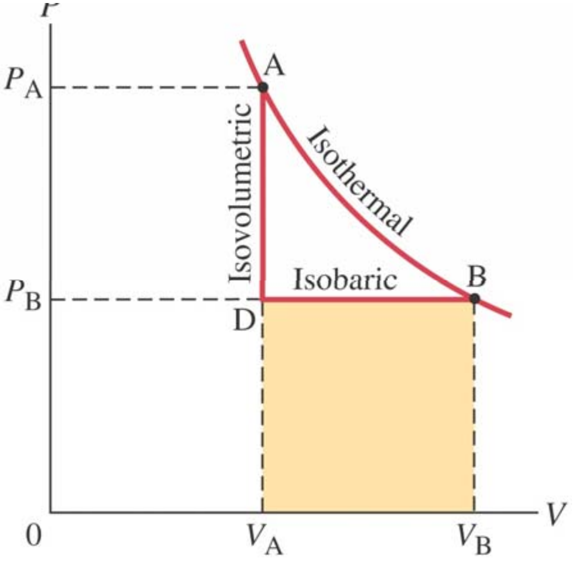
For an isothermal process, $P = nRT/V$. Integrating to find the work done in taking the gas from point A to point B gives:

$$W = \int_{V_A}^{V_B} P\,dV = nRT \int_{V_A}^{V_B} \frac{dV}{V} = nRT \ln \frac{V_B}{V_A}. \qquad \left[\begin{array}{l}\text{isothermal process;}\\ \text{ideal gas}\end{array}\right].$$



19-7 The First Law of Thermodynamics Applied; Calculating the Work

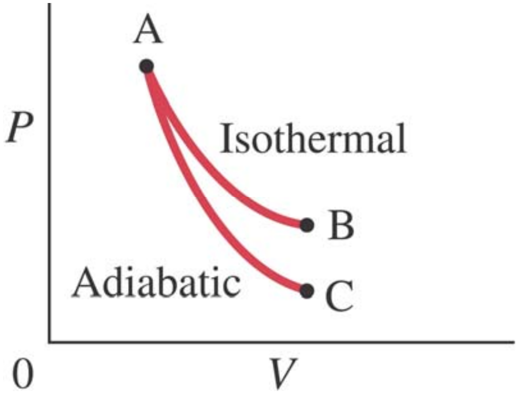
A different path takes the gas first from A to D in an isovolumetric process; because the volume does not change, no work is done. Then the gas goes from D to B at constant pressure; with constant pressure no integration is needed, and $W = P\Delta V$.



19-7 The First Law of Thermodynamics Applied; Calculating the Work

Conceptual Example 19-9: Work in isothermal and adiabatic processes.

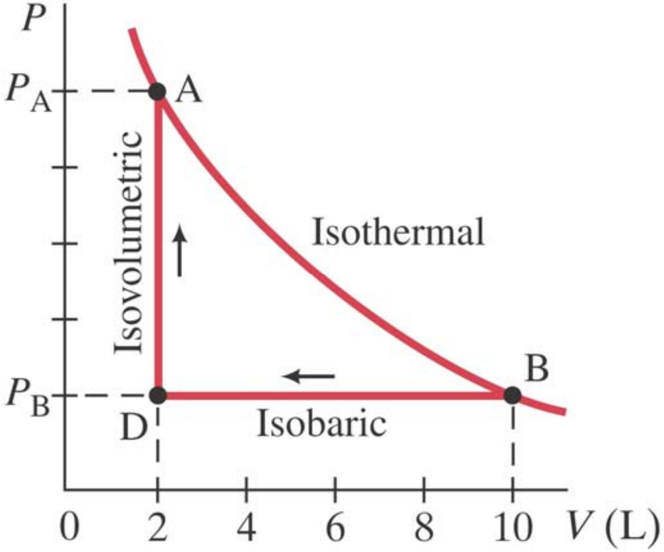
Reproduced here is the PV diagram for a gas expanding in two ways, isothermally and adiabatically. The initial volume V_A was the same in each case, and the final volumes were the same ($V_B = V_C$). In which process was more work done by the gas?



19-7 The First Law of Thermodynamics Applied; Calculating the Work

Example 19-10: First law in isobaric and isovolumetric processes.

An ideal gas is slowly compressed at a constant pressure of 2.0 atm from 10.0 L to 2.0 L. (In this process, some heat flows out of the gas and the temperature drops.) Heat is then added to the gas, holding the volume constant, and the pressure and temperature are allowed to rise (line DA) until the temperature reaches its original value ($T_A = T_B$). Calculate (a) the total work done by the gas in the process BDA, and (b) the total heat flow into the gas.



19-7 The First Law of Thermodynamics Applied; Calculating the Work

Example 19-11: Work done in an engine.

In an engine, 0.25 mol of an ideal monatomic gas in the cylinder expands rapidly and adiabatically against the piston. In the process, the temperature of the gas drops from 1150 K to 400 K. How much work does the gas do?

19-7 The First Law of Thermodynamics Applied; Calculating the Work

The following is a simple summary of the various thermodynamic processes.

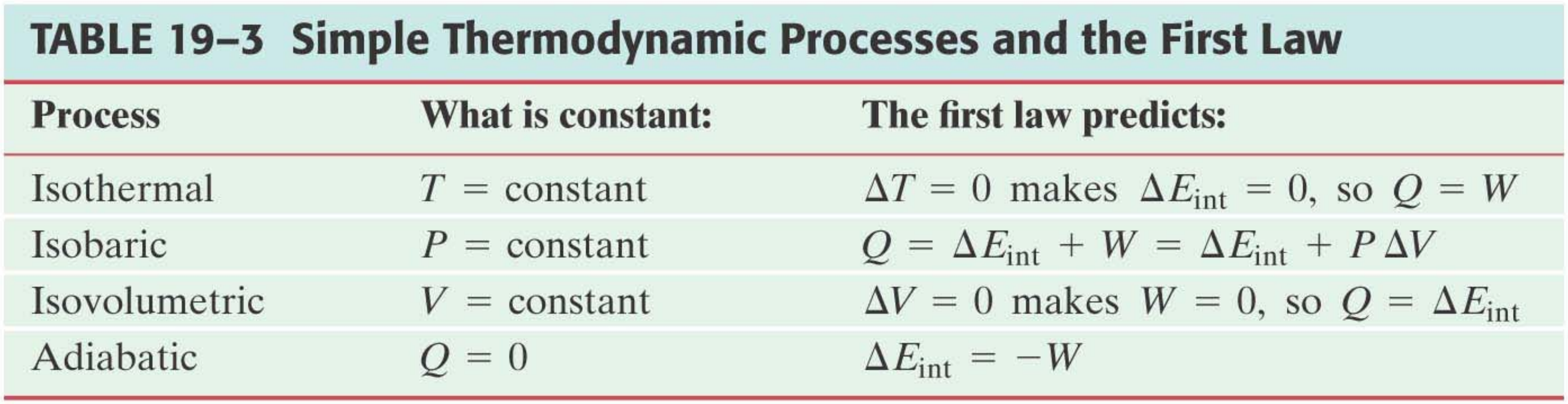


TABLE 19–3 Simple Thermodynamic Processes and the First Law

Process	What is constant:	The first law predicts:
Isothermal	T = constant	$\Delta T = 0$ makes $\Delta E_{\text{int}} = 0$, so $Q = W$
Isobaric	P = constant	$Q = \Delta E_{\text{int}} + W = \Delta E_{\text{int}} + P\,\Delta V$
Isovolumetric	V = constant	$\Delta V = 0$ makes $W = 0$, so $Q = \Delta E_{\text{int}}$
Adiabatic	$Q = 0$	$\Delta E_{\text{int}} = -W$

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For gases, the specific heat depends on the process—the isothermal specific heat is different from the isovolumetric one.

$$Q = nC_V\Delta T$$

$$Q = nC_P\Delta T$$

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

In this table, we see that the specific heats for gases with the same number of molecules are almost the same, and that the difference $C_P - C_V$ is almost exactly equal to 2 in all cases.

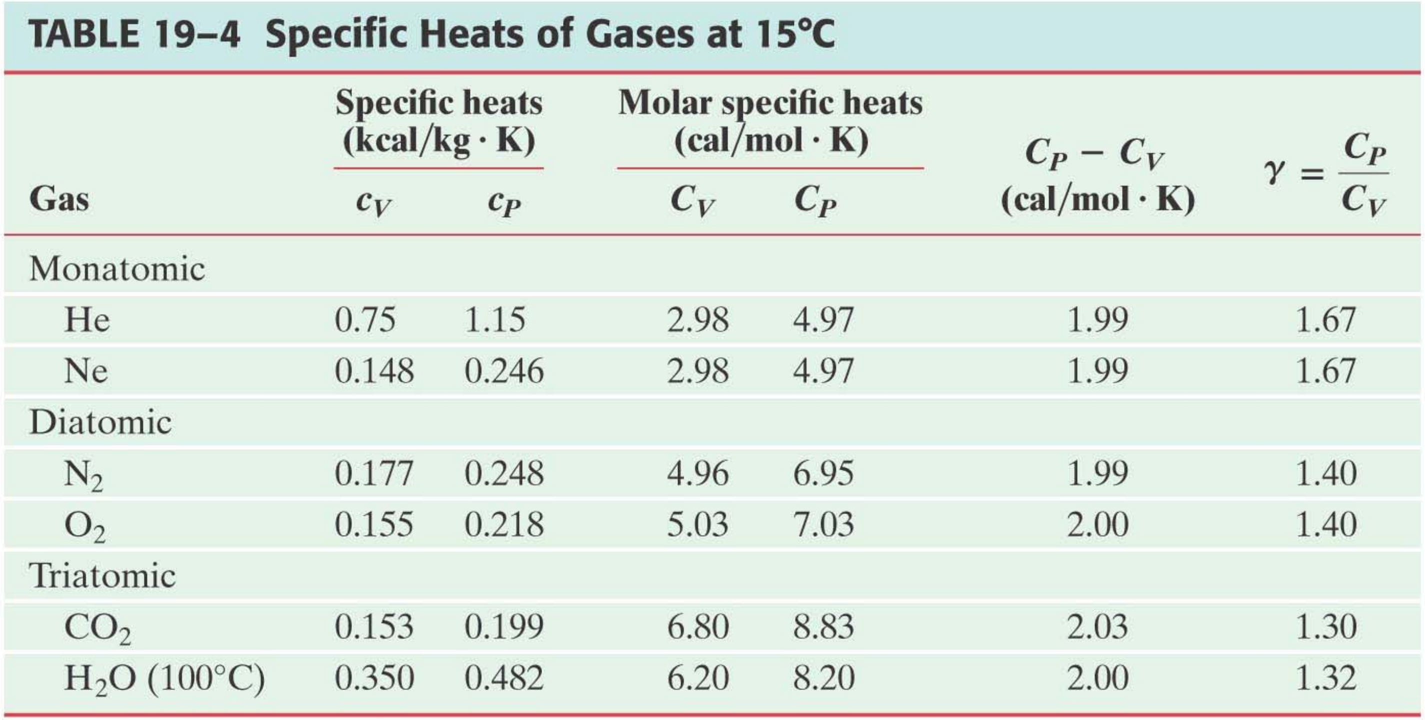


TABLE 19–4 Specific Heats of Gases at 15°C

	Specific heats (kcal/kg · K)		Molar specific heats (cal/mol · K)			
Gas	c_V	c_P	C_V	C_P	$C_P - C_V$ (cal/mol · K)	$\gamma = \frac{C_P}{C_V}$
Monatomic						
He	0.75	1.15	2.98	4.97	1.99	1.67
Ne	0.148	0.246	2.98	4.97	1.99	1.67
Diatomic						
N_2	0.177	0.248	4.96	6.95	1.99	1.40
O_2	0.155	0.218	5.03	7.03	2.00	1.40
Triatomic						
CO_2	0.153	0.199	6.80	8.83	2.03	1.30
H_2O (100°C)	0.350	0.482	6.20	8.20	2.00	1.32

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For a gas in a constant-volume process, no work is done, so $Q_V = \Delta E_{\text{int}}$.

For a gas at constant pressure, $Q_P = \Delta E_{\text{int}} + P\Delta V$.

Comparing these two processes for a monatomic gas when the temperature change is the same gives

$$C_P - C_V = R,$$

which is consistent with the measured values.

19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

In addition, since

$$\Delta E_{\text{int}} = \tfrac{3}{2} nR\,\Delta T = nC_V\,\Delta T,$$

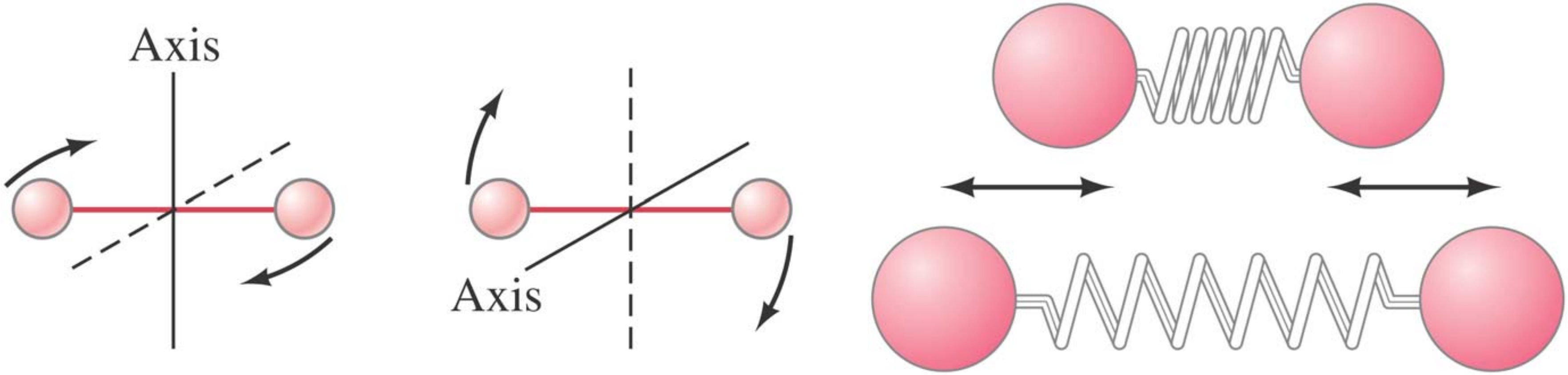
we expect that

$$C_V = \tfrac{3}{2} R.$$

This is also in agreement with measurements.

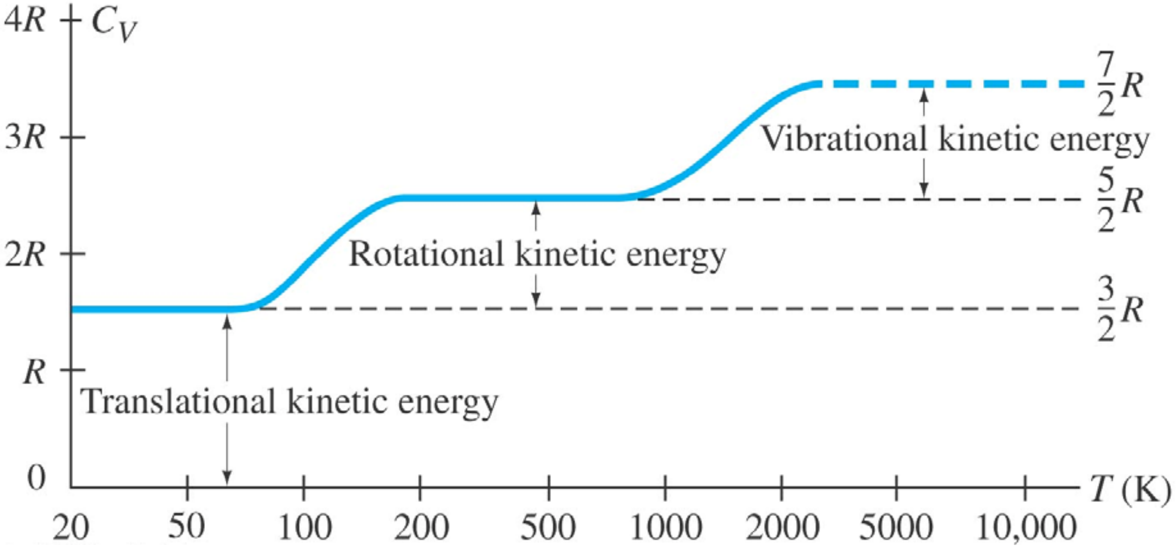
19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For a gas consisting of more complex molecules (diatomic or more), the molar specific heats increase. This is due to the extra forms of internal energy that are possible (rotational, vibrational).



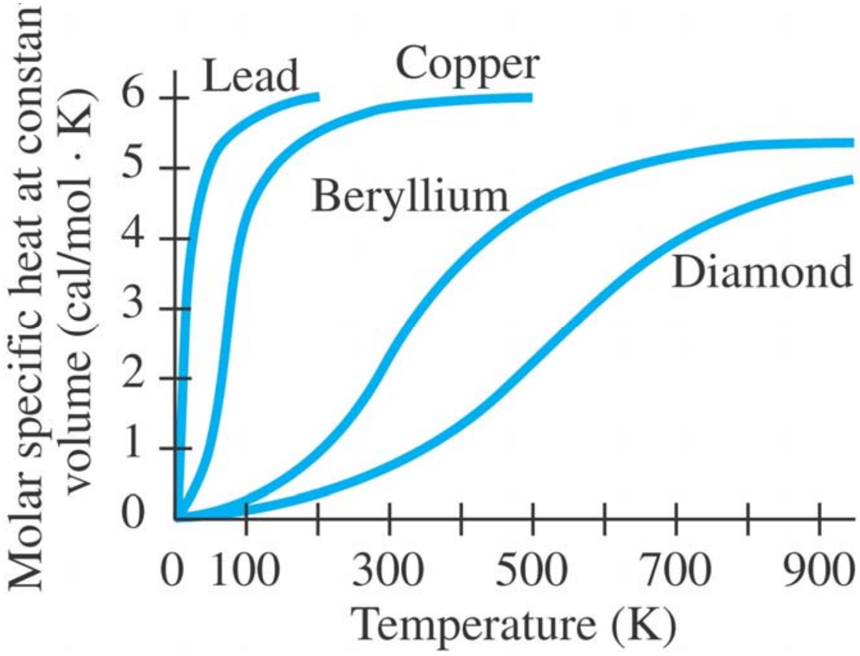
19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

Each mode of vibration or rotation is called a degree of freedom. The equipartition theorem states that the total internal energy is shared equally among the active degrees of freedom, each accounting for ½ kT. The actual measurements show a more complicated situation.



19-8 Molar Specific Heats for Gases, and the Equipartition of Energy

For solids at high temperatures, C_V is approximately $3R$, corresponding to six degrees of freedom (three kinetic energy and three vibrational potential energy) for each atom.



19-9 Adiabatic Expansion of a Gas

For an adiabatic expansion, $dE_{\mathrm{int}} = -PdV$, since there is no heat transfer.

From the relationship between the change in internal energy and the molar heat capacity, $dE_{\mathrm{int}} = nC_V dT$.

From the ideal gas law, $PdV + VdP = nRdT$.

Combining and rearranging gives $(C_P/C_V)PdV + VdP = 0$.

19-9 Adiabatic Expansion of a Gas

Define:

$$\gamma = \frac{C_P}{C_V}$$

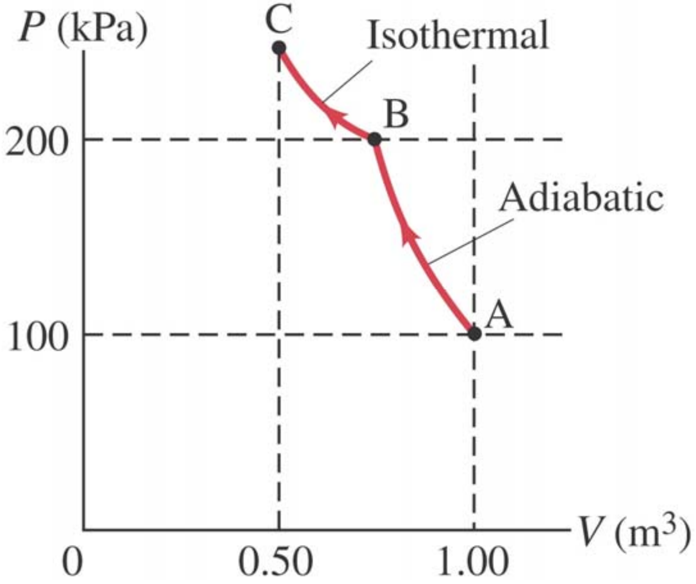
Integration then gives the result:

$$PV^{\gamma} = \text{constant.}$$

19-9 Adiabatic Expansion of a Gas

Example 19-12: Compressing an ideal gas.

An ideal monatomic gas is compressed starting at point A, where P_A = 100 kPa, V_A = 1.00 m^3, and T_A = 300 K. The gas is first compressed adiabatically to state B (P_B = 200 kPa). The gas is then further compressed from point B to point C (V_C = 0.50 m^3) in an isothermal process. (a) Determine V_B. (b) Calculate the work done on the gas for the whole process.

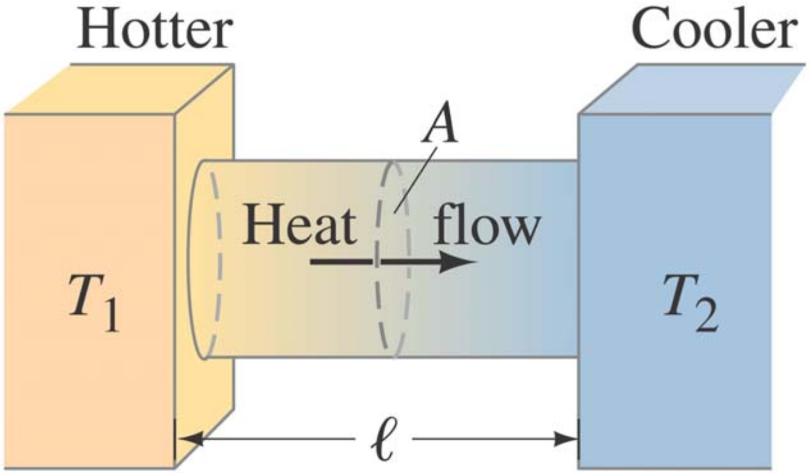


19-10 Heat Transfer: Conduction, Convection, Radiation

Heat **conduction** can be visualized as occurring through molecular **collisions**.

The **heat flow** per unit time is given by:

$$\frac{\Delta Q}{\Delta t} = kA\frac{T_1 - T_2}{\ell}.$$



19-10 Heat Transfer: Conduction, Convection, Radiation

TABLE 19–5
Thermal Conductivities

Substance	Thermal conductivity, k: $\frac{\text{kcal}}{(\text{s}\cdot\text{m}\cdot\text{C}^\circ)}$	Thermal conductivity, k: $\frac{\text{J}}{(\text{s}\cdot\text{m}\cdot\text{C}^\circ)}$
Silver	10×10^{-2}	420
Copper	9.2×10^{-2}	380
Aluminum	5.0×10^{-2}	200
Steel	1.1×10^{-2}	40
Ice	5×10^{-4}	2
Glass	2.0×10^{-4}	0.84
Brick	2.0×10^{-4}	0.84
Concrete	2.0×10^{-4}	0.84
Water	1.4×10^{-4}	0.56
Human tissue	0.5×10^{-4}	0.2
Wood	0.3×10^{-4}	0.1
Fiberglass	0.12×10^{-4}	0.048
Cork	0.1×10^{-4}	0.042
Wool	0.1×10^{-4}	0.040
Goose down	0.06×10^{-4}	0.025
Polyurethane	0.06×10^{-4}	0.024
Air	0.055×10^{-4}	0.023

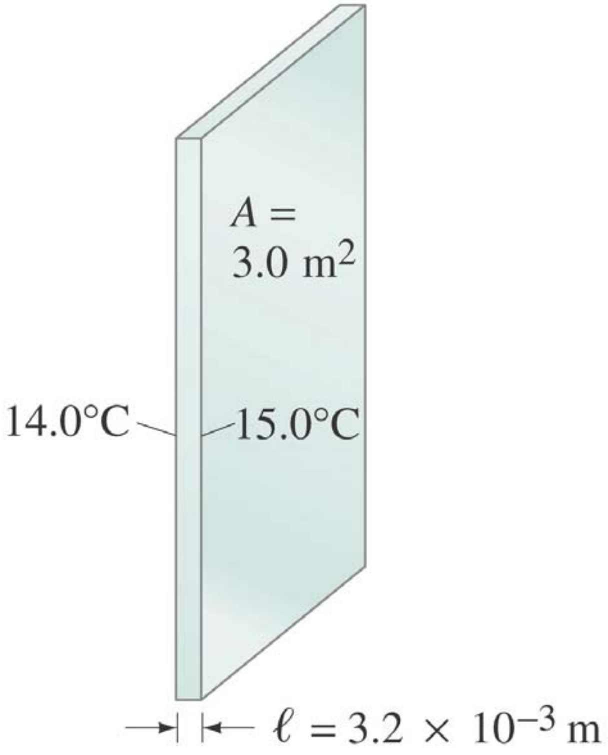
The constant k is called the **thermal conductivity**.

Materials with large k are called **conductors**; those with small k are called **insulators**.

19-10 Heat Transfer: Conduction, Convection, Radiation

Example 19-13: Heat loss through windows.

A major source of heat loss from a house is through the windows. Calculate the rate of heat flow through a glass window 2.0 m x 1.5 m in area and 3.2 mm thick, if the temperatures at the inner and outer surfaces are 15.0°C and 14.0°C, respectively.



19-10 Heat Transfer: Conduction, Convection, Radiation

Building materials are measured using *R*-values rather than thermal conductivity:

$$R = \ell/k.$$

Here, ℓ is the thickness of the material.

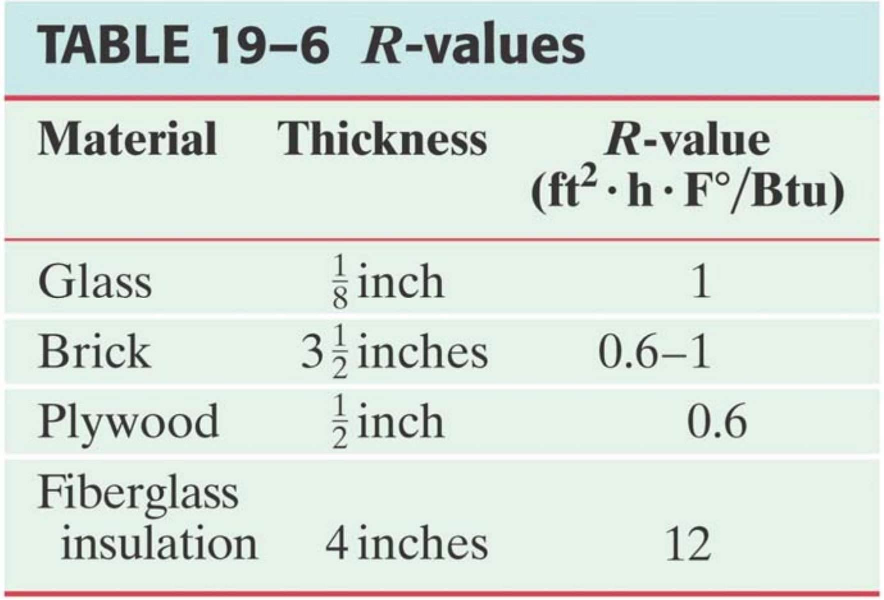
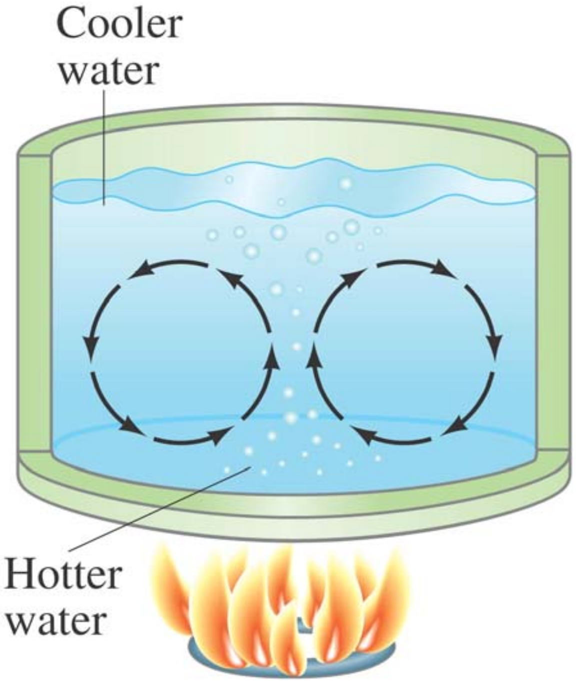


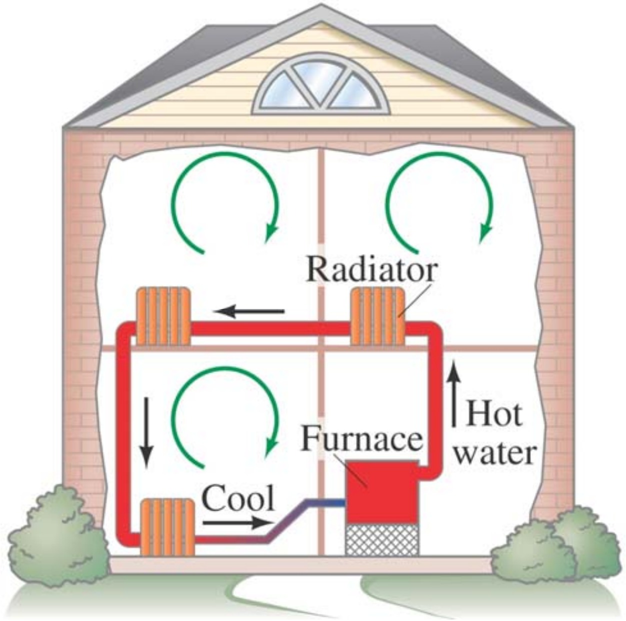
TABLE 19–6 *R*-values

Material	Thickness	*R*-value ($\mathrm{ft^2 \cdot h \cdot F^\circ/Btu}$)
Glass	$\frac{1}{8}$ inch	1
Brick	$3\frac{1}{2}$ inches	0.6–1
Plywood	$\frac{1}{2}$ inch	0.6
Fiberglass insulation	4 inches	12

19-10 Heat Transfer: Conduction, Convection, Radiation

Convection occurs when heat flows by the mass **movement** of molecules from one place to another. It may be **natural** or **forced**; both these examples are natural convection.





19-10 Heat Transfer: Conduction, Convection, Radiation

Radiation is the form of energy transfer we receive from the Sun; if you stand close to a fire, most of the heat you feel is radiated as well.

The **energy** radiated has been found to be proportional to the **fourth** power of the temperature:

$$\frac{\Delta Q}{\Delta t} = \epsilon \sigma A T^4.$$

19-10 Heat Transfer: Conduction, Convection, Radiation

The constant σ is called the **Stefan-Boltzmann** constant:

$$\sigma = 5.67 \times 10^{-8}\,\mathrm{W/m^2 \cdot K^4}.$$

The **emissivity** ε is a number between 0 and 1 characterizing the surface; black objects have an emissivity near 1, while shiny ones have an emissivity near 0. It is the same for absorption; a good emitter is also a good absorber.

19-10 Heat Transfer: Conduction, Convection, Radiation

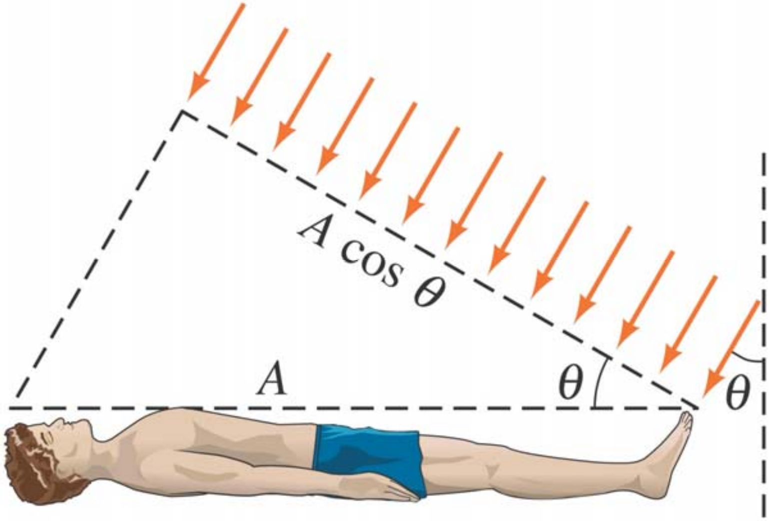
Example 19-14: Cooling by radiation.

An athlete is sitting unclothed in a locker room whose dark walls are at a temperature of 15°C. Estimate his rate of heat loss by radiation, assuming a skin temperature of 34°C and $\varepsilon = 0.70$. Take the surface area of the body not in contact with the chair to be 1.5 m^2.

19-10 Heat Transfer: Conduction, Convection, Radiation

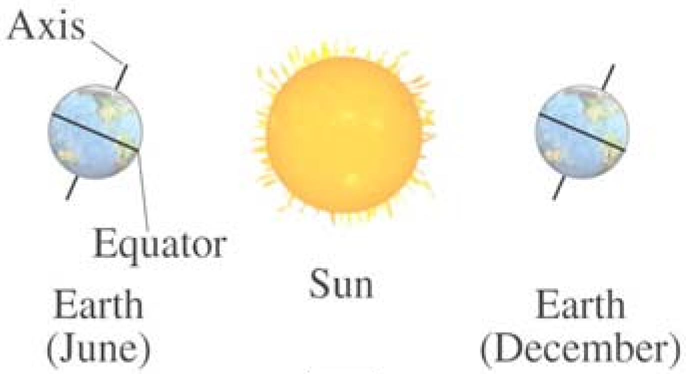
If you are in the sunlight, the Sun’s radiation will warm you. In general, you will not be perfectly perpendicular to the Sun’s rays, and will absorb energy at the rate:

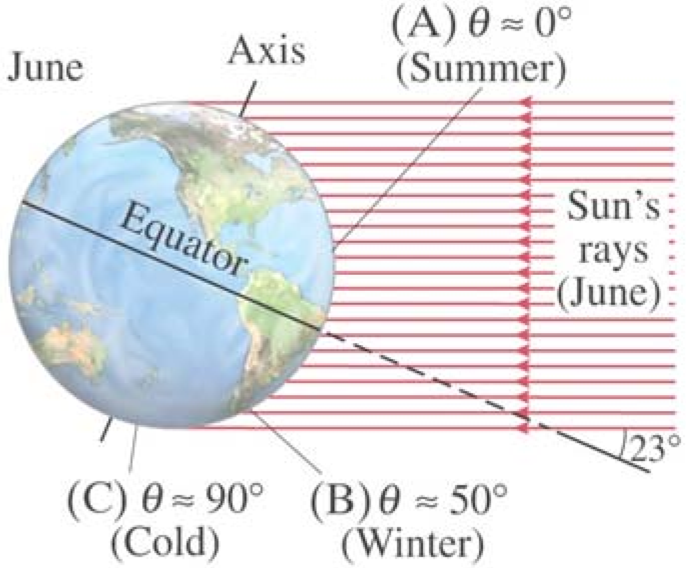
$$\frac{\Delta Q}{\Delta t} = \left(1000\ \mathrm{W/m^2}\right)\epsilon A \cos\theta .$$



19-10 Heat Transfer: Conduction, Convection, Radiation

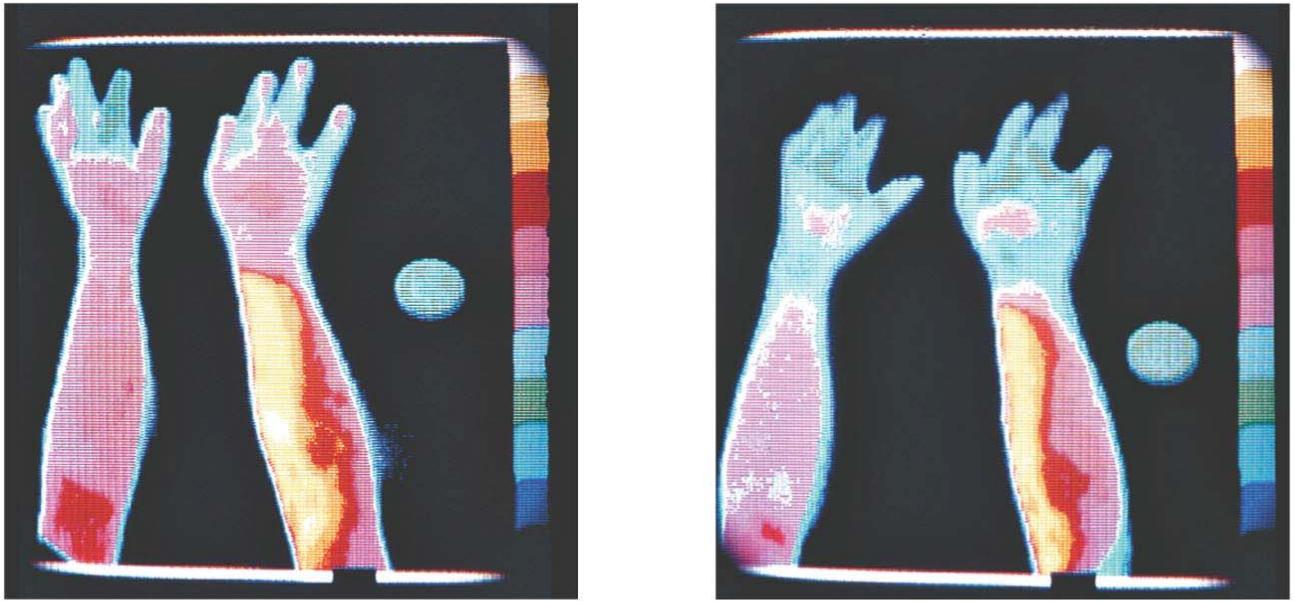
This **cos θ** effect is also responsible for the **seasons**.





19-10 Heat Transfer: Conduction, Convection, Radiation

Thermography—the detailed measurement of radiation from the body—can be used in medical imaging. Warmer areas may be a sign of **tumors** or **infection**; cooler areas on the skin may be a sign of **poor** circulation.



19-10 Heat Transfer: Conduction, Convection, Radiation

Example 19-15: Star radius.

The giant star Betelgeuse emits radiant energy at a rate 10^4 times greater than our Sun, whereas its surface temperature is only half (2900 K) that of our Sun. Estimate the radius of Betelgeuse, assuming $\varepsilon = 1$ for both. The Sun's radius is $r_S = 7 \times 10^8$ m.

Summary of Chapter 19

- **Internal energy, E_{int}, refers to the total energy of all molecules in an object. For an ideal monatomic gas,**

$$E_{int} = \tfrac{3}{2}NkT = \tfrac{3}{2}nRT.$$

- **Heat is the transfer of energy from one object to another due to a temperature difference. Heat can be measured in joules or in calories.**

- **Specific heat of a substance is the energy required to change the temperature of a fixed amount of matter by 1°C.**

Summary of Chapter 19

- In an isolated system, heat gained by one part of the system must be lost by another.
- Calorimetry measures heat exchange quantitatively.
- Phase changes require energy even though the temperature does not change.
- Heat of fusion: amount of energy required to melt 1 kg of material
- Heat of vaporization: amount of energy required to change 1 kg of material from liquid to vapor

Summary of Chapter 19

- The first law of thermodynamics:

$$\Delta E_{\text{int}} = Q - W.$$

- Thermodynamic processes: adiabatic (no heat transfer), isothermal (constant temperature), isobaric (constant pressure), isovolumetric (constant volume).

- Work done: $dW = P\,dV.$

- Molar specific heats:

$$C_P - C_V = R.$$

Summary of Chapter 19

- Heat transfer takes place by conduction, convection, and radiation.
- In conduction, energy is transferred through the collisions of molecules in the substance.
- In convection, bulk quantities of the substance flow to areas of different temperature.
- Radiation is the transfer of energy by electromagnetic waves.