Chapter 15

The Laws of Thermodynamics

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- Thermodynamic Processes and the First Law
- Human Metabolism and the First Law
- The Second Law of Thermodynamics – Introduction
- Heat Engines
- Refrigerators, Air Conditioners, and Heat Pumps

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- **Entropy and the Second Law of Thermodynamics**
- **Order to Disorder**
- **Unavailability of Energy; Heat Death**
- **Evolution and Growth; “Time’s Arrow”**
- **Statistical Interpretation of Entropy and the Second Law**
- **Thermal Pollution and Global Warming**

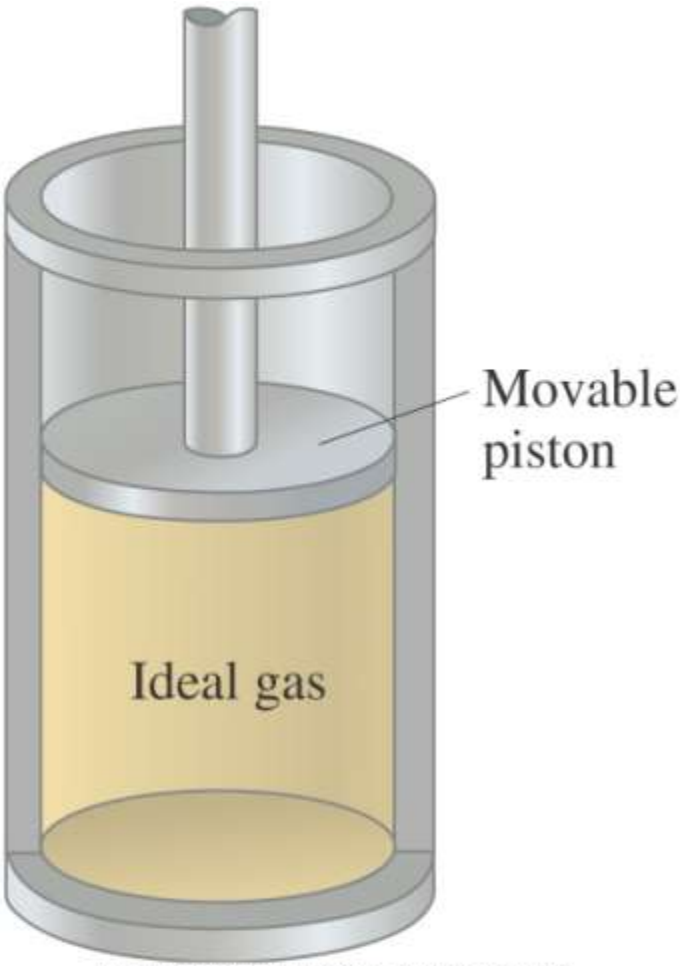
15-1 The First Law of Thermodynamics

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.

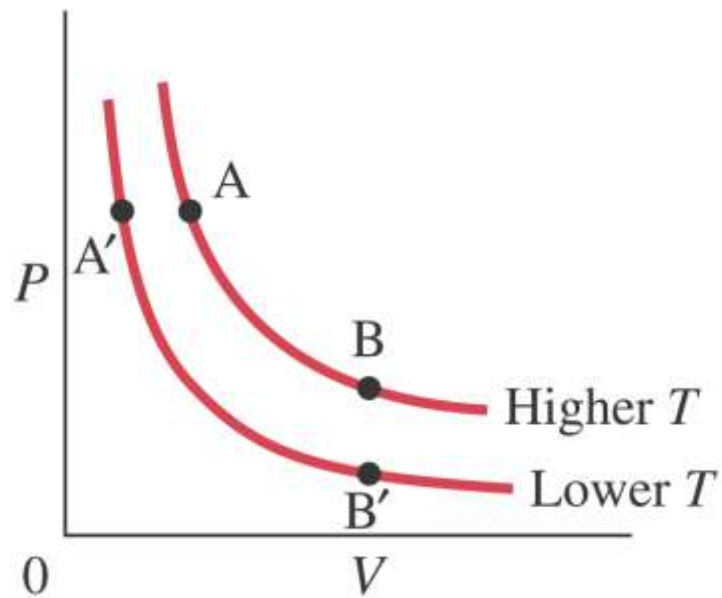
$$\Delta U = Q - W \qquad (15\text{-}1)$$

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

15-2 Thermodynamic Processes and the First Law



An **isothermal** process is one where the **temperature** does not change.



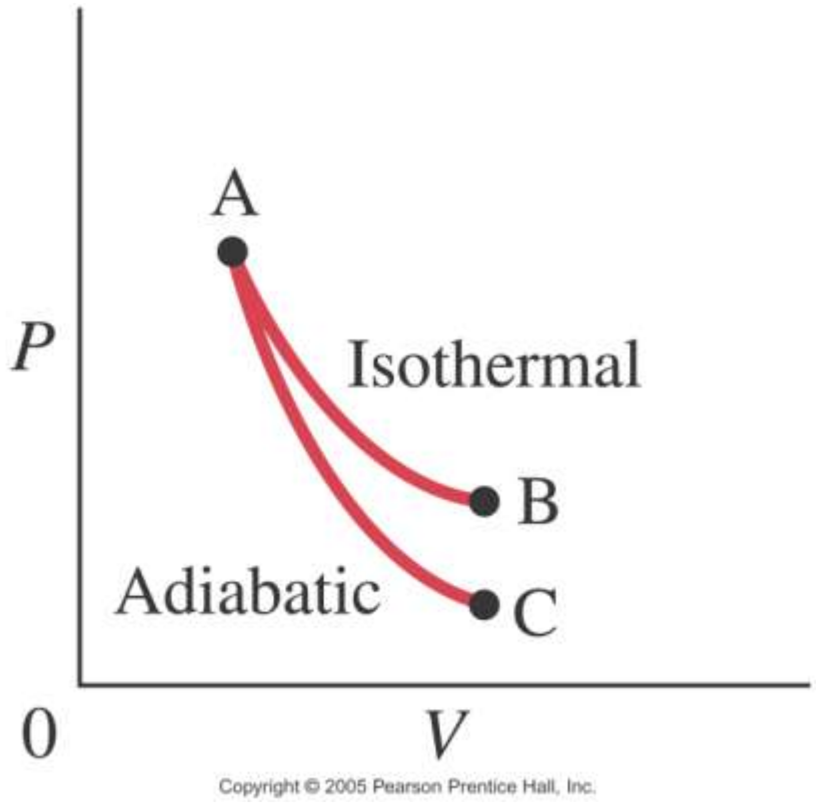
15-2 Thermodynamic Processes and the First Law

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.

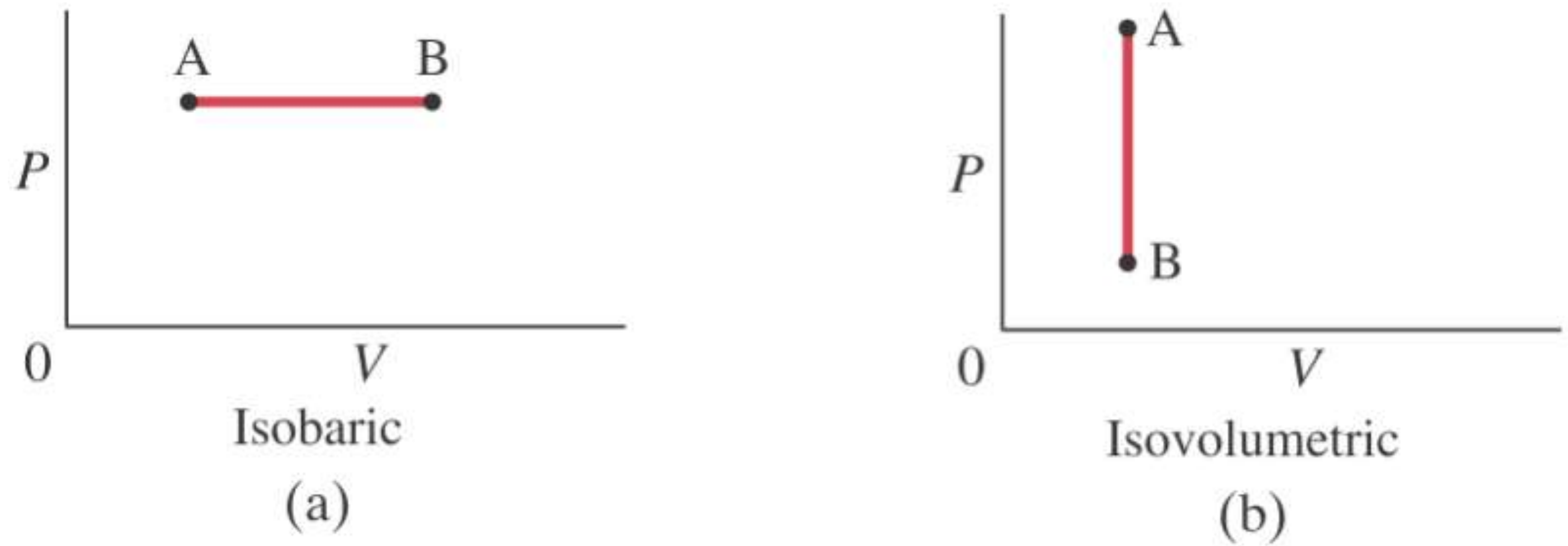
15-2 Thermodynamic Processes and the First Law

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



15-2 Thermodynamic Processes and the First Law

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



15-2 Thermodynamic Processes and the First Law

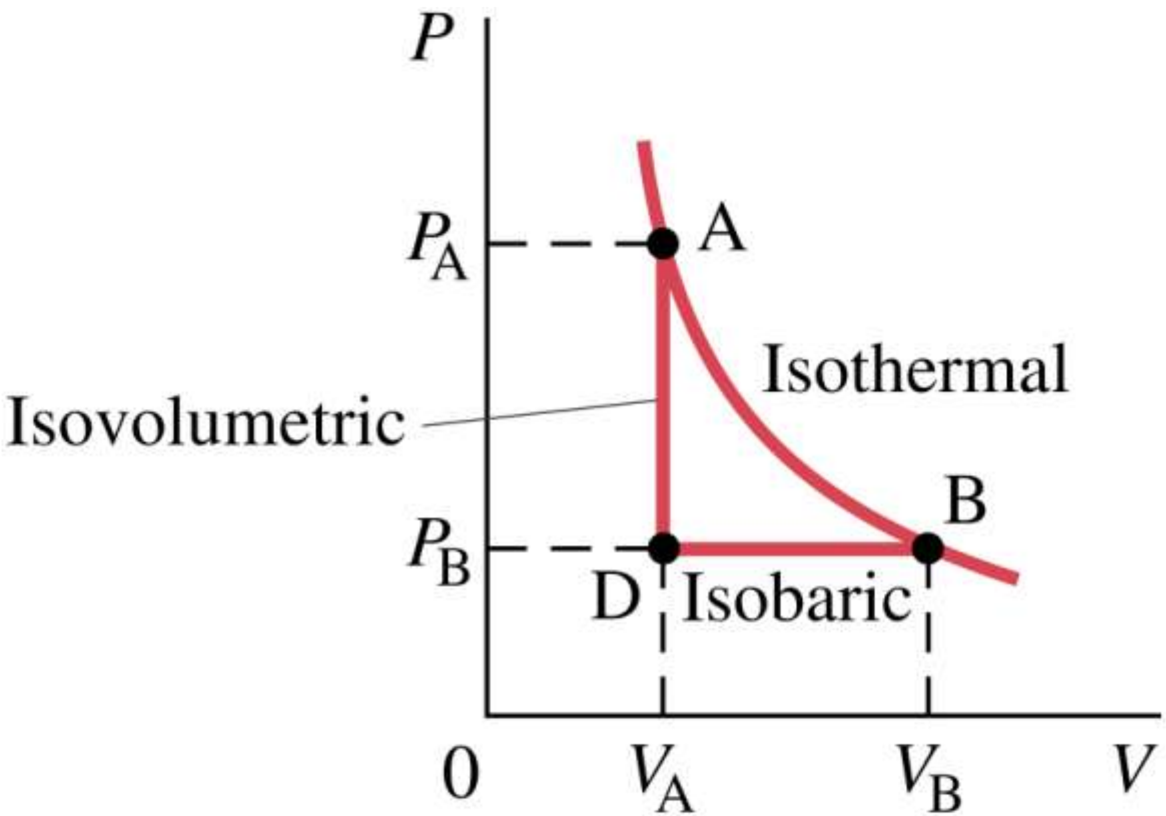
If the **pressure** is constant, the **work** done is the pressure multiplied by the change in volume:

$$W = P\,\Delta V \qquad \text{(15-3)}$$

In an **isometric** process, the volume does not change, so the work done is **zero**.

15-2 Thermodynamic Processes and the First Law

For processes where the pressure varies, the work done is the area under the *P*-*V* curve.



15-2 Thermodynamic Processes and the First Law

TABLE 15–1 Simple Thermodynamic Processes and the First Law

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

15-3 Human Metabolism and the First Law

If we apply the first law of thermodynamics to the human body:

$$\Delta U = Q - W$$

we know that the body can do work. If the internal energy is not to drop, there must be energy coming in. It isn't in the form of heat; the body loses heat rather than absorbing it. Rather, it is the chemical potential energy stored in foods.

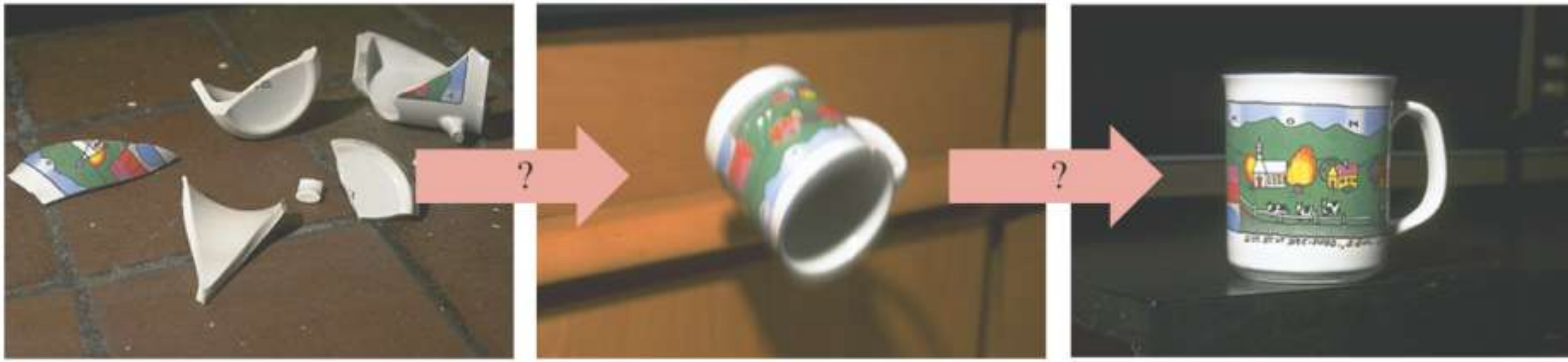
15-3 Human Metabolism and the First Law

The **metabolic rate** is the rate at which internal energy is transformed in the body.

TABLE 15–2
Metabolic Rates (65-kg human)

Activity	Metabolic Rate (approximate) kcal/h	Metabolic Rate (approximate) watts
Sleeping	60	70
Sitting upright	100	115
Light activity (eating, dressing, household chores)	200	230
Moderate work (tennis, walking)	400	460
Running (15 km/h)	1000	1150
Bicycling (race)	1100	1270

15-4 The Second Law of Thermodynamics – Introduction



(a) Initial state.

(b) Later: cup reassembles and rises up.

(c) Later still: cup lands on table.

The absence of the process illustrated above indicates that **conservation of energy** is not the whole story. If it were, movies run backwards would look perfectly normal to us!

15-4 The Second Law of Thermodynamics – Introduction

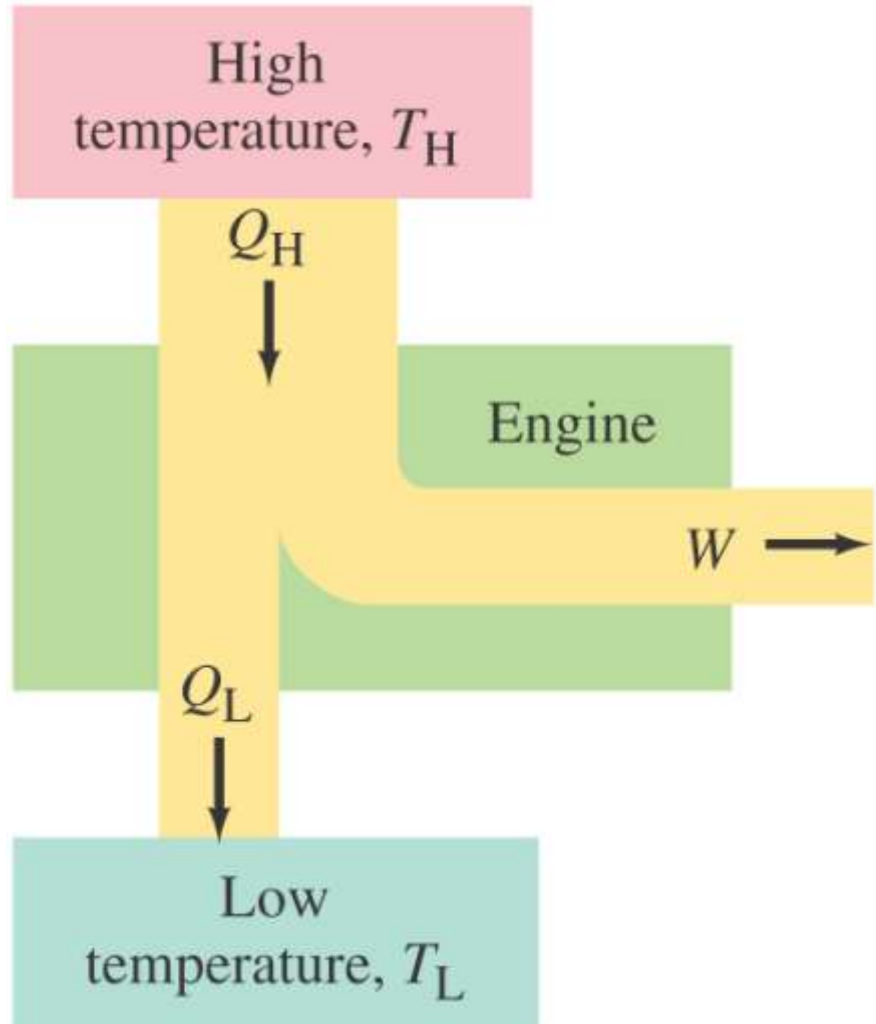
The **second law of thermodynamics** is a statement about which processes occur and which do not. There are many ways to state the second law; here is one:

Heat can flow spontaneously from a hot object to a cold object; it will not flow spontaneously from a cold object to a hot object.

15-5 Heat Engines

It is easy to produce **thermal energy** using work, but how does one produce **work** using thermal energy?

This is a **heat engine**; mechanical energy can be obtained from thermal energy only when heat can **flow** from a **higher** temperature to a **lower** temperature.



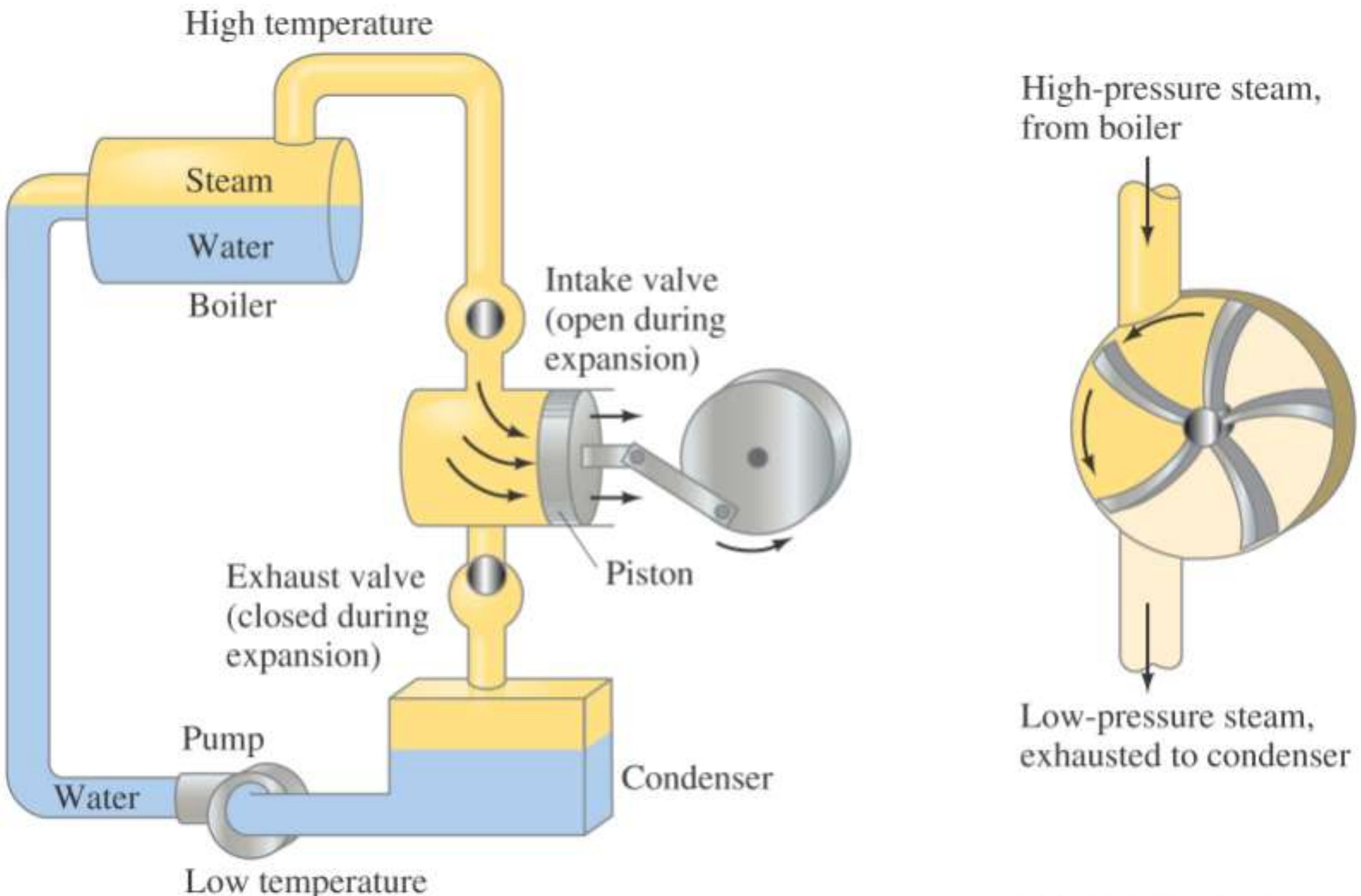
15-5 Heat Engines

We will discuss only engines that run in a **repeating** cycle; the change in internal energy over a cycle is **zero**, as the system returns to its initial state.

The **high** temperature reservoir transfers an amount of heat Q_H to the engine, where part of it is transformed into work W and the rest, Q_L, is exhausted to the **lower** temperature reservoir. Note that all three of these quantities are positive.

15-5 Heat Engines

A **steam** engine is one type of heat engine.

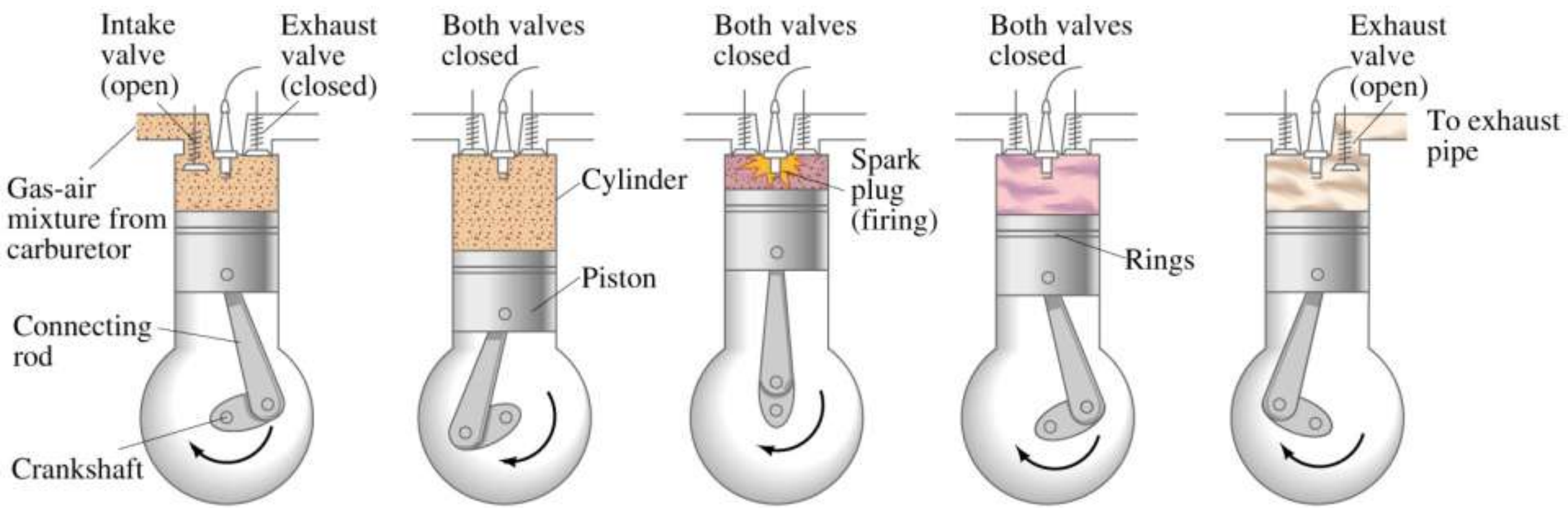


(a) Reciprocating type

(b) Turbine (boiler and condenser not shown)

15-5 Heat Engines

The **internal combustion** engine is a type of heat engine as well.



(a) Intake (b) Compression (c) Ignition (d) Expansion (power stroke) (e) Exhaust

15-5 Heat Engines

Why does a heat engine need a temperature difference?

Otherwise the work done on the system in one part of the cycle will be equal to the work done by the system in another part, and the net work will be zero.

15-5 Heat Engines

The **efficiency** of the heat engine is the ratio of the **work done** to the **heat input**:

$$e = \frac{W}{Q_{\mathrm{H}}}$$

Using conservation of energy to eliminate *W*, we find:

$$e = \frac{W}{Q_{\mathrm{H}}} \qquad \text{(15-4a)}$$

$$= \frac{Q_{\mathrm{H}} - Q_{\mathrm{L}}}{Q_{\mathrm{H}}} = 1 - \frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}} \qquad \text{(15-4b)}$$

15-5 Heat Engines

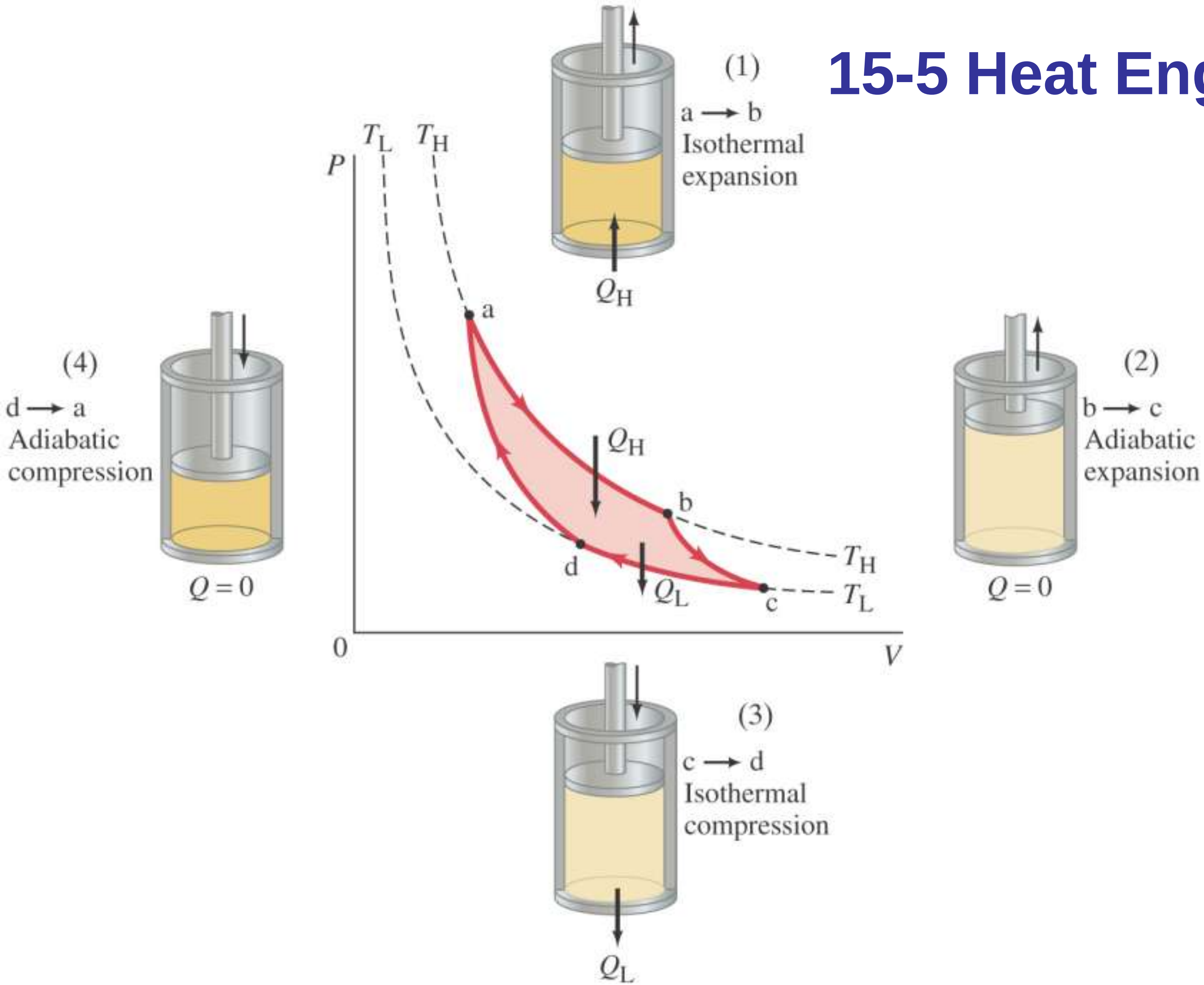
The **Carnot** engine was created to examine the efficiency of a heat engine. It is idealized, as it has no friction. Each leg of its cycle is **reversible**.

The Carnot cycle consists of:

- Isothermal expansion
- Adiabatic expansion
- Isothermal compression
- Adiabatic compression

An example is on the next slide.

15-5 Heat Engines



15-5 Heat Engines

For an ideal reversible engine, the efficiency can be written in terms of the temperature:

$$e_{\text{ideal}} = \frac{T_{\text{H}} - T_{\text{L}}}{T_{\text{H}}} = 1 - \frac{T_{\text{L}}}{T_{\text{H}}} \qquad \text{(15-5)}$$

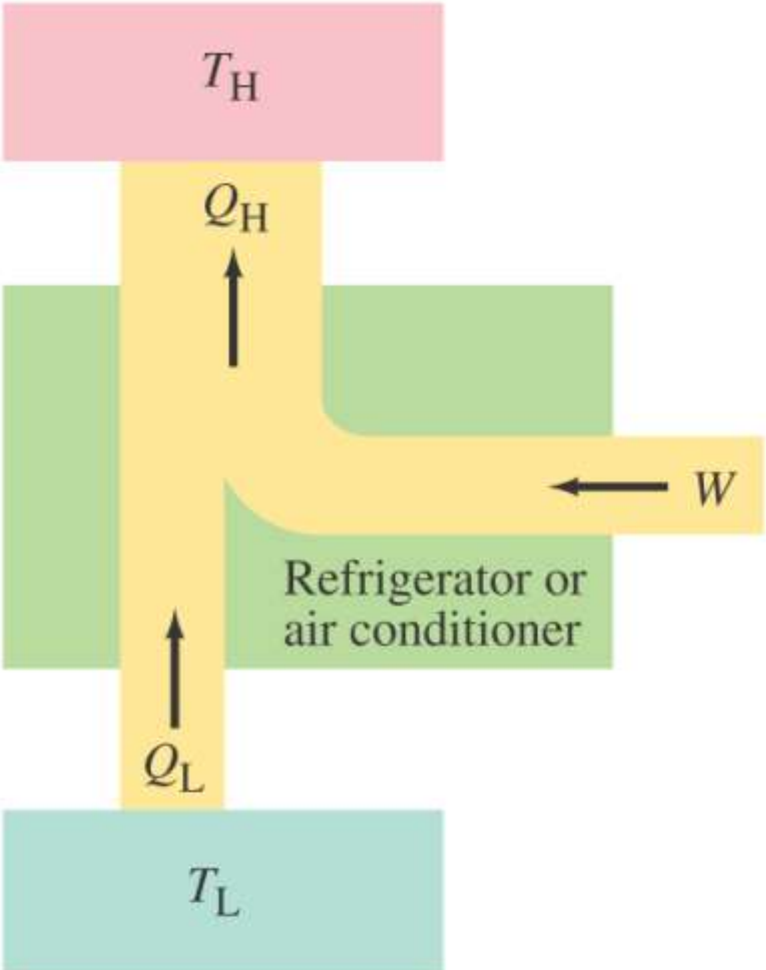
From this we see that 100% efficiency can be achieved only if the cold reservoir is at absolute zero, which is impossible.

Real engines have some frictional losses; the best achieve 60-80% of the Carnot value of efficiency.

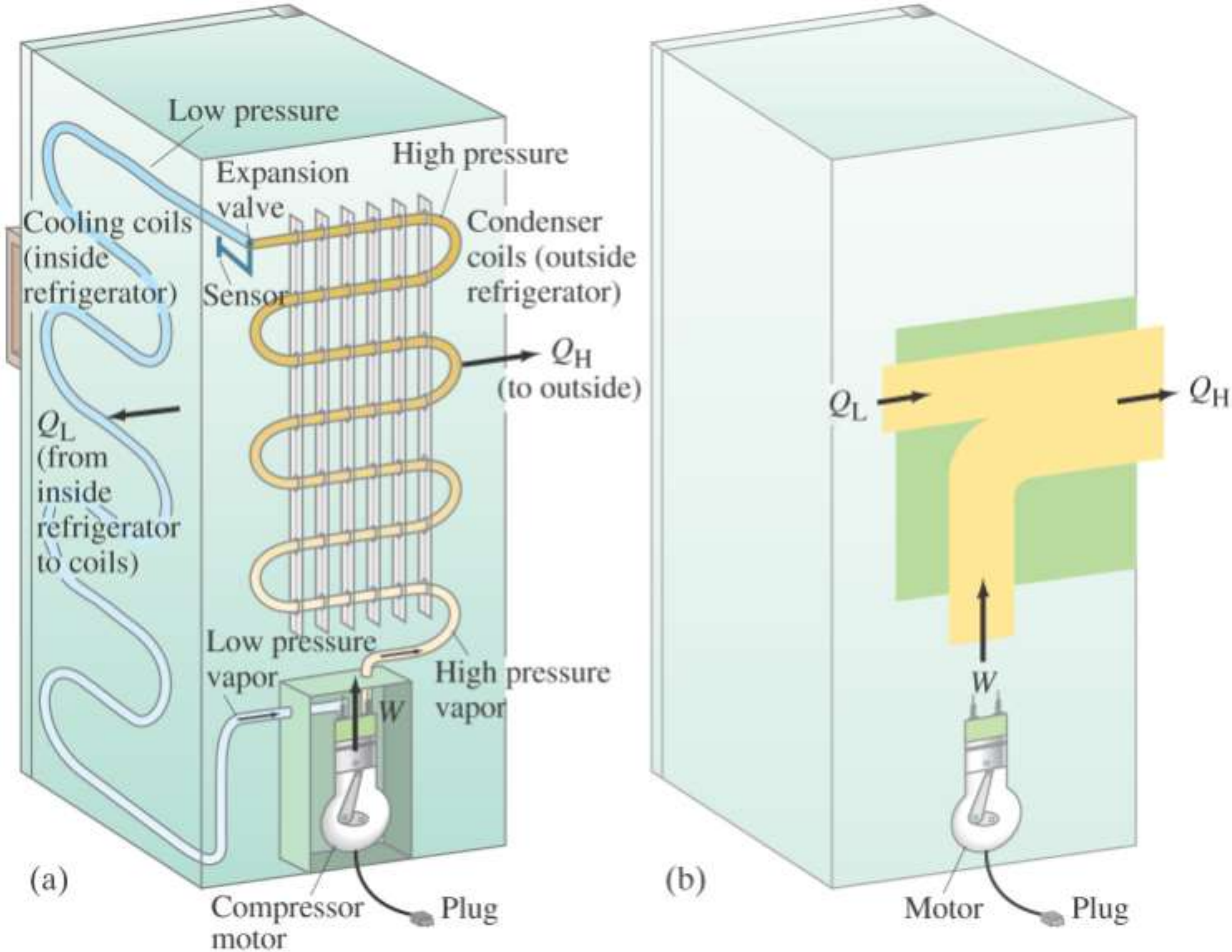
15-6 Refrigerators, Air Conditioners, and Heat Pumps

These appliances can be thought of as heat engines operating in **reverse**.

By doing **work**, heat is **extracted** from the cold reservoir and **exhausted** to the hot reservoir.



15-6 Refrigerators, Air Conditioners, and Heat Pumps



15-6 Refrigerators, Air Conditioners, and Heat Pumps

Refrigerator **performance** is measured by the coefficient of performance (**COP**):

$$\mathrm{COP} = \frac{Q_{\mathrm{L}}}{W} \qquad \textbf{(15-6a)}$$

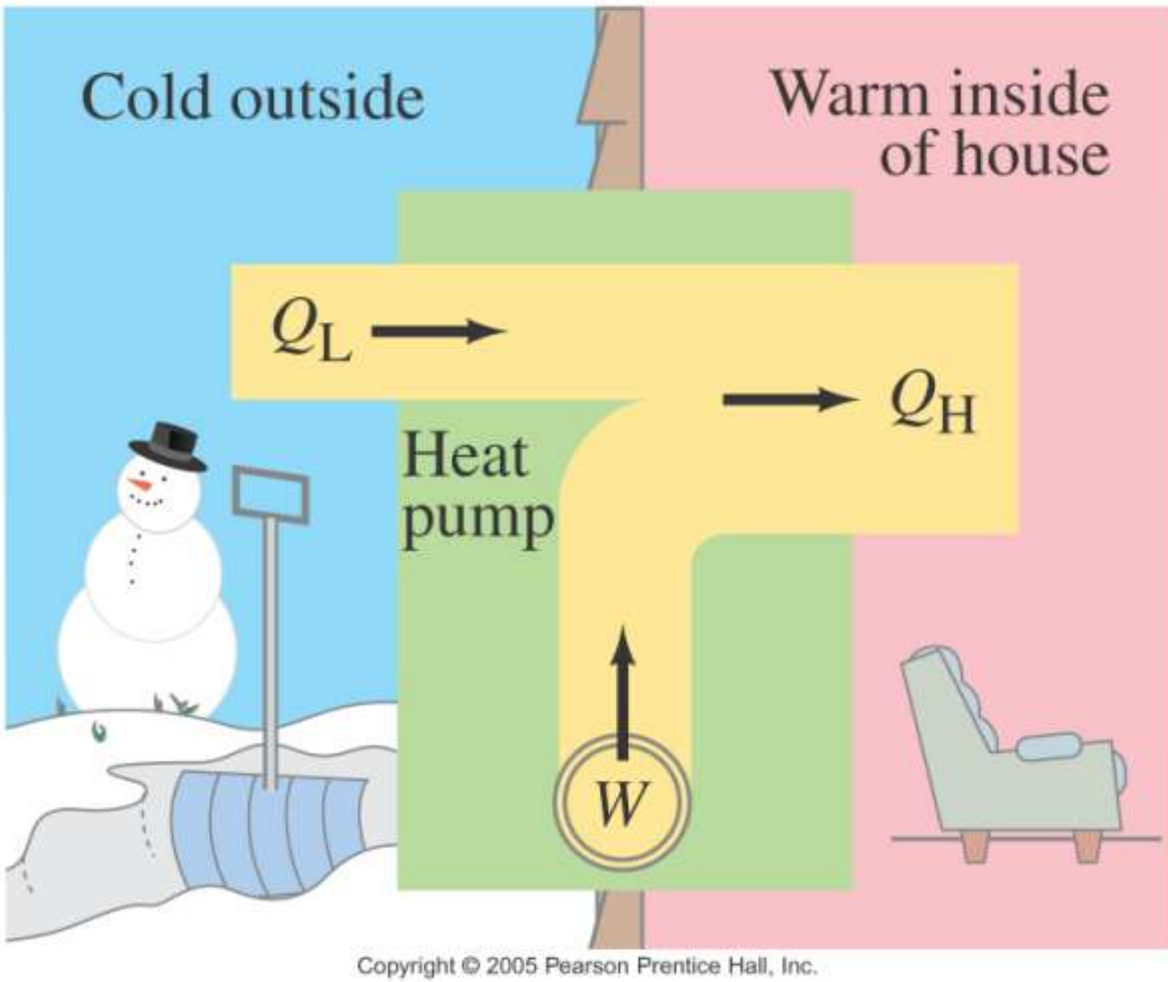
Substituting:

$$\mathrm{COP} = \frac{Q_{\mathrm{L}}}{W} = \frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}} - Q_{\mathrm{L}}} \qquad \textbf{(15-6b)}$$

$$\mathrm{COP}_{\mathrm{ideal}} = \frac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}} \qquad \textbf{(15-6c)}$$

15-6 Refrigerators, Air Conditioners, and Heat Pumps

A **heat pump** can heat a house in the winter:



$$\mathrm{COP} = \frac{Q_H}{W} \quad (15\text{-}7)$$

15-7 Entropy and the Second Law of Thermodynamics

Definition of the change in entropy S when an amount of heat Q is added:

$$\Delta S = \frac{Q}{T} \qquad \textbf{(15-8)}$$

Another statement of the second law of thermodynamics:

The total entropy of an isolated system never decreases.

15-8 Order to Disorder

Entropy is a measure of the **disorder** of a system. This gives us yet another statement of the **second** law:

Natural processes tend to move toward a state of greater disorder.

Example: If you put milk and sugar in your coffee and stir it, you wind up with coffee that is uniformly milky and sweet. No amount of stirring will get the milk and sugar to come back out of solution.

15-8 Order to Disorder

Another example: when a tornado hits a building, there is major damage. You never see a tornado approach a pile of rubble and leave a building behind when it passes.

Thermal equilibrium is a similar process – the uniform final state has more disorder than the separate temperatures in the initial state.

15-9 Unavailability of Energy; Heat Death

Another **consequence** of the second law:

In any natural process, some energy becomes **unavailable** to do useful work.

If we look at the universe as a whole, it seems inevitable that, as more and more energy is converted to unavailable forms, the ability to do work anywhere will gradually vanish. This is called the **heat death** of the universe.

15-10 Evolution and Growth; "Time's Arrow"

Growth of an individual, and evolution of a species, are both processes of increasing order. Do they violate the second law of thermodynamics?

No! These are not isolated systems. Energy comes into them in the form of food, sunlight, and air, and energy also leaves them.

The second law of thermodynamics is the one that defines the arrow of time – processes will occur that are not reversible, and movies that run backward will look silly.

15-11 Statistical Interpretation of Entropy and the Second Law

A **macrostate** of a system is specified by giving its macroscopic **properties** – temperature, pressure, and so on.

A **microstate** of a system describes the position and velocity of **every** particle.

For every macrostate, there are **one or more** microstates.

15-11 Statistical Interpretation of Entropy and the Second Law

A simple example: tossing four coins. The macrostates describe how many heads and tails there are; the microstates list the different ways of achieving that macrostate.

Macrostate	Possible Microstates (H = heads, T = tails)	Number of Microstates
4 heads	H H H H	1
3 heads, 1 tail	H H H T, H H T H, H T H H, T H H H	4
2 heads, 2 tails	H H T T, H T H T, T H H T, H T T H, T H T H, T T H H	6
1 head, 3 tails	T T T H, T T H T, T H T T, H T T T	4
4 tails	T T T T	1

15-11 Statistical Interpretation of Entropy and the Second Law

We assume that each microstate is equally probable; the probability of each macrostate then depends on how many microstates are in it.

The number of microstates quickly becomes very large if we have even 100 coins instead of four; the table on the next slide lists some macrostates, how many microstates they have, and the relative probability that each macrostate will occur. Note that the probability of getting fewer than 20 heads or tails is extremely small.

15-11 Statistical Interpretation of Entropy and the Second Law

TABLE 15–3
Probabilities of Various Macrostates for 100 Coin Tosses

Macrostate			
heads	tails	Number of microstates	Probability
100	0	1	8.0×10^{-31}
99	1	1.0×10^{2}	8.0×10^{-29}
90	10	1.7×10^{13}	1.0×10^{-17}
80	20	5.4×10^{20}	4.0×10^{-10}
60	40	1.4×10^{28}	0.01
55	45	6.1×10^{28}	0.05
50	50	1.0×10^{29}	0.08
45	55	6.1×10^{28}	0.05
40	60	1.4×10^{28}	0.01
20	80	5.4×10^{20}	4.0×10^{-10}
10	90	1.7×10^{13}	1.0×10^{-17}
1	99	1.0×10^{2}	8.0×10^{-29}
0	100	1	8.0×10^{-31}

15-11 Statistical Interpretation of Entropy and the Second Law

Now we can say that the second law does not **forbid** certain processes; all microstates are equally likely. However, some of them have an extraordinarily **low** probability of occurring – a lake freezing on a hot summer day, broken crockery re-assembling itself; all the air in a room moving into a single corner.

Remember how low some probabilities got just in going from four coins to 100 – if we are dealing with **many moles** of material, they can become so rare as to be effectively impossible.

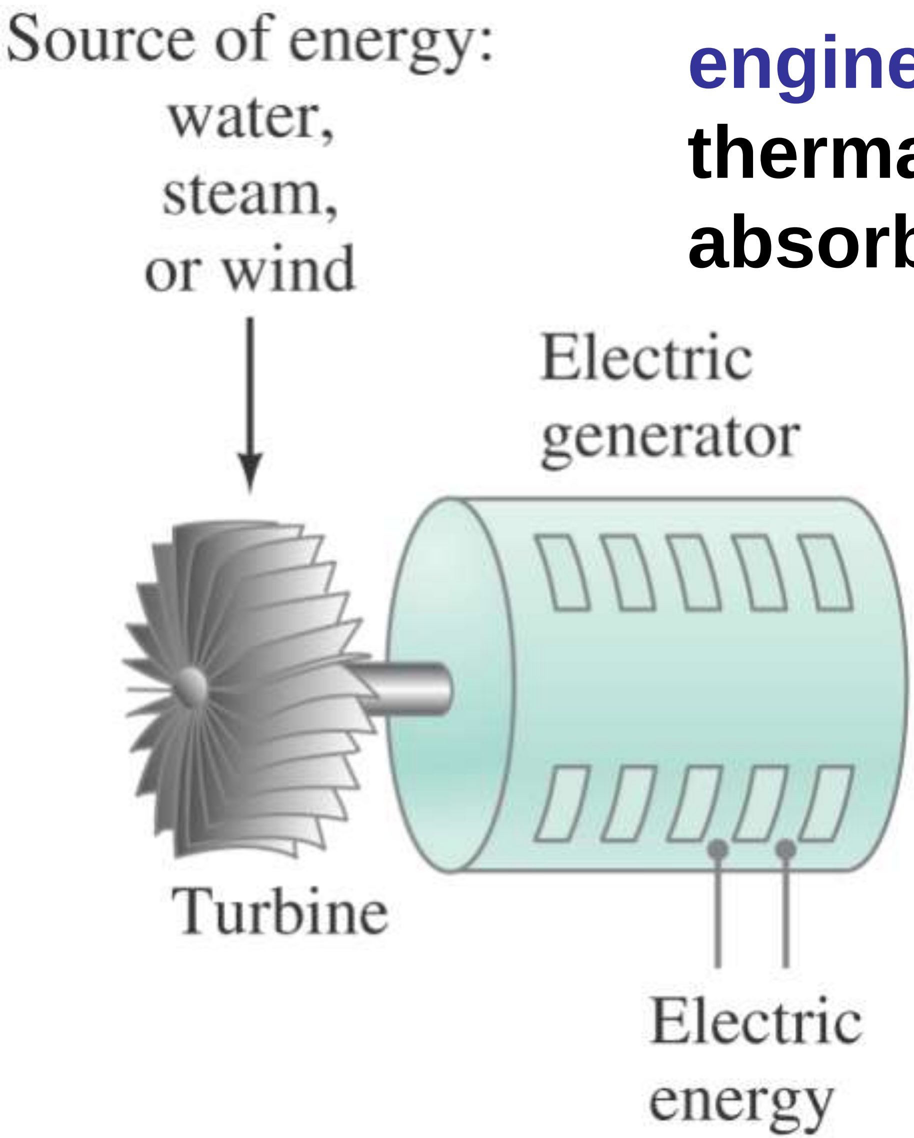
15-12 Thermal Pollution and Global Warming

The **generation** of electricity using **solar** energy (a) does not involve a **heat** engine, but **fossil-fuel** plants (b) and **nuclear** plants (c) do.

(a) (b) (c)

15-12 Thermal Pollution and Global Warming

The **heat output** of any heat engine, Q_L, is referred to as **thermal pollution**, as it must be **absorbed** by the environment.



15-12 Thermal Pollution and Global Warming

Air pollution is also emitted by power plants, industries, and consumers. Some of this pollution results in a buildup of CO_2 in the atmosphere, contributing to **global warming**. This can be **minimized** through careful choices of fuels and processes.

The **thermal pollution**, however, is a consequence of the **second law**, and is **unavoidable**; it can be reduced only by **reducing** the amount of energy we use.

15-12 Thermal Pollution and Global Warming

Problem solving:

1. **Define** what is part of the **system** and what is part of the **surroundings**.
2. Be careful of the **signs** for work and heat when using the first law of thermodynamics.
3. Be careful about **units**; be sure that you are using the same ones throughout the problem.
4. Express temperatures in **kelvins**.

15-12 Thermal Pollution and Global Warming

5. **Efficiency** is always less than 1.

6. Entropy **increases** when heat is added, and **decreases** when heat is removed.

Summary of Chapter 15

- First law of thermodynamics: $\Delta U = Q - W$
- Isothermal process: temperature is constant.
- Adiabatic process: no heat is exchanged.
- Work done by gas at constant pressure:

$$W = P\,\Delta V$$

- Heat engine changes heat into useful work; needs temperature difference.
- Efficiency of a heat engine: $e = \frac{W}{Q_{\mathrm{H}}} = 1 - \frac{Q_{\mathrm{L}}}{Q_{\mathrm{H}}}$

Summary of Chapter 15

- **Upper limit on efficiency:**

$$e_{\text{ideal}} = 1 - \frac{T_{\text{L}}}{T_{\text{H}}}$$

- **Refrigerators and air conditioners do work to extract heat from a cooler region and send it to a warmer region:**

$$\text{COP} = \frac{Q_{\text{L}}}{W}$$

- **A heat pump is similar:**

$$\text{COP} = \frac{Q_{\text{H}}}{W}$$

Summary of Chapter 15

- Second law of thermodynamics:
  - heat flows spontaneously from a hot object to a cold one, but not the reverse
  - a given amount of heat cannot be changed entirely to work
  - natural processes tend to increase entropy.
- Change in entropy: $\Delta S = \frac{Q}{T}$
- Entropy is a measure of disorder.
- As time goes on, less and less energy is available to do useful work.