Lecture 41

(Ch. 12: 5-6)

Topic Summary

- **Thermal Processes in Gases**
  - **Isobaric**

$$W = -P\Delta V; \quad Q = nC_p\Delta T; \quad C_p = C_v + R$$
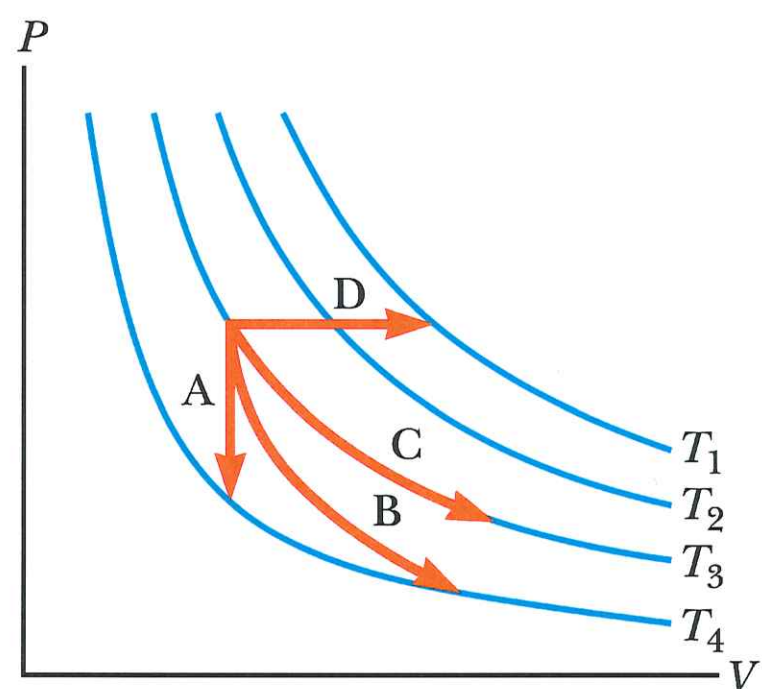
  - **Adiabatic**

$$Q = 0; \quad \Delta U = W; \quad \gamma = \frac{C_p}{C_v}$$

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

  - **Isovolumetric**

$$\Delta U = Q$$

  - **Isothermal**

$$W_{\text{env}} = nRT\ln\left(\frac{V_f}{V_i}\right)$$

Topic Summary
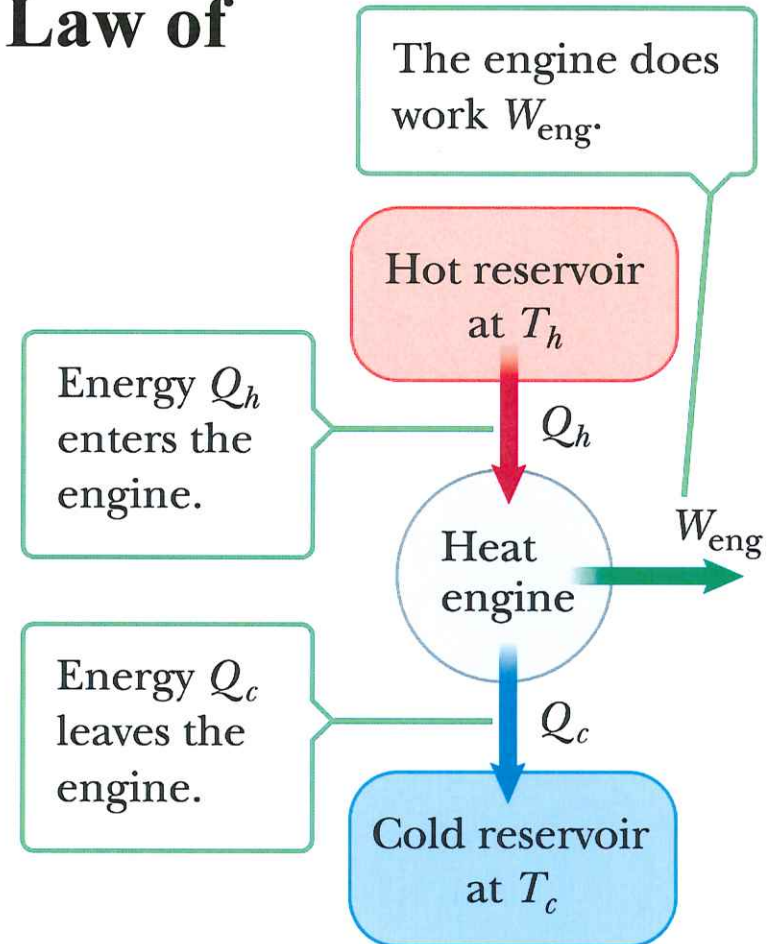
- **Heat Engines and the Second Law of Thermodynamics**

$$\Delta U = 0 \rightarrow Q = W_{eng}$$

- **Heat Engine**

$$W_{eng} = |Q_h| - |Q_c|$$

- **Thermal Efficiency**

$$e \equiv \frac{W_{eng}}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

The engine does work W_{eng}.

Hot reservoir at T_h

Energy Q_h enters the engine.

Q_h

Heat engine

W_{eng}

Energy Q_c leaves the engine.

Q_c

Cold reservoir at T_c

The Second Law of Thermodynamics

$$e = \frac{W_{\text{eng}}}{|Q_h|} < 1$$

- The first law says **we can't get a greater amount of energy out of a cyclic process than we put in.**
- The second law says **we can't break even.**

Chapter 12: Thermodynamics

Reversible and irreversible processes

With respect to time, any process falls under one of these two cases:

- The laws of physics are not broken when doing a time-reversal of a process.

- A time-reversal of a process breaks physical symmetries and laws.

  The concepts of **time arrow** and **time-reversal** are related to how a system can reach an equilibrium state.

Chapter 12: Thermodynamics

Reversible and irreversible processes

A process is **reversible** if it does not violate any law of physics when it is run backwards in time.

For example an ice cube placed on a countertop in a warm room will melt. The reverse process cannot occur: an ice cube will not form out of the puddle of water on the countertop in a warm room.

A collision between two billiard balls is reversible. Momentum is conserved if time is run forward; momentum is still conserved if time runs backwards.
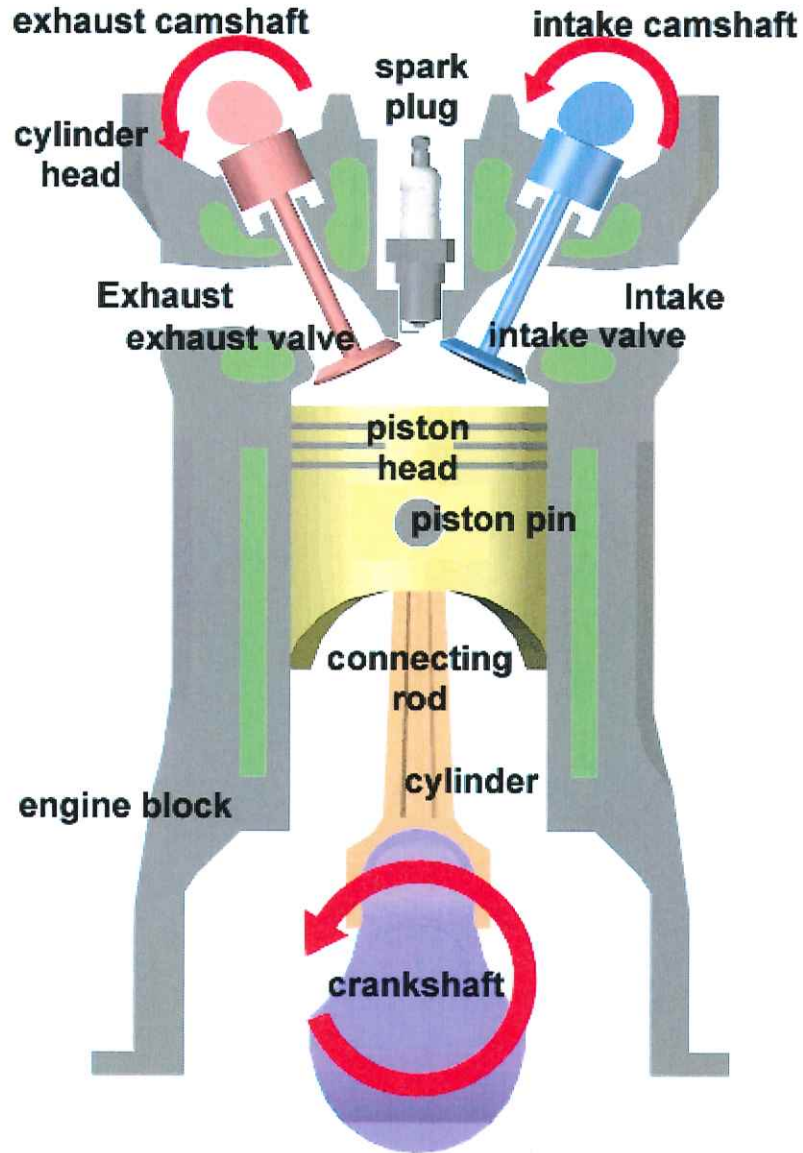
Chapter 12: Thermodynamics

Reversible and irreversible processes

A process is **not reversible** if it violates any law of physics when it is run backwards in time.

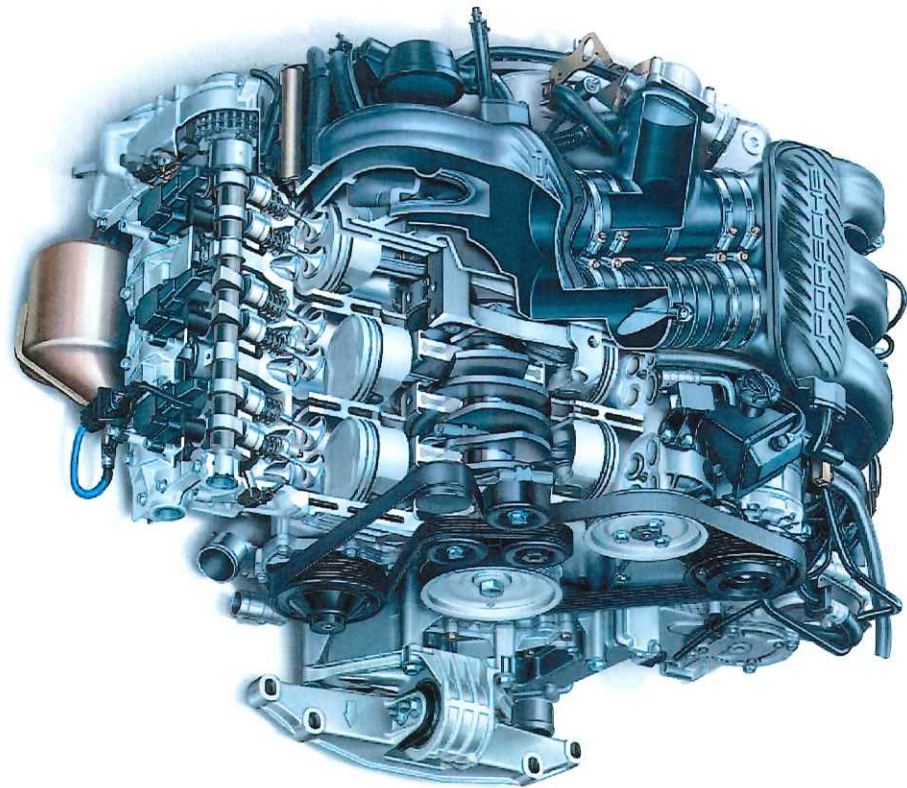Any process that involves dissipation of energy is not reversible.

Any process that involves heat transfer from a hotter object to a colder object is not reversible.
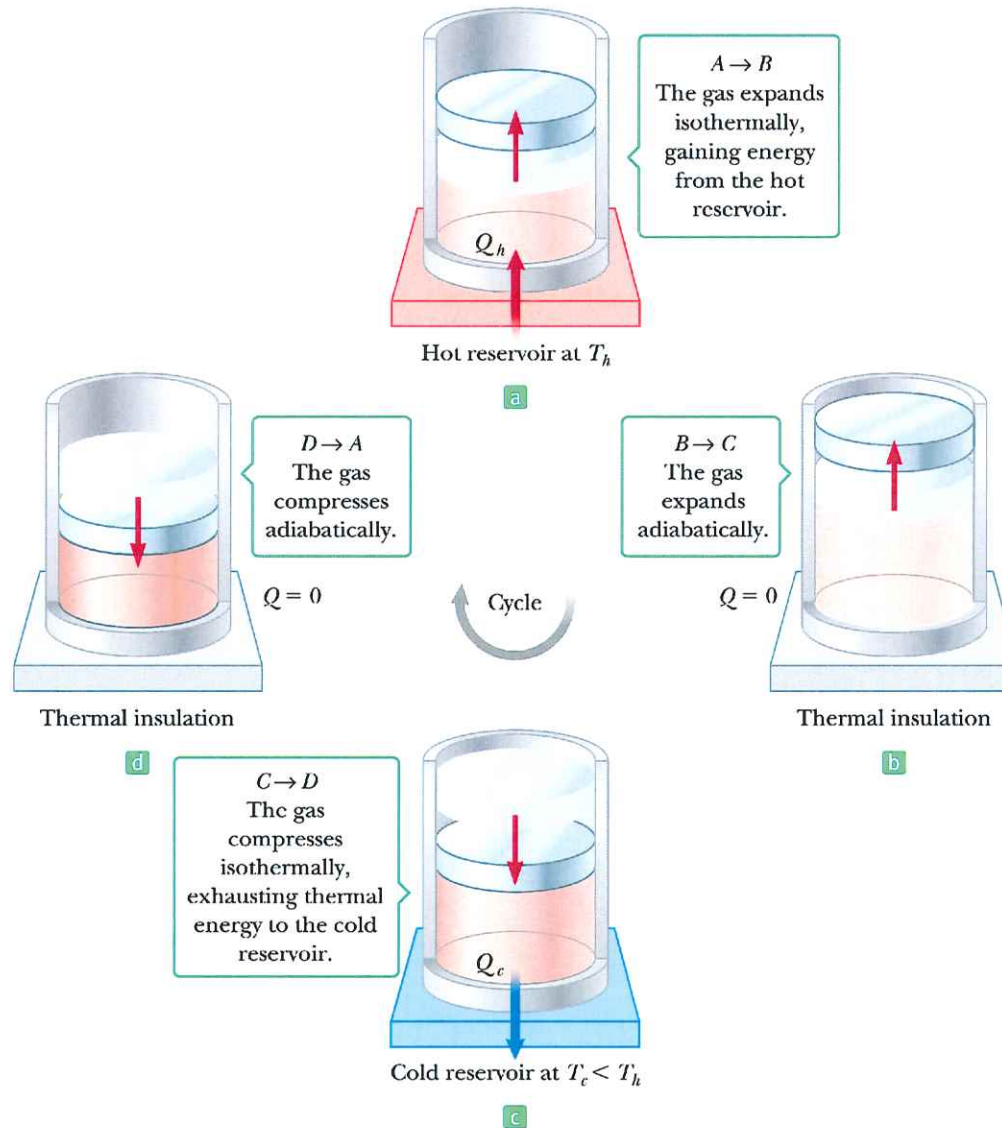
Chapter 12: Thermodynamics

exhaust camshaft

intake camshaft

spark plug

cylinder head

exhaust camshaft

Exhaust
exhaust valve

Intake
intake valve

piston head

piston pin

connecting rod

cylinder

engine block

crankshaft

CAR ENGINE

The four–stroke OTTO cycle of a conventional petrol engine

The Carnot Engine

$A \rightarrow B$
The gas expands isothermally, gaining energy from the hot reservoir.

Q_h

Hot reservoir at T_h

a

$D \rightarrow A$
The gas compresses adiabatically.

$Q = 0$

Cycle

Thermal insulation

d

$B \rightarrow C$
The gas expands adiabatically.

$Q = 0$

Thermal insulation

b

$C \rightarrow D$
The gas compresses isothermally, exhausting thermal energy to the cold reservoir.

Q_c

Cold reservoir at $T_c < T_h$

c

©Cengage

The Carnot Engine

Chapter 12: Thermodynamics

Otto Cycle

$$e = 1 - \frac{1}{r^{\gamma-1}}$$

P

IGNITION fuel combustion

3

Q_H

adiabatic   isothermals

power stroke

2

compression stroke W

cooling of exhaust gases

4

Q_C

released to surroundings

5

1

P_o

V

V_2

intake stroke
exhaust stroke

$V_1 = r\,V_2$

r = compression ratio
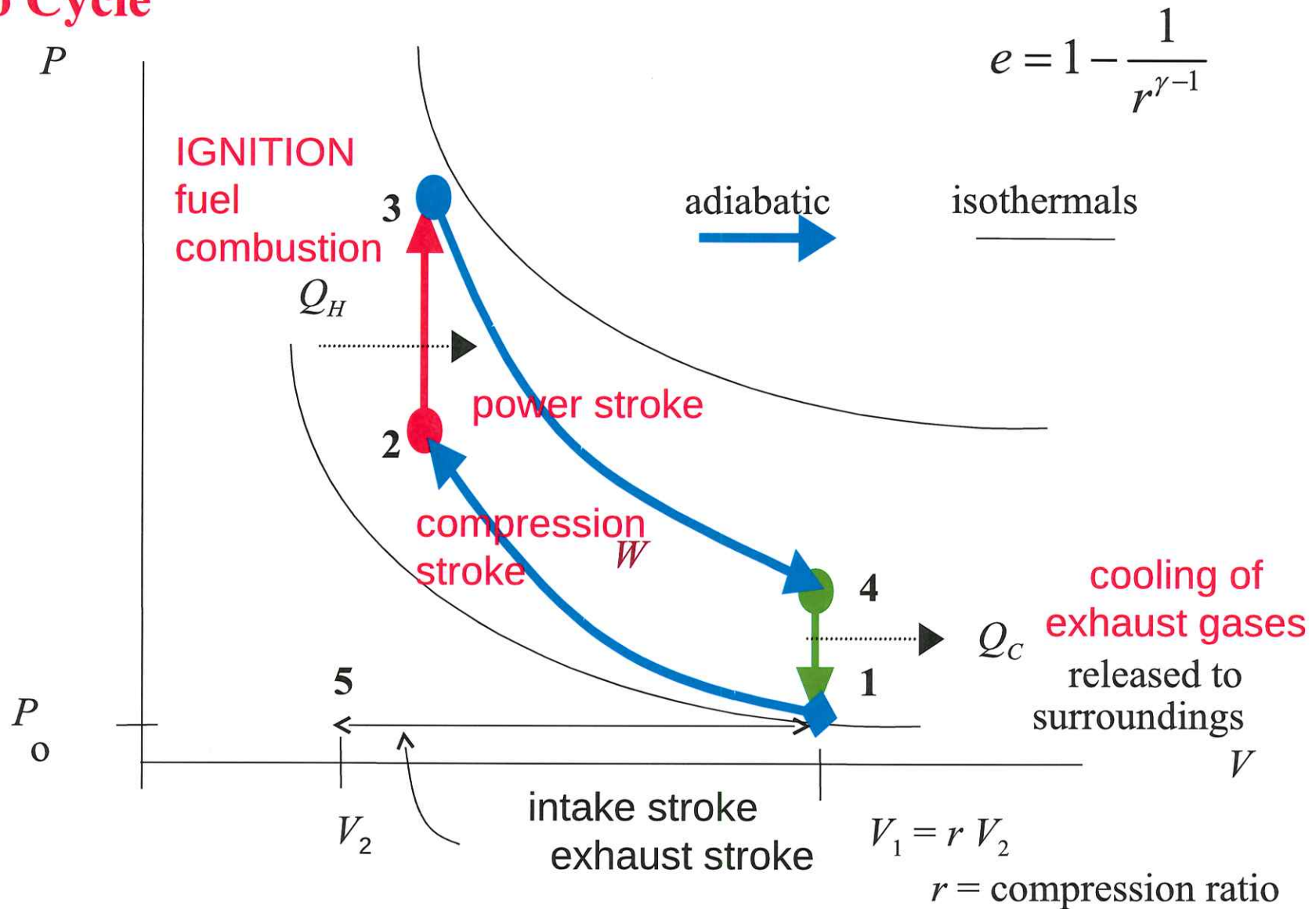
The Carnot Engine

$$\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$$

$$e \equiv \frac{W_{\text{eng}}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|} \rightarrow e_C = 1 - \frac{T_c}{T_h}$$

- All Carnot engines operating reversibly between the same two temperatures have the same efficiency.

- All real engines operate irreversibly, due to friction and the brevity of their cycles, and are therefore *less* efficient than the Carnot engine.

Chapter 12: Thermodynamics

The Carnot Engine

The **Carnot Engine** is a theoretical engine that achieves maximum efficiency. This sets a limit for how efficient a thermal engine can be. ***Any real engine has an efficiency that is lower than the one of a Carnot Engine working in the same temperature difference***. The Carnot engine is a four-step process that takes place between a hot side and a cold side, called the **Carnot cycle**. Its efficiency depends on the temperatures and increases with the increase of the difference between the two.

$$e_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

Take note that the temperatures have to be Kelvin!

Sample Problem

Imagine a Carnot engine that operates between the temperatures $T_H = 850$ K and $T_L = 300$ K. The engine performs 1200 J of work each cycle, which takes 0.25 s.

(a) What is the efficiency of this engine?

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300\,K}{850\,K} = 0.647$$

(b) What is the average power of this engine?

$$P = \frac{W}{t} = \frac{1200\,J}{0.25\,s} = 4800\,W = 4.8\,kW$$

Sample Problem 20-5

An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and the freezing points of water. Is this possible?

$$\varepsilon \le \varepsilon_{Carnot} = 1 - \frac{T_L}{T_H} = 1 - \frac{(0+273)\,K}{(100+273)\,K} = 0.268 \approx 27\%$$

NO !

Find the maximum possible efficiency of a heat engine operating between the freezing (0 °C) and boiling (100 °C) points of water. Note $T_K = T_C + 273.15$

The maximum efficiency is that of a Carnot engine, one minus the temperature (in K) ratio between the cold and hot reservoirs.

Known: $T_C = 0°C; T_H = 100°C.$

SOLVE   The maximum efficiency is:

$$e_{Carnot} = 1 - \frac{T_C}{T_H} = 1 - \frac{(0°C)}{(100°C)} = 1 - \frac{(273\ K)}{(373\ K)} = 0.268$$

Chapter 12: Thermodynamics

The *first law* allows us to calculate the energy changes in processes. However, these changes do not suggest any spontaneity. The only condition required is that of energy conservation.

A distinction between spontaneous and non-spontaneous comes in the form of the *second law of thermodynamics*:

Heat never flows spontaneously from a colder body to a hotter body.

Heat flows spontaneously only from hotter to cooler objects.

Chapter 12: Thermodynamics

Entropy

The second law of thermodynamics may seem rather qualitative and imprecise, but the concept of **entropy** (symbol **S**) makes it quantitative.

Entropy is a state variable. It is often difficult to compute entropy. What is more important is that the change in entropy that takes place when heat flows. That change is :

$$\Delta S = \frac{Q}{T}, \text{ entropy change; in SI: J/K}$$

The **net entropy change** is always positive.

$$\Delta S_{net} = \Delta S_{cool} + \Delta S_{hot} > 0$$

Entropy

$$\Delta S \equiv \frac{Q_r}{T} \quad \text{SI unit}: \text{joules} / \text{kelvin} \left(J / K \right)$$

The entropy of the Universe increases in all natural processes.

Chapter 12: Thermodynamics

Entropy is not conserved!

Various other expressions for the second law of thermodynamics:

Heat flow is accompanied by an increase in the entropy of the universe.

No device can exceed 100% efficiency.

Energy differences can only come from transport and conversions, not spontaneous generation.

Chapter 12: Thermodynamics

Suppose you have two large objects in thermal contact, one at $T_1 = 300$ K and the other at $T_2 = 400$ K.

The second law of thermodynamics says that heat flows from the hotter to the cooler object.

Suppose that after a short time, 24kJ of heat has flowed.

$T_1 = 300$ K $\quad Q = 24$ kJ $\quad T_2 = 400$ K
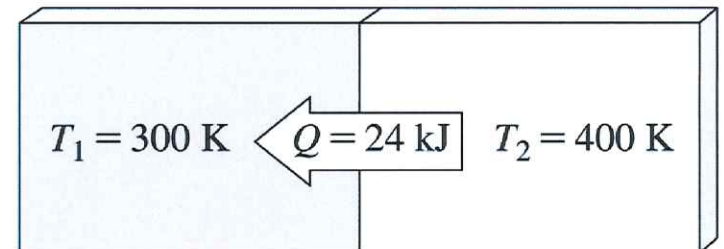
The entropy changes of the two objects:

$$\Delta S_{cool} = \frac{Q}{T_{cool}} = \frac{24,000J}{300K} = 80J/K$$

$$\Delta S_{hot} = \frac{Q}{T_{hot}} = \frac{-24,000J}{400K} = -60J/K$$

$$\Delta S_{total} = \Delta S_{cool} + \Delta S_{hot} = 80J/K - 60J/K = +20J/K$$

That illustrates a general rule: Heat flow from a hotter to a cooler body is accompanied by <u>an increase in the system's total entropy</u>.

Problem # 2 How much energy must be transferred as heat for a reversible isothermal expansion of an ideal gas at 132° C if the entropy of the gas increases by 46 J/K ?

- From Eq. 20-2, $\Delta S = S_f - S_i = \dfrac{Q}{T}$

we obtain

$$Q = T\Delta S = (405 \text{ K})(46.0 \text{ J/K}) = 1.86 \times 10^4 \text{ J}.$$

48. A 65-g ice cube is initially at 0.0°C.

  a. Find the change in entropy of the cube after it melts completely at 0.0°C.

  b. What is the change in entropy of the environment in this process? *Hint:* The latent heat of fusion for water is 3.33×10^5 J/kg.

12.48 **(a)** The energy transferred to the ice cube as it melts at a constant

  temperature of $T = 0.0°C = 273$ K is $Q_{ice} = +m_{ice}L_f$ and the change in

  entropy of the ice cube is

$$\Delta S_{env} = \frac{Q_{ice}}{T} = \frac{m_{ice}L_f}{T} = \frac{(0.065 \text{ kg})(3.33 \times 10^5 \text{ J/kg})}{273 \text{ K}} = \boxed{+79 \text{ J/K}}$$

  (b) The energy transferred to the environment during this melting

  process is $Q_{env} = -Q_{ice} = -m_{ice}L_f$ and the change in entropy of the

  environment is

$$\Delta S_{env} = \frac{Q_{env}}{T} = \frac{-m_{ice}L_f}{T} = \boxed{-79 \text{ J/K}}$$

53. **T** The surface of the Sun is approximately at 5.70×10^3 K, and the temperature of the Earth's surface is approximately 290. K. What entropy change occurs when 1.00×10^3 J of energy is transferred by heat from the Sun to the Earth?

12.53 A quantity of energy, of magnitude Q, is transferred from the Sun and

added to Earth. Thus, $\Delta S_{Sun} = \dfrac{-Q}{T_{Sun}}$ and $\Delta S_{Earth} = \dfrac{+Q}{T_{Earth}}$, so the total

change in entropy is

$$\Delta S_{total} = \Delta S_{Earth} + \Delta S_{Sun} = \frac{Q}{T_{Earth}} - \frac{Q}{T_{Sun}}$$

$$= (1\ 000\ J)\left(\frac{1}{290\ K} - \frac{1}{5\ 700\ K}\right) = \boxed{+3.27\ J/K}$$

Entropy and Disorder

Isolated systems tend toward greater disorder $\rightarrow$ entropy is a measure of that disorder.

$$S = k_B \ln W$$

$$k_B = 1.38 \times 10^{-23} \text{ J}/\text{K}$$

Chapter 12: Thermodynamics

Boltzmann's equation for entropy (yes, the one on the tombstone).

The entropy of a macrostate that consists of Ω microstates is:

$$S = k. \log W$$

$$S = k_B \ln \Omega$$

If there is just one microstate, than the entropy is 0. This means that the system is maximally ordered in that macrostate that can only have one microstate.
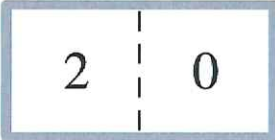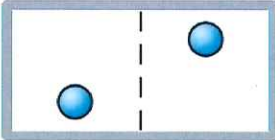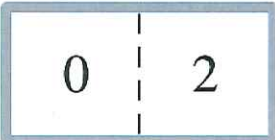
Another 2nd law: Natural processes tend to evolve toward a state of maximum entropy (min. order = max. disorder).

Chapter 12: Thermodynamics

Statistical Interpretation of Entropy

Microstates and *macrostates*, plus probabilities.

In this two-molecule ideal gas we have a total of 4 microstates and 3 macrostates.

Microstates (ways of distributing the two atoms in the two halves of the box)	Macrostates (number of atoms in each half)		

In macrostate 1 there is one microstate out of 4. The probability is ¼.
For MS 2 there are 2 microstates out of 4, so the probability is ½.
Microstate 3 has, again, a probability of ¼.
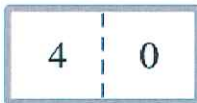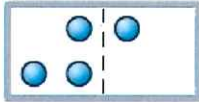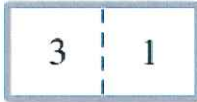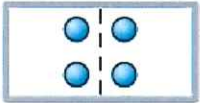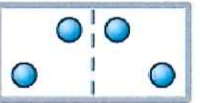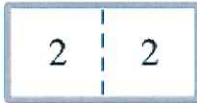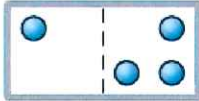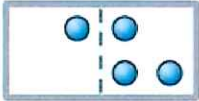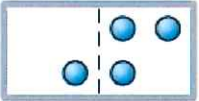
Chapter 12: Thermodynamics

Statistical Interpretation of Entropy

Microstates and *macrostates*, plus probabilities.

In a four-molecule ideal gas we have a total of 16 microstates and 5 macrostates.

Microstates (16 total)	Macrostates	Probability of macrostate
	4 ⦙ 0	$\frac{1}{16} = 0.06$
	3 ⦙ 1	$\frac{4}{16} = 0.25$
	2 ⦙ 2	$\frac{6}{16} = 0.38$
	1 ⦙ 3	$\frac{4}{16} = 0.25$
	0 ⦙ 4	$\frac{1}{16} = 0.06$

Entropy and Disorder
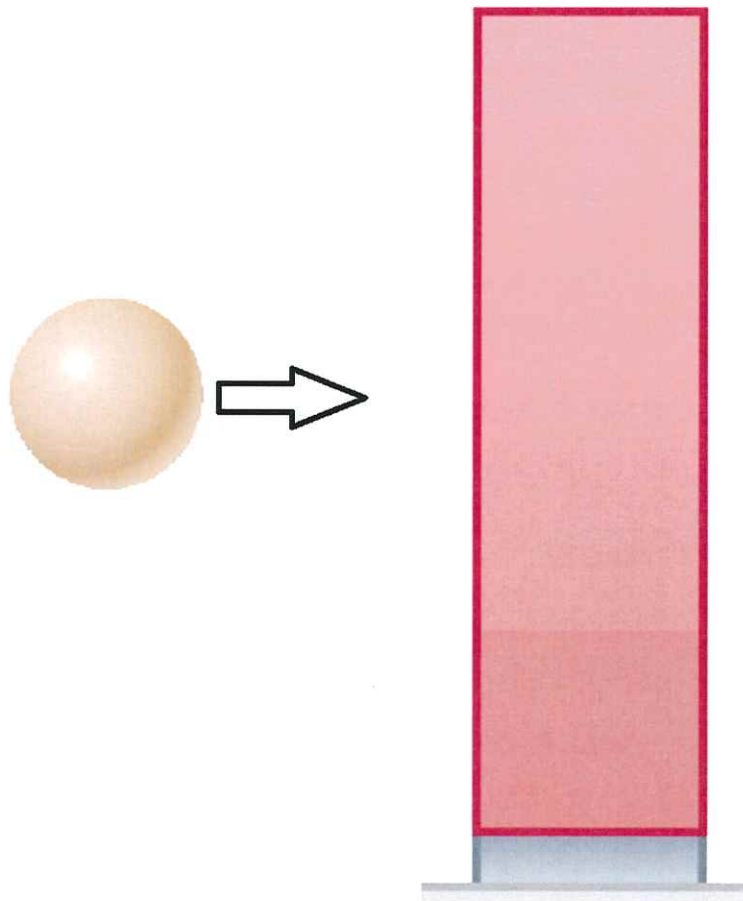
In all real processes, the energy available for doing work decreases.

The entropy of the Universe always increases.

Figure 14.17
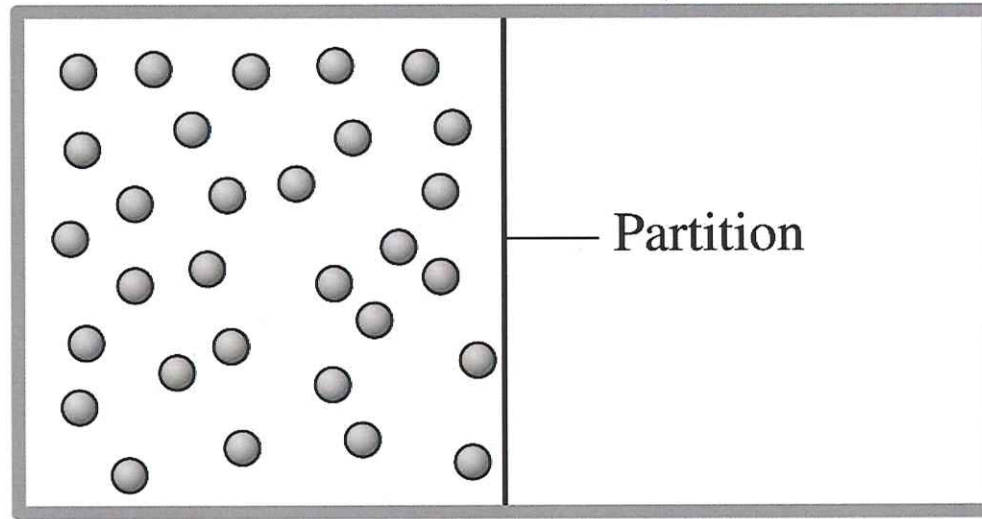
Partition

When the partition is removed, the molecules spread evenly through the container.

S↑

so with diffusion

S↑

© 2010 Pearson Education, Inc.

Figure 14.18

Cold (slower average speed)   Hot (faster average speed)
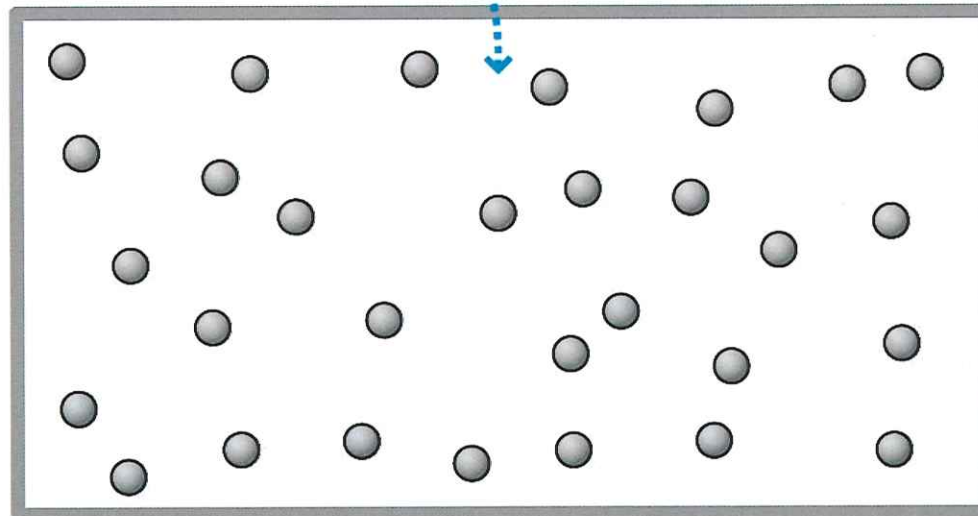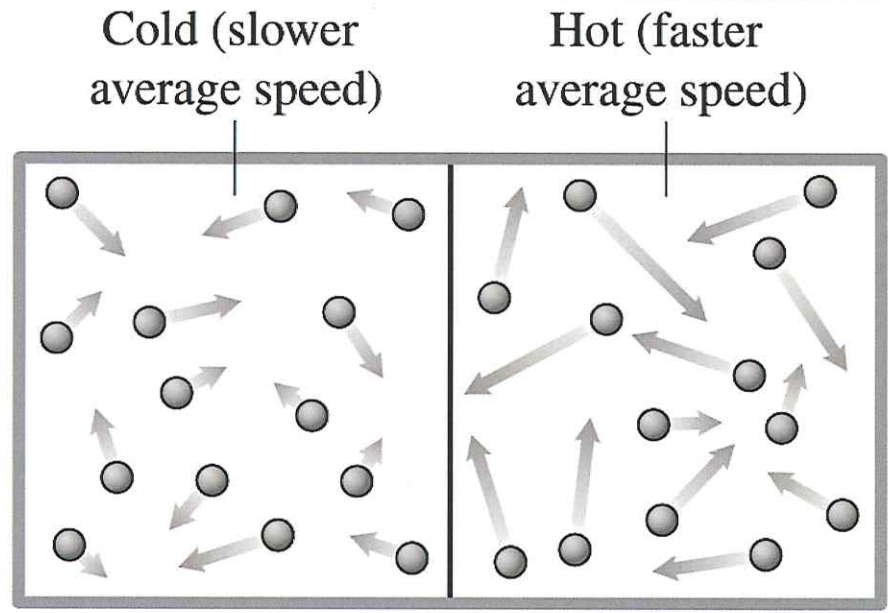
Entropy increases

→ low S, ordered state

After mixing, average molecular speed is intermediate throughout the container.

→ high S, disordered state

But

So with Q, SP

Q

© 2010 Pearson Education, Inc.
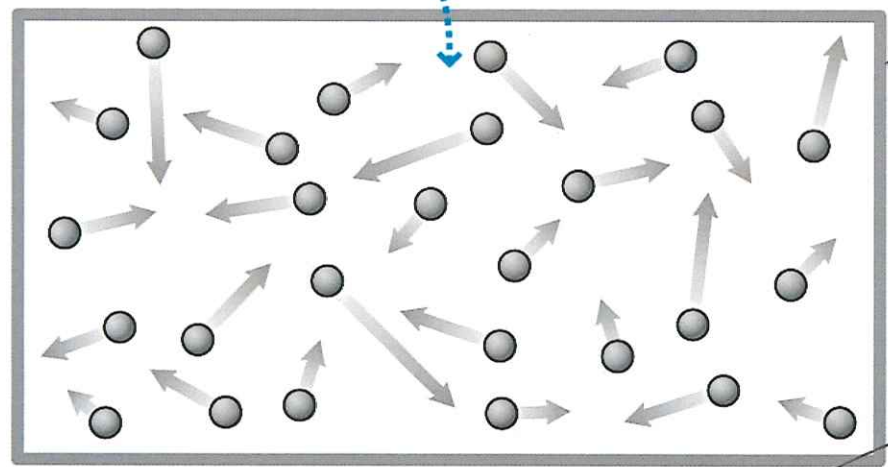
Human Metabolism

$$\frac{\Delta U}{\Delta t} = \frac{Q}{\Delta t} + \frac{W}{\Delta t}$$

Measuring the Metabolic Rate $\Delta U / \Delta t$

Laurent/B./American Hospital of Paris/Science Source

The metabolic rate is directly proportional to the rate of oxygen consumption by volume.

$$\frac{\Delta U}{\Delta t} = 4.8 \frac{\Delta V_{O_2}}{\Delta t}$$

Metabolic Rate, Activity, and Weight Gain

Table 12.4 Oxygen Consumption and Metabolic Rates for Various Activities for a 65-kg Male[a]

Activity	O_2 Use Rate (mL/min · kg)	Metabolic Rate (kcal/h)	Metabolic Rate (W)
Sleeping	3.5	70	80
Light activity (dressing, walking slowly, desk work)	10	200	230
Moderate activity (walking briskly)	20	400	465
Heavy activity (basketball, swimming a fast breaststroke)	30	600	700
Extreme activity (bicycle racing)	70	1 400	1 600

[a]*Source: A Companion to Medical Studies*, 2/e, R. Passmore, Philadelphia, F. A. Davis, 1968.

1 lb fat $\rightarrow$ 4100 kcal

Run 1 mile/day: 35 days×120 kcal/day = 4200 kcal

Eat 2 fewer slices of bread per day:

35 days×2 slices/day×60 kcal/slice = 4200 kcal

Physical Fitness and Efficiency of the Human Body as a Machine

Table 12.5 Physical Fitness and Maximum Oxygen Consumption Rate[a]

Fitness Level	Maximum Oxygen Consumption Rate (mL/min · kg)
Very poor	28
Poor	34
Fair	42
Good	52
Excellent	70

[a] *Source: Aerobics*, K. H. Cooper, Bantam Books, New York, 1968.

$$\frac{\Delta U}{\Delta t} = \frac{Q}{\Delta t} + \frac{W}{\Delta t}$$

e = body's efficiency

$$= \frac{|W/\Delta t|}{|\Delta U/\Delta t|}$$

Physical Fitness and Efficiency of the Human Body as a Machine

Table 12.6 Metabolic Rate, Power Output, and Efficiency for Different Activities[a]

Activity	Metabolic Rate $\dfrac{\Delta U}{\Delta t}$ (watts)	Power Output $\dfrac{W}{\Delta t}$ (watts)	Efficiency e
Cycling	505	96	0.19
Pushing loaded coal cars in a mine	525	90	0.17
Shoveling	570	17.5	0.03

[a] *Source:* "Inter- and Intra-Individual Differences in Energy Expenditure and Mechanical Efficiency," C. H. Wyndham et al., *Ergonomics* **9**, 17 (1966).

59. **BIO** Sweating is one of the main mechanisms with which the body dissipates heat. Sweat evaporates with a latent heat of 2 430 kJ/kg at body temperature, and the body can produce as much as 1.5 kg of sweat per hour. If sweating were the only heat dissipation mechanism, what would be the maximum sustainable metabolic rate, in watts, if 80% of the energy used by the body goes into waste heat?

12.59   The maximum rate at which the body can dissipate waste heat by sweating is

$$\frac{\Delta Q}{\Delta t} = \left(\frac{\Delta m}{\Delta t}\right) L_v = \left(1.5\frac{kg}{h}\right)\left(2\ 430\times10^3\frac{J}{kg}\right)\left(\frac{1\ h}{3\ 600\ s}\right) = 1.0\times10^3\ W$$

If this represents 80% of the maximum sustainable metabolic rate [i.e.,

$\Delta Q/\Delta t = 0.80(\Delta U/\Delta t)_{max}$], then that maximum rate is

$$\left(\frac{\Delta U}{\Delta t}\right)_{max} = \frac{\Delta Q/\Delta t}{0.80} = \frac{1.0\times10^3\ W}{0.80} = \boxed{1.3\times10^3\ W}$$

60. **BIO** A woman jogging has a metabolic rate of 625 W.

a. Calculate her volume rate of oxygen consumption in L/s.

b. Estimate her required respiratory rate in breaths/min if her lungs inhale 0.600 L of air in each breath and air is 20.9% oxygen.

12.60 The metabolic rate equation requires a metabolic rate in units of kcal/s.

Convert 625 W to kcal/s:

$$625 \text{ W} = 625 \text{ J/s}\left(\frac{1 \text{ kcal}}{4186 \text{ J}}\right) = 0.149 \text{ kcal/s}$$

(a) Her volume rate of oxygen consumption is then

$$\frac{\Delta U}{\Delta t} = 4.8 \frac{\Delta V_{O_2}}{\Delta t} \rightarrow \frac{\Delta V_{O_2}}{\Delta t} = \frac{1}{4.8}\frac{\Delta U}{\Delta t} = \frac{1}{4.8}(0.149 \text{ kcal/s}) = \boxed{3.10\times10^{-2} \text{ L/s}}$$

(b) Finding the respiratory rate R in breaths/min requires a unit conversion from L/s to breaths/min:

$$R = 3.10\times10^{-2} \frac{L_{O_2}}{s}\left(\frac{1 \text{ breath}}{0.600 \text{ L}_{air}}\right)\left(\frac{1 \text{ L}_{air}}{0.209 \text{ L}_{O_2}}\right)\left(\frac{60 \text{ s}}{1 \text{ min}}\right) = \boxed{14.8 \text{ breaths/min}}$$

61. **BIO** Suppose a highly trained athlete consumes oxygen at a rate of 70.0 mL/(min · kg) during a 30.0-min workout. If the athlete's mass is 78.0 kg and their body functions as a heat engine with a 20.0% efficiency, calculate

    a. their metabolic rate in kcal/min and

       Answer ↓

    b. the thermal energy in kcal released during the workout.

12.61 (a) The 78.0-kg athlete consumes oxygen at a rate of

$$\frac{\Delta V_{O_2}}{\Delta t} = \left(70.0\frac{mL}{min \cdot kg}\right)(78.0 \text{ kg})\left(\frac{10^{-3} \text{ L}}{1 \text{ mL}}\right)\left(\frac{1 \text{ min}}{60 \text{ s}}\right) = 9.10 \times 10^{-2} \text{ L/s}$$

with a metabolic rate of

$$\frac{\Delta U}{\Delta t} = 4.8\frac{\Delta V_{O_2}}{\Delta t} = (4.8)(9.10 \times 10^{-2} \text{ L/s}) = 0.437 \text{ kcal/s} = \boxed{26.2 \text{ kcal/min}}$$

(b) Treating the athlete as a heat engine operating for 30.0 min with an efficiency of 20.0%, $|Q_h| = \Delta U = 26.2 \text{ kcal/min}(30.0 \text{ min}) = 786 \text{ kcal} \cdot$

Applying the definition of efficiency gives the energy released to the environment (the cold reservoir):

$$e = 1 - \frac{\Delta U}{|Q_c|} \quad \rightarrow \quad |Q_c| = (1-e)\Delta U$$

$$|Q_c| = (1-0.200)(786 \text{ kcal}) = \boxed{629 \text{ kcal}}$$