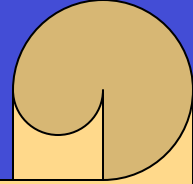# Chapter 15: Thermodynamics

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

Work is energy transferred from one object to another by mechanical means

FIRST LAW OF THERMODYNAMICS

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

$$\Delta U = Q - W$$

Careful with signs: for example, if work is **done TO** the system use Q+W

U, V, P, T, m, n are quantities that describe a state of the system: **state variables**
Q and W change state of the system, they are not state variables

Ex. 15-1   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?

4300J

Thermodynamic Processes

Movable piston

Ideal gas

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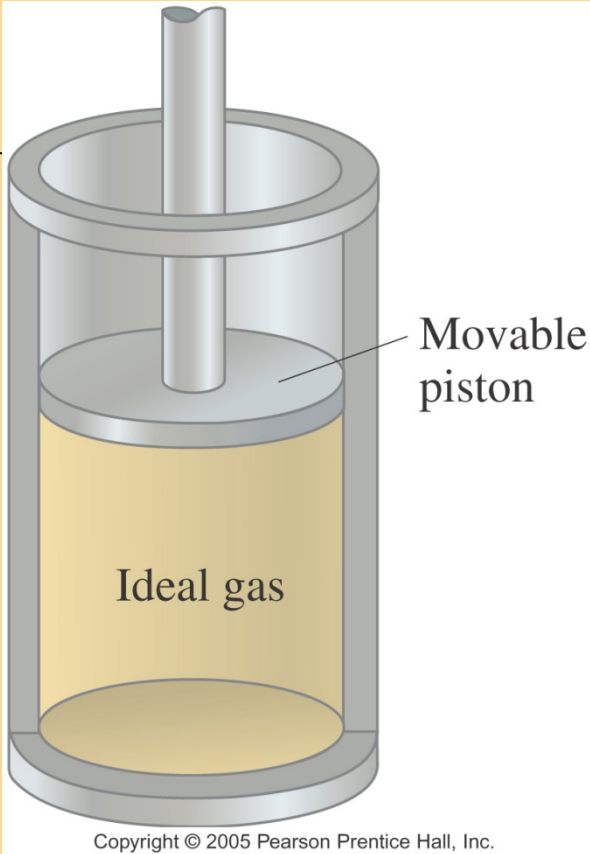
$$\Delta U = 3nR\Delta T / 2$$

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

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 (process very slow).

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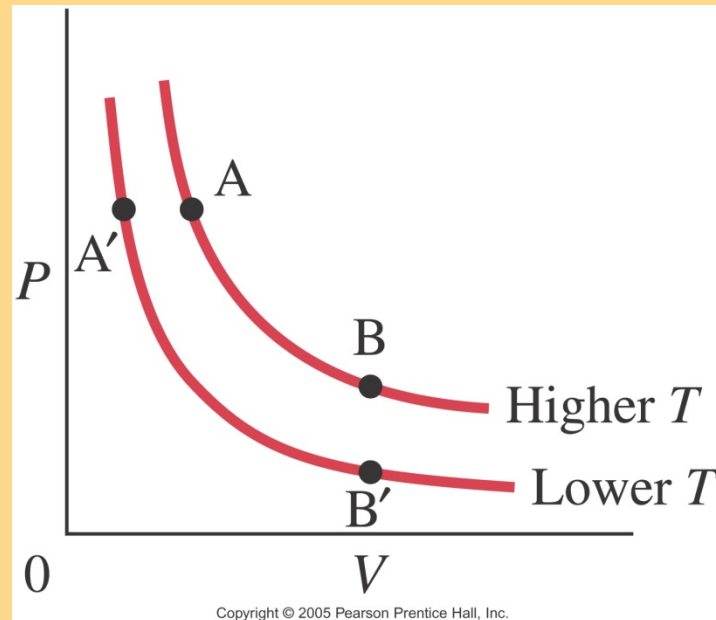
PV=constant curves are **isotherms** System starts at A. If Q is added, then P and V change, the gas expands and do work on the surroundings. Since T is constant, internal energy does not change and so **Q=W**
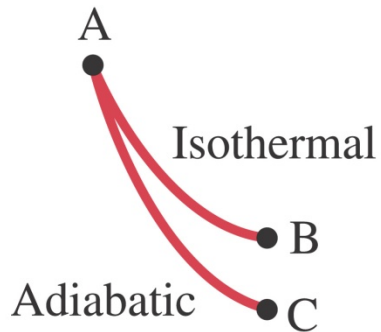
Thermodynamics Processes
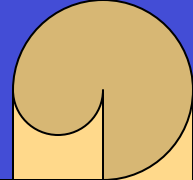
An **adiabatic** process is one where there is no heat flow into or out of the system, Q=0. -- system is very isolated or process is very fast (diesel engine)
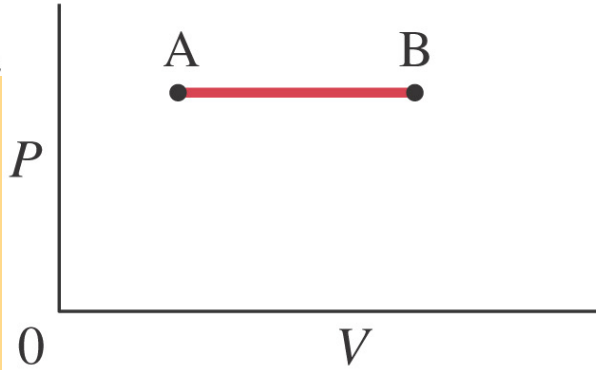
$$\Delta U = -W$$

Internal energy decreases as gas expands; hence T decreases and so does PV, which explains why C is below B

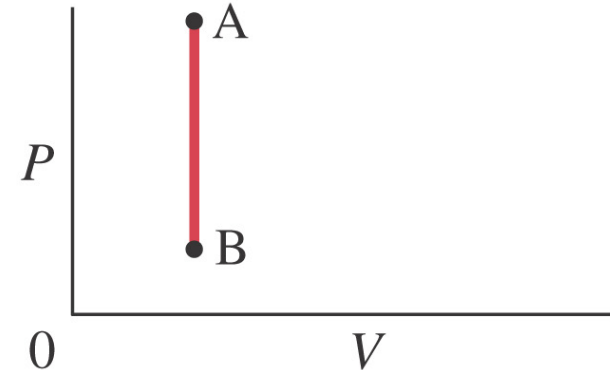An **isobaric** process (a) occurs at constant pressure; an **isovolumetric** one (b) at constant volume.

P

A

Isothermal

B

Adiabatic

C

0   V

A   B

P

0   V

Isobaric

(a)

A

P

B

0   V
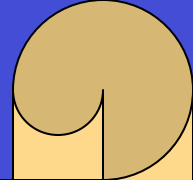
Isovolumetric

(b)

Thermodynamics Processes

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

$$W = Fd = PAd \Rightarrow \boxed{W = P\,\Delta V}$$

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

Work done is the area under the P-V curve -- only way to solve it if P varies as in isothermal processes
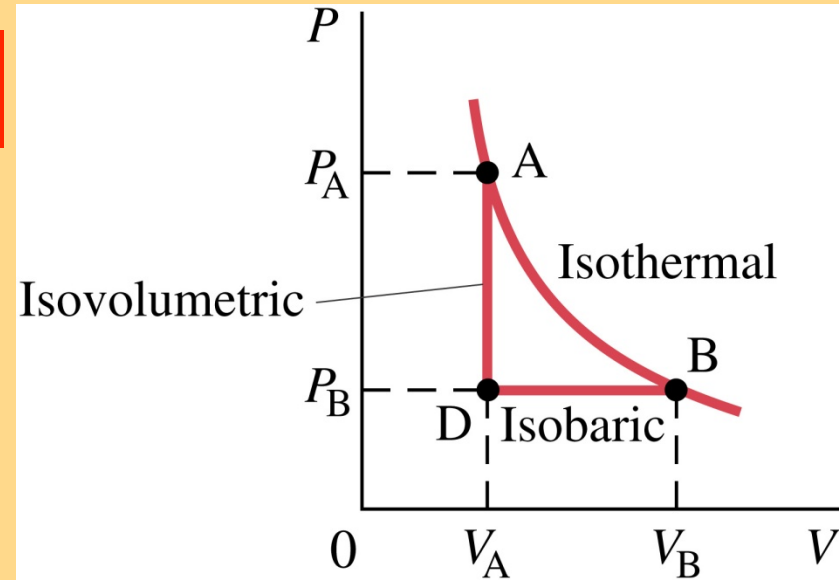
TABLE 15–1 Simple Thermodynamic Processes and the First Law

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	$Q = 0$	$\Delta U = -W$

Ex. 15-3 Suppose the initial volume is the same in both an isothermal and in an adiabatic process. If the final volume is also the same, in which process was more work done by the gas?

In the isothermal process – larger area

Ex. 15-4 Example of an adiabatic process: hold a thin rubber with two hands and gauge its temperature with your lips. Stretch the rubber band suddenly and again touch it with your lips. Why the temperature increases?

Q=0 because the process is fast, no time for heat to enter or leave the system. We do work on the system, $\Delta U = +W$ so the temperature increases

Ex. 15-5 An ideal gas is slowly compressed at a constant pressure of 2.0 atm from 10.0 L to 2.0 L (B to D in figure). 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 (line DA) until initial T is reached. Calculate (a) the total work done by the gas in the process BDA, and (b) the total heat flow into the gas

$$1atm = 1.01 \times 10^5 \, N/m^2$$
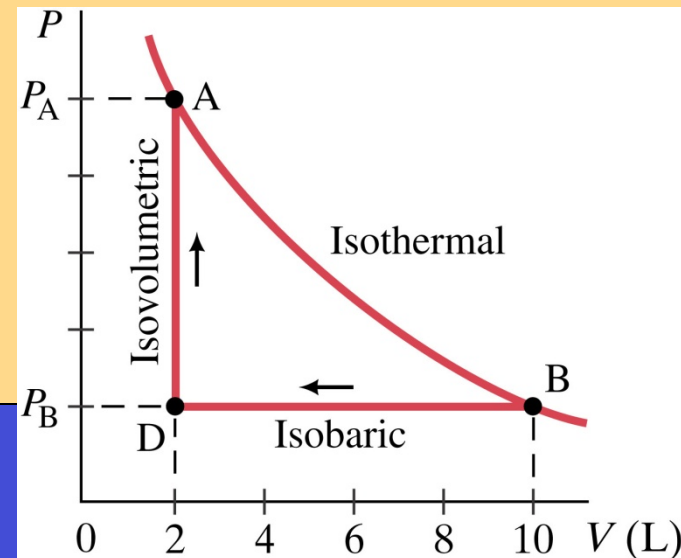
$$(a) W = -1.6 \times 10^3 J \quad (b)\Delta U = 0 \Rightarrow Q = -1.6 \times 10^3 J (out \ of \ gas)$$

Ex. 15-6 In an engine, 0.25 moles 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?

$$\Delta U = 3nR(T_f - T_i)/2 \Rightarrow W = 2300J$$

Ex. 15-7 Determine the change in internal energy of 1.00 liter of water (mass 1.00 kg) at 100oC when it is fully boiled from liquid to gas, which results in 1671 liters of steam at 100oC. The process is done at atmospheric pressure.

$$1atm = 1.01 \times 10^5 N/m^2 \qquad 1L = 10^{-3} m \qquad L_v = 22.6 \times 10^5 J/kg$$

$$Q = mL, \ W = P\Delta V \Rightarrow \Delta U = 20.9 \times 10^5 J$$

Second Law
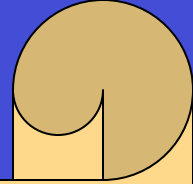
According to the first law, energy is conserved. There are however processes that would conserve energy, but never happens.
Examples: heat flow from cold to hot object; salt and pepper separating in water.
Lack of reversibility – *2nd law* of thermodynamics

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.

But we need a more general statement applied to other processes too.

The development of a general statement derived from the study of **heat engines**

A heat engine is any device that changes **thermal** energy into mechanical **work**

Heat Engines

High temperature, T_H

Q_H

Engine

W

Q_L
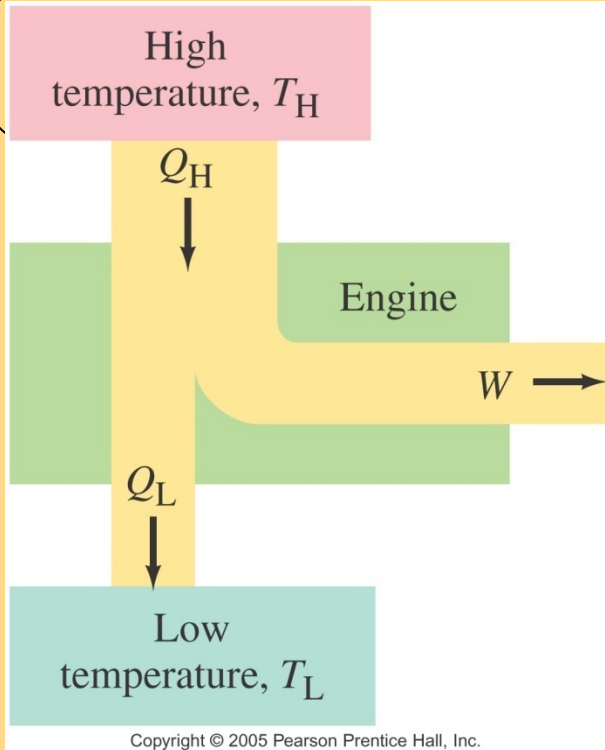
Low temperature, T_L

Easy to produce thermal energy doing work, the other way round is more difficult -- 1700: 1st steam engine

As heat flows from high to low temperature, some of the heat can be **transformed** to mechanical work.

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.*

$$Q_H = W + Q_L$$

Steam Engine

Steam heated by combustion of coal, oil, gas, or nuclear energy

High temperature

Steam

Water

Boiler

Intake valve (open during expansion)

Piston

Exhaust valve (closed during expansion)

Pump

Water

Condenser

Low temperature

(a) Reciprocating type

High-pressure steam, from boiler

Low-pressure steam, exhausted to condenser
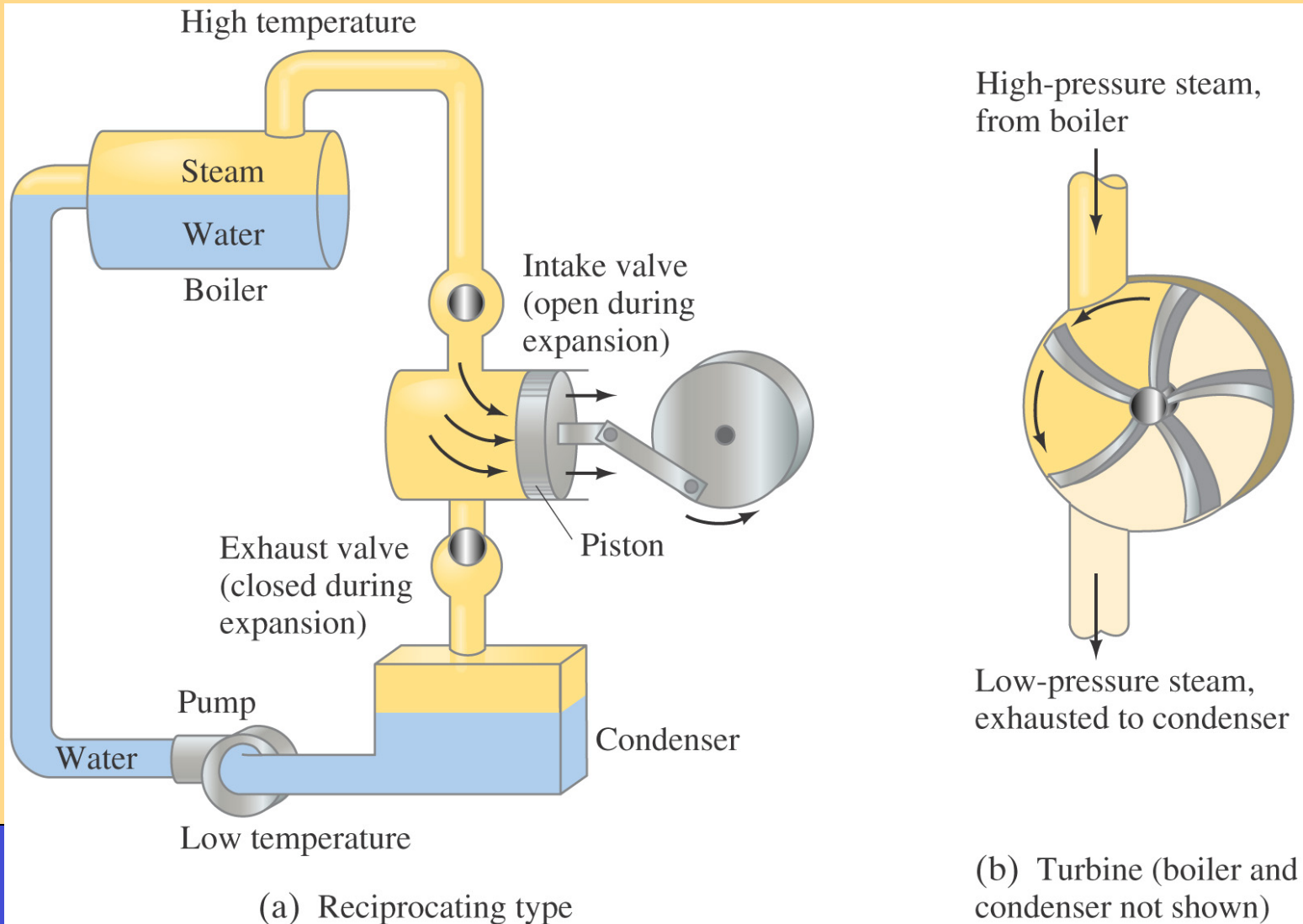
(b) Turbine (boiler and condenser not shown)

High temperature is achieved by burning the gasoline-air mixture in the cylinder

Intake valve (open) Exhaust valve (closed)

Gas-air mixture from carburetor

Connecting rod

Crankshaft

(a) Intake

Both valves closed

Cylinder

Piston

(b) Compression

Both valves closed

Spark plug (firing)

(c) Ignition

Both valves closed

Rings

(d) Expansion (power stroke)

Exhaust valve (open)

To exhaust pipe

(e) Exhaust
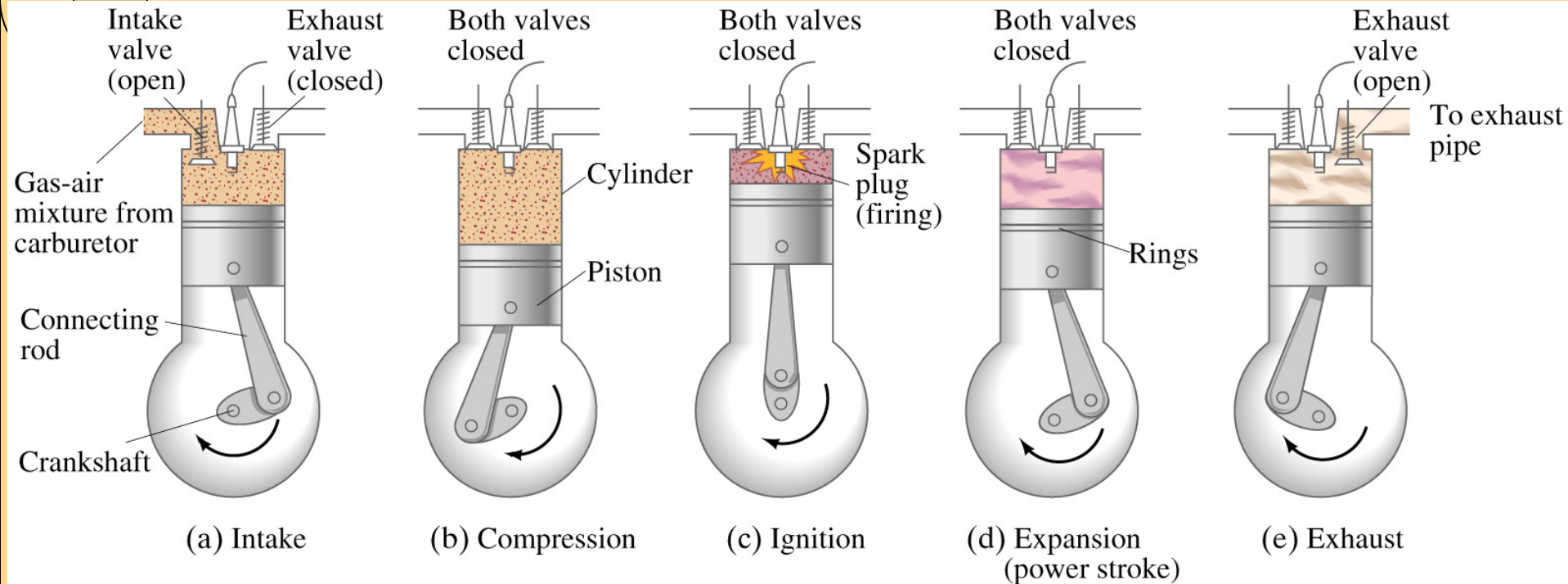
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Temperature difference is necessary for **net work** to be different from zero, otherwise the work done on the system in one part of the cycle would be equal to the work done by the system in another part, and the net work will be zero.

10

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

$$e = \frac{W}{Q_H}$$

$$Q_H = W + Q_L$$

$$e = \frac{W}{Q_H}$$

$$= \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

Ex. 15-9 An automobile engine has an efficiency of 20% and produces an average of 23000J of mechanical work per second during operation. (a) How much heat input is required, and (b) how much heat is discharged as waste heat from this engine per second?

$$Q_H = \frac{W}{e} = 115 kJ$$

$$\frac{Q_L}{Q_H} = 1 - e = 92 kJ$$

11

Carnot Engine

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

(1) a → b Isothermal expansion

(2) b → c Adiabatic expansion

(3) c → d Isothermal compression

(4) d → a Adiabatic compression

$Q = 0$

Q_H

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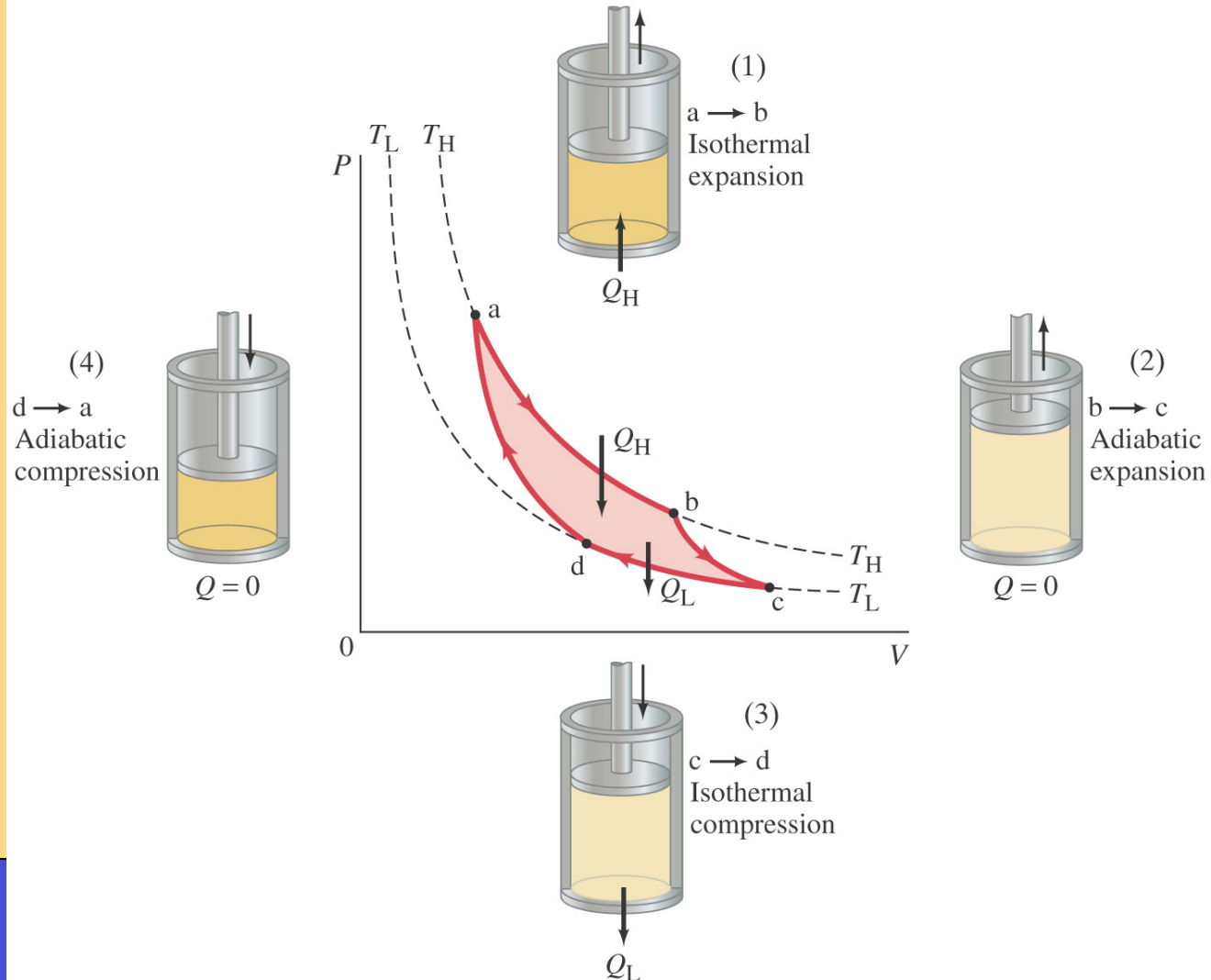
For an **ideal reversible engine**, the efficiency can be written in terms of the **temperature**:

$$e_{ideal} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_L}{T_H}$$

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.

Ex. 15-10 A steam engine operates between 500oC and 270oC. What is the maximum possible efficiency of this engine?

e_{ideal}=0.30=30%

Realistically an engine might achieve 0.70 of this value=21%

Ex. 15-11 An engine manufacturer makes the following claims: An engine's heat input per second is 9.0kJ at 435 K. The heat output per second is 4.0kJ at 285K. Do you believe these claim? (compare the efficiency with the ideal one)

$e = 0.56$

$e_{ideal} = 0.34$

It violates the 2nd law of thermodynamics

Refrigerators, Air Conditioners

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They are just the reverse of heat engines

By doing work, heat is extracted from the cold reservoir and exhausted to the hot reservoir.
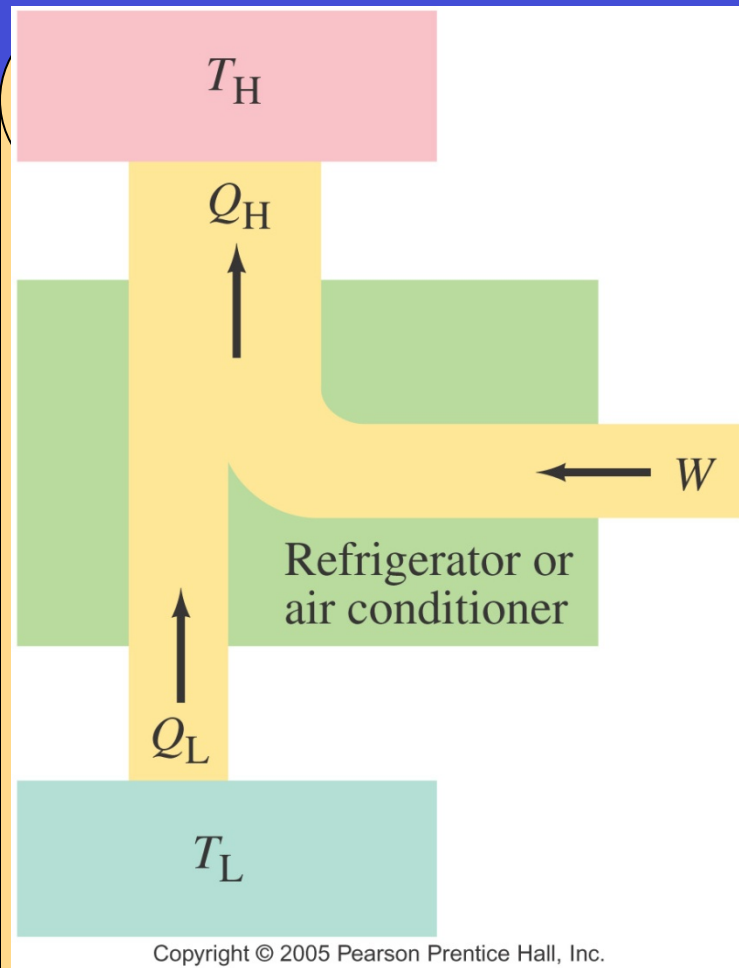
Refrigerator performance is measured by the coefficient of performance (COP):

$$\text{COP} = \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$\text{COP}_{\text{ideal}} = \frac{T_L}{T_H - T_L}$$

For a **heat pump**

$$\text{COP} = \frac{Q_H}{W}$$

Ex. 15-12 A freezer has a COP of 3.8 and uses 200 W of power. How long would it take to freeze an ice-cube tray that contains 600 g of water at 0oC? L=333 kJ/kg

$$P = \frac{W}{t} \Rightarrow t = \frac{W}{200J/s} = \frac{Q_L/COP}{200J/s} = 260s$$

Ex. 15-13 A heat pump has a coefficient of performance of 3.0 and is rated to do work at 1500 W. (a) How much heat can it add to a room per second? (b) If the heat pump were turned around to act as an air conditioner in the summer, what would you expect its coefficient of performance to be, assuming all else stays the same?

$$Q_H = COP \times W = 4500J$$

$$Q_L = Q_H - W = 3000J \Rightarrow COP = \frac{Q_L}{W} = 2.0$$

Entropy and the 2nd Law of Thermo

Thus a living organism continually increases its entropy -or, as you may say, produces positive entropy -and thus tends to approach the dangerous state of maximum entropy, which is of death. It can only keep aloof from it, i.e. alive, by continually drawing from its environment negative entropy -which is something very positive as we shall immediately see.

Erwin Schrodinger – **What is life?**   **http://home.att.net/~p.caimi/schrodinger.html**

General statement of the second law of thermodynamics:

The total entropy of any system plus that of its environment increases as a result of any natural process.

$$\Delta S = \frac{Q}{T}$$ **T is KELVIN**

Entropy is a measure of the **disorder of a system**. Natural processes tend to move toward a state of greater disorder. Examples: salt+pepper, falling object
Thermal equilibrium is a similar process – the uniform final state has more disorder than the separate temperatures in the initial state.
The 2nd law of thermodynamics define an **ARROW OF TIME** – processes occur that are **NOT REVERSIBLE**

The ideas of entropy and disorder are made clearer with the use of a statistical analysis of the molecular state of a system - Boltzmann

Ex. 15-14 An ice cube of mass 56 g is taken from a storage compartment at 0oC and placed in a paper cup. After a few minutes, exactly half of the mass of the ice cube has melted, becoming water at 0oC. Find the change in entropy of the ice/water.

L=333 kJ/kg

$$\Delta S = 34 J / K$$

Ex. 15-15 A sample of 50.0 kg of water at 20.00 C is mixed with 50.0 kg of water at 24.00 C. Estimate the change in entropy.

Final temperature will 22.00 oC – same amounts of water

$$Q = mc\Delta T = (50.0 kg)(4186 J / kg C^o)(2.00 C^o) = 4.186 \times 10^5 J$$

$$\Delta S = \Delta S_H + \Delta S_C$$

$$\Delta S_H \approx \frac{4.186 \times 10^5 J}{(23 + 273)K} = -1414 J / K < 0$$

$$\Delta S_C \approx \frac{4.186 \times 10^5 J}{(21 + 273)K} = 1424 J / K > 0$$

Net change in entropy of the whole system is positive

$$\Delta S = \Delta S_H + \Delta S_C \approx 10 J / K > 0$$

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.

There are too many particles in a system to be able to provide all microstates. Many different microstates correspond to the same macrostate. We deal with probabilties.

Example: tossing 4 coins. Macrostates describe how many heads and tails there are; the microstates list the different ways of achieving that macrostate.

All heads or all tails: most orderly arrangement but lowest probability

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

Statistical Interpretation

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

Macrostate		Number of	Probability
heads	tails	microstates	
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}

Statistical Interpretation

TABLE 15–3
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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}

The second law **does not forbid** certain processes; 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.

Form of Electric Energy Production	U.S.	World	Advantages	Disadvantages
Fossil-fuel steam plants: burn coal, oil, or natural gas to boil water, producing high-pressure steam that turns a turbine of a generator (Figs. 15–12b, 15–21); uses heat engine.	87	86	We know how to build them; for now relatively inexpensive.	Air pollution; thermal pollution; limited efficiency; land devastation from extraction of raw materials (mining); global warming; accidents such as oil spills at sea; limited fuel supply (estimates range from a couple of decades to a few centuries).
Nuclear energy:				
Fission: nuclei of uranium or plutonium atoms split ("fission") with release of energy (Chapter 31) that heats steam; uses heat engine.	8	6	Normally almost no air pollution; less contribution to global warming; relatively inexpensive.	Thermal pollution; accidents can release damaging radioactivity; difficult disposal of radioactive by-products; possible diversion of nuclear material by terrorists; limited fuel supply.
Fusion: energy released when isotopes of hydrogen (or other small nuclei) combine or "fuse" (Chapter 31).	0	0	Relatively "clean"; vast fuel supply (hydrogen in water molecules in oceans); less contribution to global warming.	Not yet workable.
Hydroelectric: Falling water turns turbines at the base of a dam.	4	7	No heat engine needed; no air, water, or thermal pollution; relatively inexpensive; high efficiency; dams can control flooding.	Reservoirs behind dams inundate scenic land or canyons; dams block upstream migration of salmon and other fish for reproduction; few locations remain for new dams; drought.
Geothermal: natural steam from inside the Earth comes to the surface (hot springs, geysers, steam vents); or cold water passed down into contact with hot, dry rock is heated to steam.	<1	<1	No heat engine needed; little air pollution; good efficiency; relatively inexpensive and "clean."	Few appropriate sites; small production; mineral content of spent hot water can pollute.
Wind power: 3-kW to 5-MW windmills (vanes up to 50 m wide) turn a generator.	<1	<1	No heat engine; no air, water or thermal pollution; relatively inexpensive.	Large array of big windmills might affect weather and be eyesores; hazardous to migratory birds; winds not always strong.
Solar energy:	<0.1	<1		
Active solar heating: rooftop solar panels absorb the Sun's rays, which heat water in tubes for space heating and hot water supply.			No heat engine needed; no air or thermal pollution; unlimited fuel supply.	Space limitations; may require back-up; relatively expensive; less effective when cloudy.
Passive solar heating: architectural devices—windows along southern exposure, sunshade over windows to keep Sun's rays out in summer.			No heat engine needed; no air or thermal pollution; relatively inexpensive.	Almost none, but other methods needed too.
Solar cells (photovoltaic cells): convert sunlight directly into electricity without use of heat engine.			No heat engine; thermal, air, and water pollution very low; good efficiency (>30% and improving).	Expensive; chemical pollution at manufacture; large land area needed as Sun's energy not concentrated.