

• PROGRAM OF “PHYSICS”

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PHYSICS 2

(FLUID MECHANICS AND THERMAL PHYSICS)

02 credits (30 periods)

Chapter 1 Fluid Mechanics

**Chapter 2 Heat, Temperature and the Zeroth
Law of Thermodynamics**

**Chapter 3 Heat, Work and the First Law of
Thermodynamics**

Chapter 4 The Kinetic Theory of Gases

**Chapter 5 Entropy and the Second Law of
Thermodynamics**

Chapter 5

Heat Engine, Entropy and the Second Law of Thermodynamics

- 1 Heat Engines and
the Second Law of Thermodynamics**
- 2 Reversible and Irreversible Processes**
- 3 The Carnot Engine**
- 4 Gasoline and Diesel Engines**
- 5 Heat Pumps and Refrigerators**
- 6 Entropy**

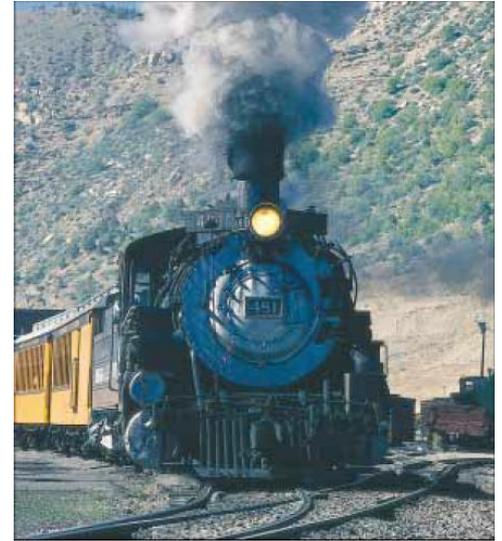
1 Heat Engines and the Second Law of Thermodynamics

1.1 Notion

A *heat engine* is a device that converts internal energy (heat) to other useful forms, such as electrical or mechanical energy

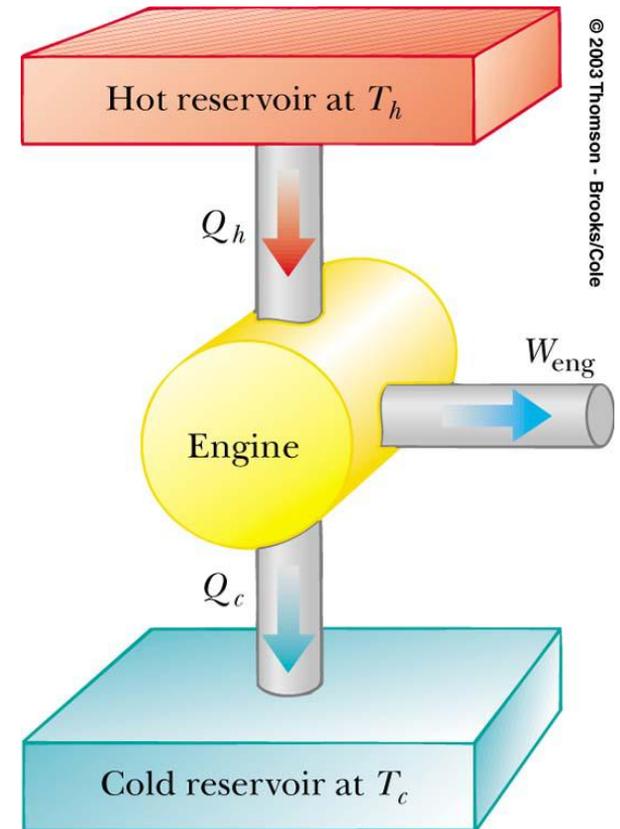
A heat engine carries some **working substance** through a **cyclical process**

In internal-combustion engines, such as those used in automobiles, the working substance is a mixture of air and fuel; in a steam turbine it is water.



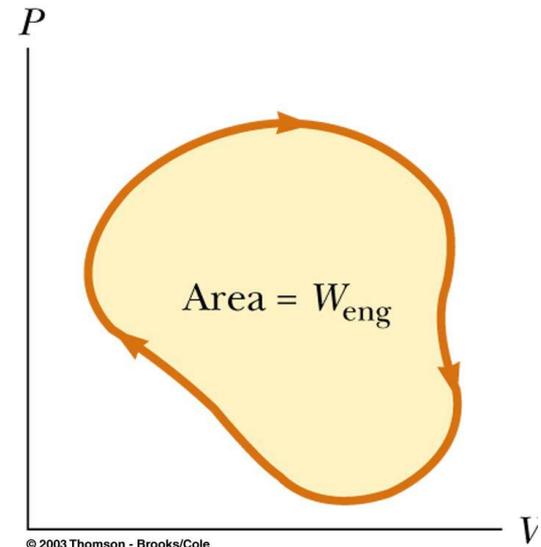
1.2 Working principle of a heat engine

- ▶ Energy is transferred from a source at a high temperature (Q_h)
- ▶ Work is done by the engine (W_{eng})
- ▶ Energy is expelled to a source at a lower temperature (Q_c)



Schematic representation of a heat engine

- ▶ Since it is a cyclical process, $\Delta U = 0$
 - Its initial and final internal energies are the same
- ▶ Therefore, from the first law of thermodynamics :
$$\Delta U = Q_{\text{net}} - W_{\text{eng}} = 0$$
$$\rightarrow Q_{\text{net}} = W_{\text{eng}} ; Q_{\text{h}} - Q_{\text{c}} = W$$
- ▶ The **work done** by the engine equals the **net energy** absorbed by the engine
- ▶ The work is equal to the area enclosed by the curve of the PV diagram

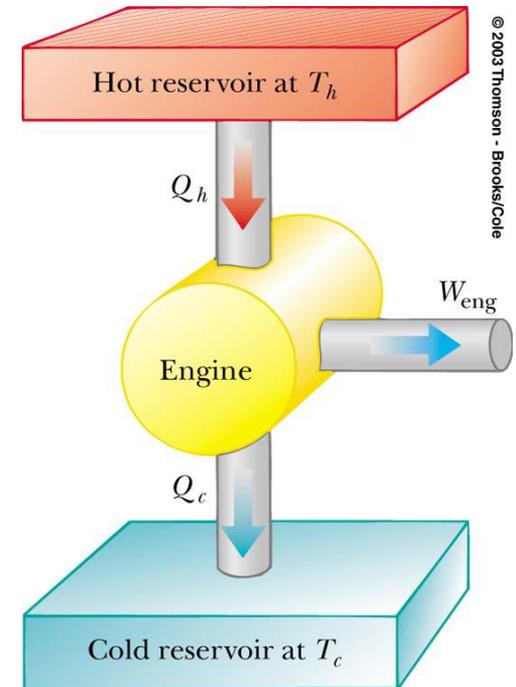


1.3 Thermal Efficiency of a Heat Engine

- ▶ Thermal efficiency is defined as the ratio of the work done by the engine to the energy absorbed at the higher temperature

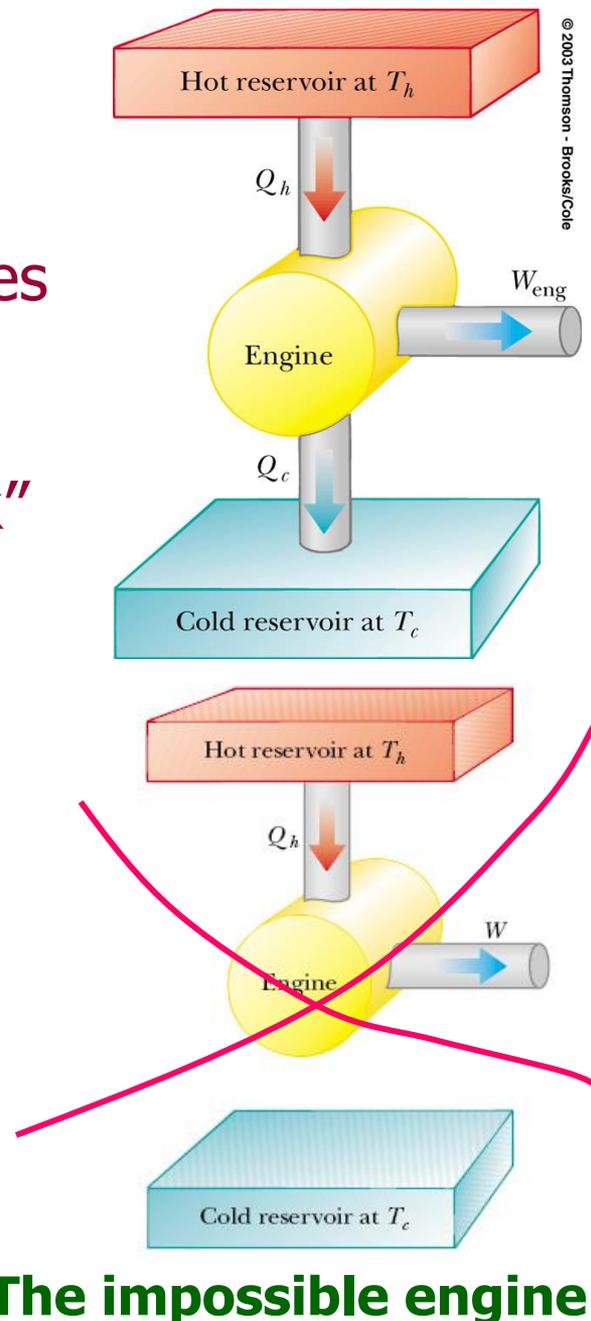
$$e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

- ▶ $e = 1$ (100% efficiency) only if $Q_c = 0$
 - No energy expelled to cold reservoir



1.4 Second Law of Thermodynamics

- ▶ “It is **impossible** to construct a heat engine that, operating in a cycle, produces no other effect than the absorption of energy from a reservoir and the performance of an equal amount of work”
 - Means that Q_c cannot equal 0
 - ▶ Some Q_c must be expelled to the environment
 - Means that e cannot equal 100%



PROBLEM 1 Find the efficiency of a heat engine that absorbs 2 000 J of energy from a hot reservoir and exhausts 1500 J to a cold reservoir.

SOLUTION

$$e = 1 - \frac{Q_c}{Q_h} = 1 - \frac{1\,500\text{ J}}{2\,000\text{ J}} = 0.25, \text{ or } 25\%$$

- PROBLEM 2** A diesel engine performs 2200 J of mechanical work and discards 4300 J of heat each cycle.
- (a)** How much heat must be supplied to the engine in each cycle?
- (b)** What is the thermal efficiency of the engine?

SOLUTION

(a) $Q_H = W + |Q_C| = 6500 \text{ J}.$

(b) $e = \frac{2200 \text{ J}}{6500 \text{ J}} = 0.34 = 34\%.$

PROBLEM 3 An aircraft engine takes in 9000 J of heat and discards 6400 J each cycle.

(a) What is the mechanical work output of the engine during one cycle?

(b) What is the thermal efficiency of the engine?

SOLUTION

(a) $W = 9000 \text{ J} - 6400 \text{ J} = 2600 \text{ J}.$

(b) $e = \frac{W}{Q_H} = \frac{2600 \text{ J}}{9000 \text{ J}} = 0.29 = 29\%.$

PROBLEM 4 A gasoline engine has a power output of 180 kW (about 241 hp). Its thermal efficiency is 28.0%.

(a) How much heat must be supplied to the engine per second?

(b) How much heat is discarded by the engine per second?

SOLUTION

$$\text{(a)} \quad Q_H = \frac{W}{e} = \frac{180 \times 10^3 \text{ J}}{0.280} = 6.43 \times 10^5 \text{ J}.$$

$$\text{(b)} \quad |Q_C| = |Q_H| - W = 6.43 \times 10^5 \text{ J} - 1.80 \times 10^5 \text{ J} = 4.63 \times 10^5 \text{ J}.$$

PROBLEM 5 A gasoline engine in a large truck takes in 10,000 J of heat and delivers 2000 J of mechanical work per cycle. The heat is obtained by burning gasoline with heat of combustion $L_C = 5.0 \times 10^4 \text{ J/g}$.

(a) What is the thermal efficiency of this engine?

(b) How much heat is discarded in each cycle?

(c) How much gasoline is burned in each cycle?

(d) If the engine goes through 25 cycles per second, what is its power output in watts? In horsepower?

SOLUTION

$$\mathbf{(a)} \quad e = \frac{W}{Q_H} = \frac{2000 \text{ J}}{10,000 \text{ J}} = 0.20 = 20\%$$

$$\begin{aligned} \mathbf{(b)} \quad Q_C &= W - Q_H = 2000 \text{ J} - 10,000 \text{ J} \\ &= -8000 \text{ J} \end{aligned}$$

PROBLEM 5 A gasoline engine in a large truck takes in 10,000 J of heat and delivers 2000 J of mechanical work per cycle. The heat is obtained by burning gasoline with heat of combustion $L_c = 5.0 \times 10^4 \text{ J/g}$.

(a) What is the thermal efficiency of this engine?

(b) How much heat is discarded in each cycle?

(c) How much gasoline is burned in each cycle?

(d) If the engine goes through 25 cycles per second, what is its power output in watts? In horsepower?

SOLUTION

$$\text{(c)} \quad Q_H = mL_c \quad m = \frac{Q_H}{L_c} = \frac{10,000 \text{ J}}{5.0 \times 10^4 \text{ J/g}} = 0.20 \text{ g}$$

$$\begin{aligned} \text{(d)} \quad P &= (2000 \text{ J/cycle})(25 \text{ cycles/s}) = 50,000 \text{ W} = 50 \text{ kW} \\ &= (50,000 \text{ W}) \frac{1 \text{ hp}}{746 \text{ W}} = 67 \text{ hp} \end{aligned}$$

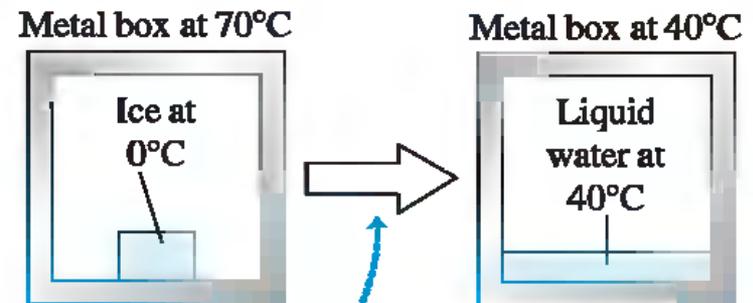
2 Reversible and Irreversible Processes

Thermodynamic processes that occur in nature are all **irreversible processes**.

These are processes that proceed spontaneously **in one direction** but not the other

EXAMPLE :

- The flow of heat from a hot body to a cooler body
- Sliding a book across a table converts mechanical energy into heat by friction (a book initially at rest on the table would spontaneously start moving and the table and book would cool down ?).
- A block of ice melts irreversibly when we place it in a hot (70°C) metal box.



Heat flows from the box into the ice and water, never the reverse.

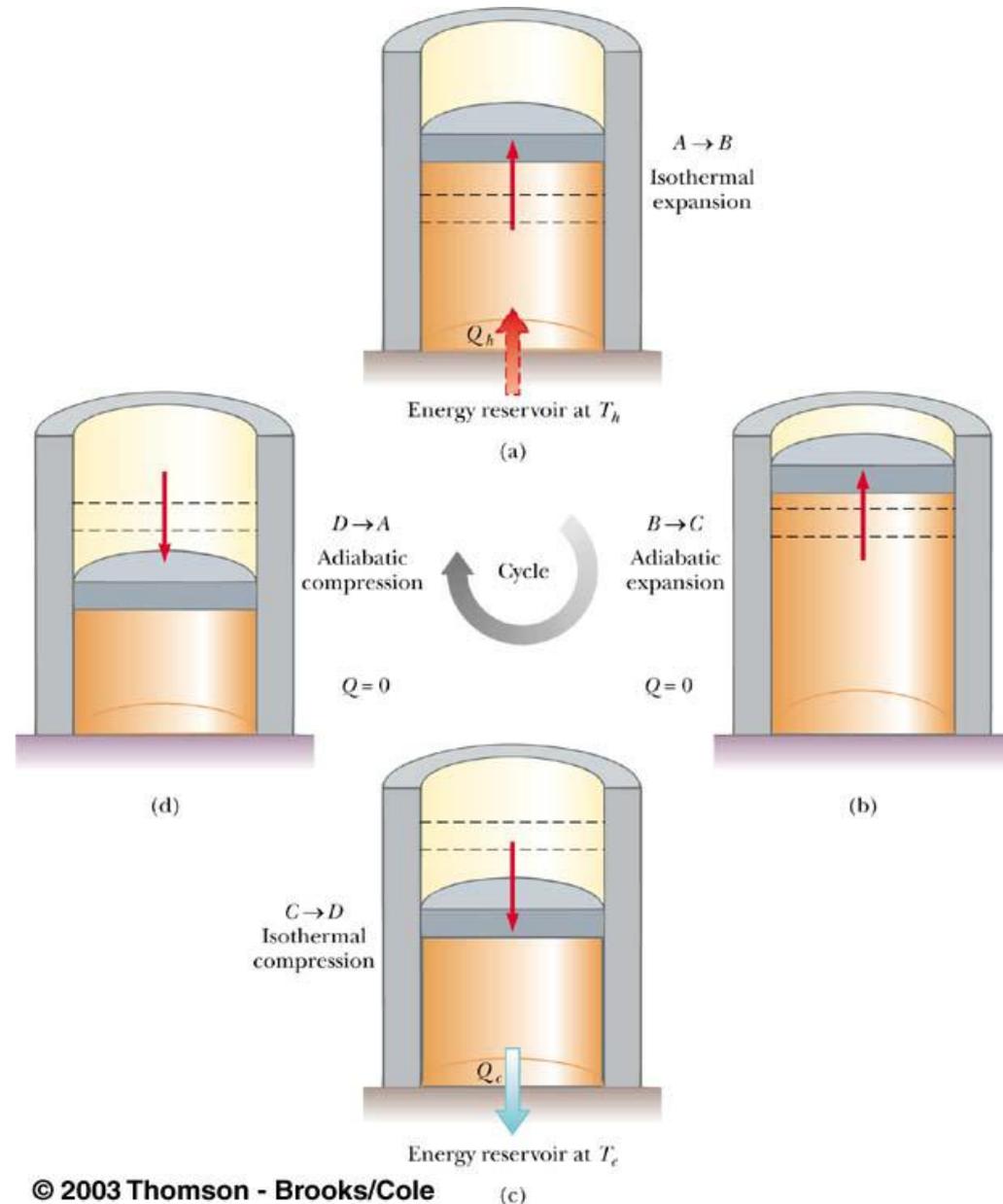
2 Reversible and Irreversible Processes

- ▶ A *reversible* process is one in which every state along some path is an equilibrium state
 - And one for which the system can be returned to its initial state along the same path
- ▶ An *irreversible* process does not meet these requirements
 - Most natural processes are irreversible
 - Reversible processes are an idealization, but some real processes are good approximations

Reversible processes are thus equilibrium processes, with the system always **in thermodynamic equilibrium.**

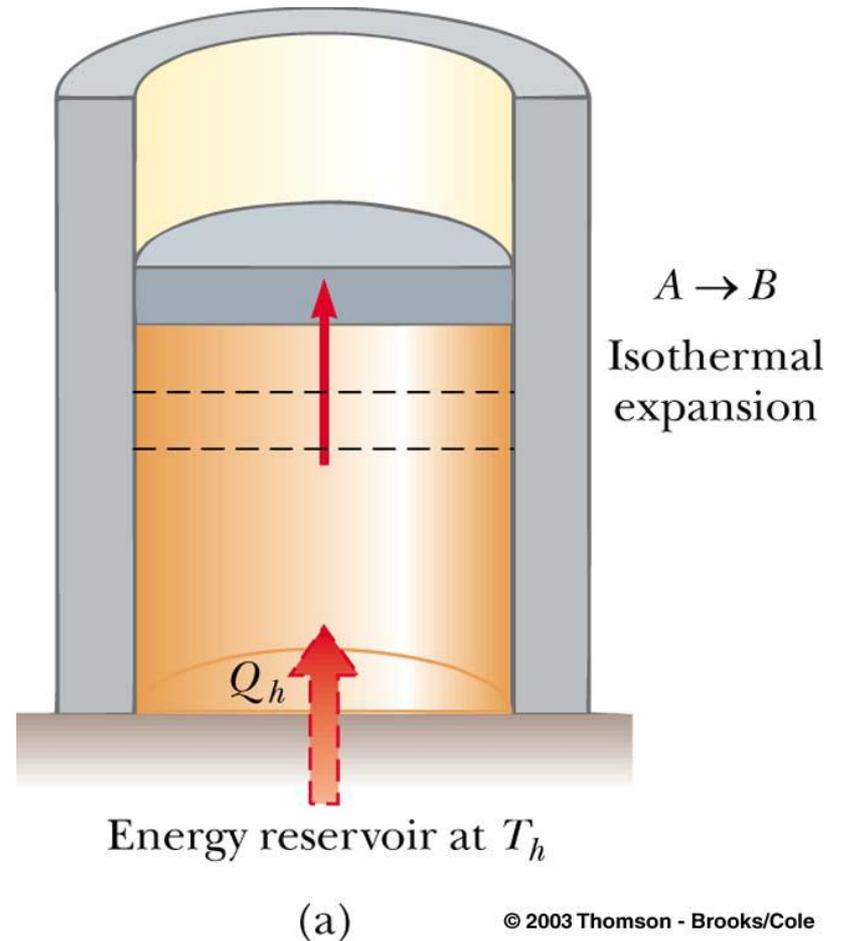
3 THE CARNOT ENGINE

- ▶ A theoretical engine developed by Sadi Carnot
- ▶ A heat engine operating in an **ideal, reversible cycle** (now called a *Carnot Cycle*) between two reservoirs is the most efficient engine possible
- ▶ **Carnot's Theorem** : **No real engine operating between two energy reservoirs can be more efficient than a Carnot engine operating between the same two reservoirs**



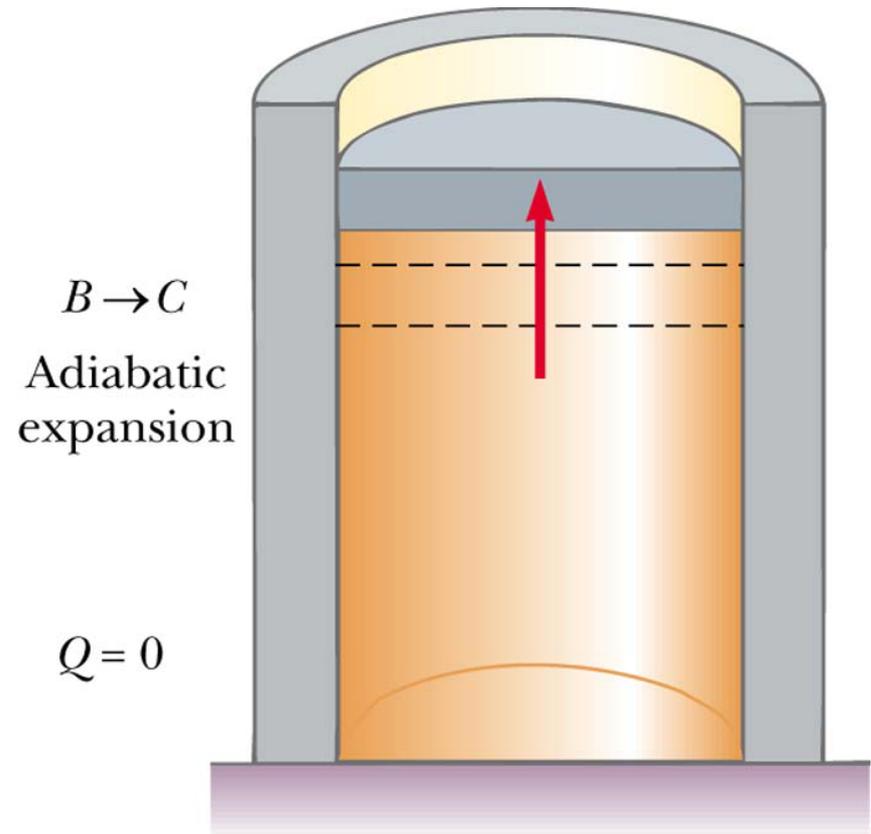
Carnot Cycle, A to B

- ▶ A to B is an isothermal expansion
- ▶ The gas is placed in contact with the high temperature reservoir
- ▶ The gas absorbs heat Q_h
- ▶ The gas does work W_{AB} in raising the piston



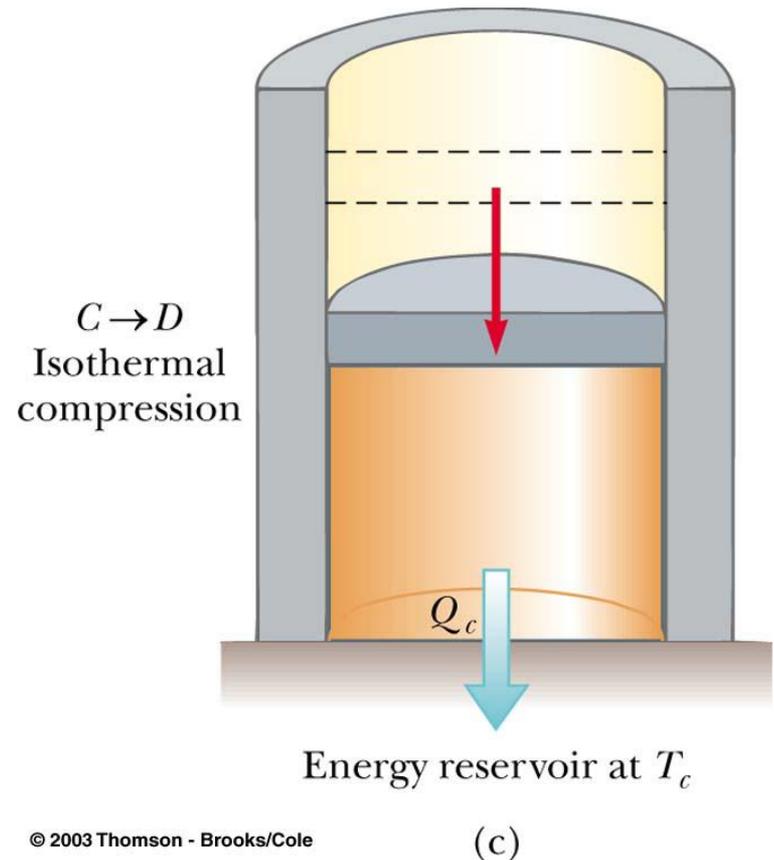
Carnot Cycle, B to C

- ▶ B to C is an adiabatic expansion
- ▶ The base of the cylinder is replaced by a thermally nonconducting wall
- ▶ No heat enters or leaves the system
- ▶ The temperature falls from T_h to T_c
- ▶ The gas does work W_{BC}



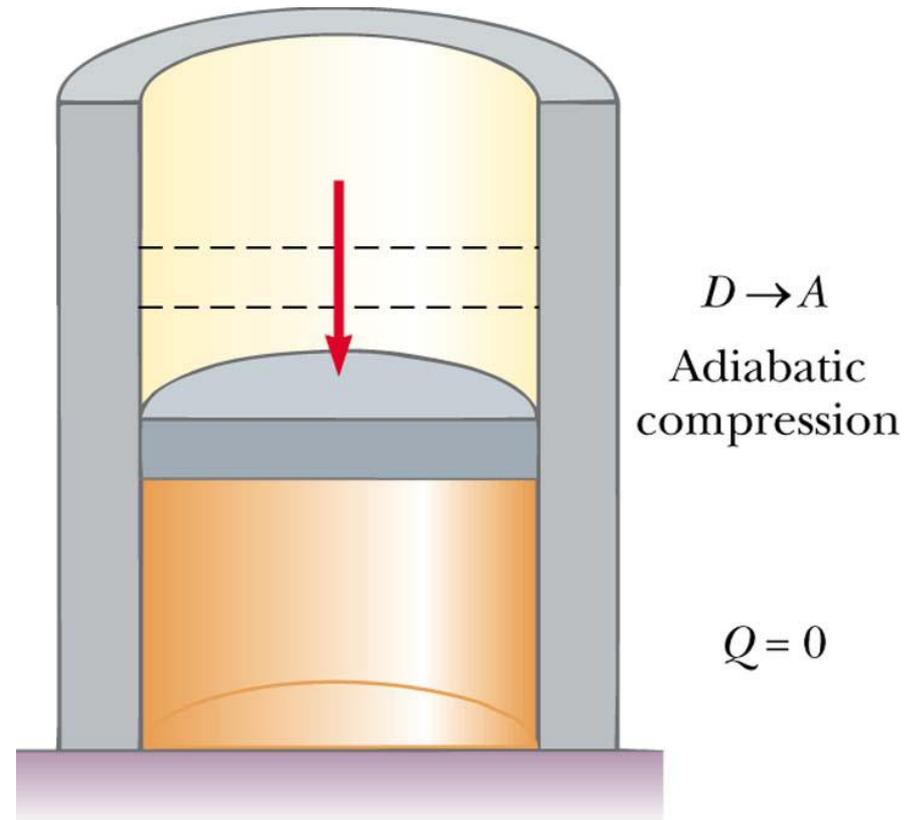
Carnot Cycle, C to D

- ▶ The gas is placed in contact with the cold temperature reservoir
- ▶ C to D is an isothermal compression
- ▶ The gas expels energy Q_c
- ▶ Work W_{CD} is done on the gas



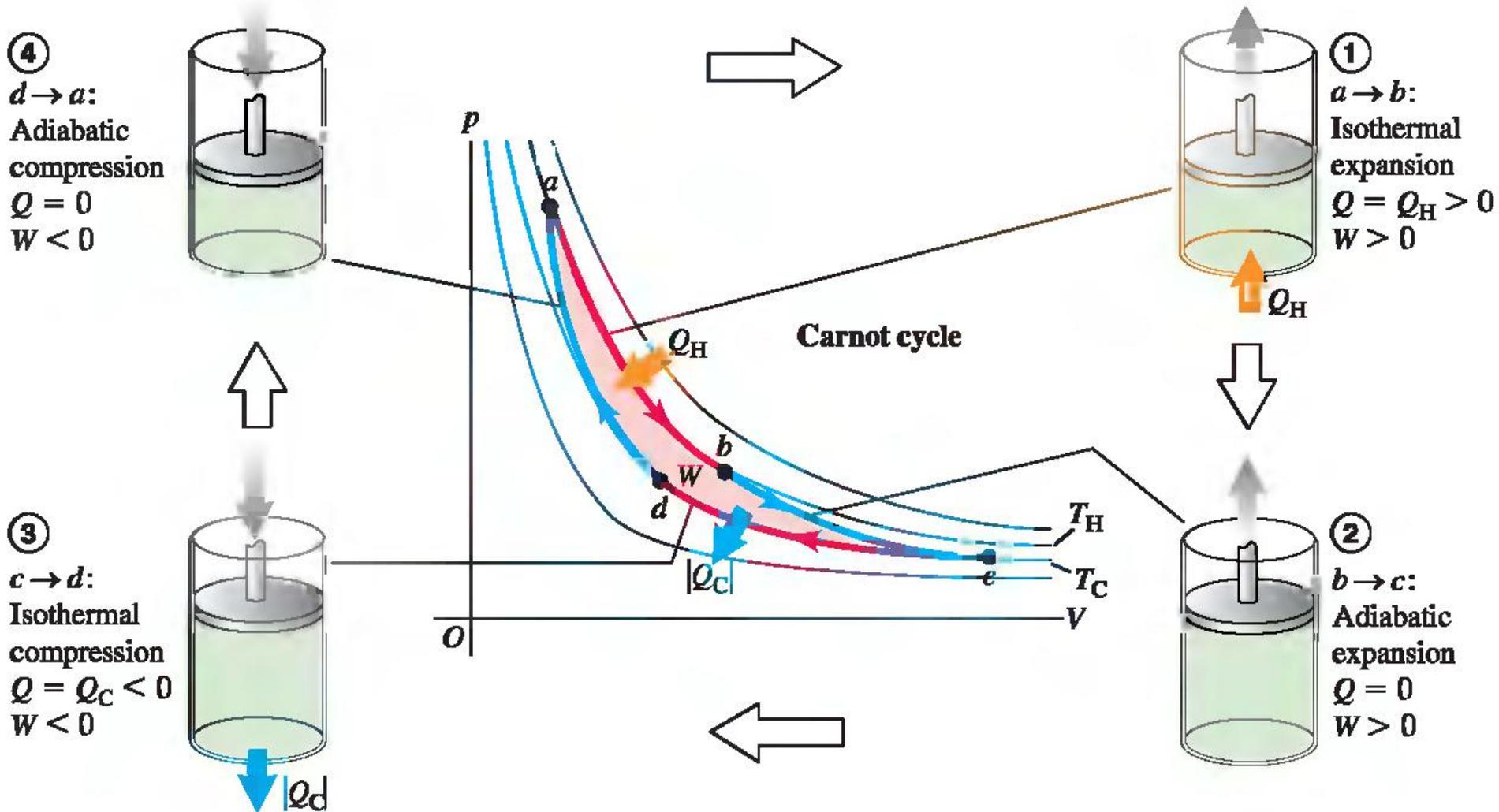
Carnot Cycle, D to A

- ▶ D to A is an adiabatic compression
- ▶ The gas is again placed against a thermally nonconducting wall
 - So no heat is exchanged with the surroundings
- ▶ The temperature of the gas increases from T_C to T_h
- ▶ The work done on the gas is W_{CD}



(d)

→ The Carnot cycle consists of two reversible isothermal and two reversible adiabatic processes.



Carnot Cycle, PV Diagram

- ▶ The work done by the engine is shown by the area enclosed by the curve
- ▶ The net work is equal to $Q_h - Q_c$
- ▶ The thermal efficiency of the engine :

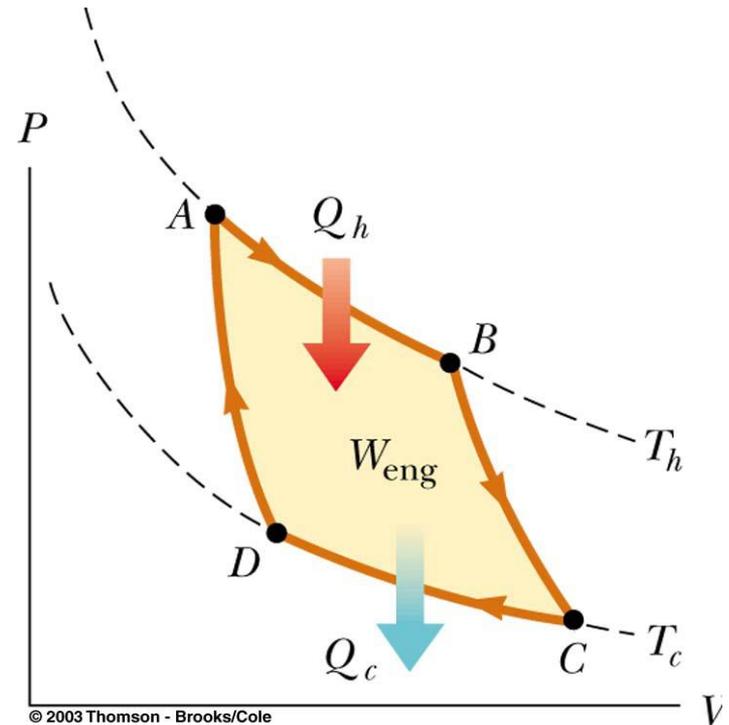
$$e = \frac{W_{eng}}{|Q_h|} = \frac{|Q_h| - |Q_c|}{|Q_h|} = 1 - \frac{|Q_c|}{|Q_h|}$$

- ▶ We can demonstrate : $\frac{|Q_c|}{|Q_h|} = \frac{T_c}{T_h}$

→ The thermal efficiency of a Carnot engine :

$$e_c = 1 - \frac{T_c}{T_h}$$

(The efficiency of a Carnot engine depends only on the temperatures of the two heat reservoirs)



Notes About Carnot Efficiency

- ▶ Efficiency is 0 if $T_h = T_c$
- ▶ Efficiency is 100% only if $T_c = 0$ K
 - Such reservoirs are not available
- ▶ The efficiency increases as T_c is lowered and as T_h is raised
- ▶ In most practical cases, T_c is near room temperature, 300 K
 - So generally **T_h is raised to increase efficiency**
- ▶ All real engines are less efficient than the Carnot engine
 - Real engines are irreversible because of friction
 - Real engines are irreversible because they complete cycles in short amounts of time

PROBLEM 6 A steam engine has a boiler that operates at 500 K. The energy from the burning fuel changes water to steam, and this steam then drives a piston. The cold reservoir's temperature is that of the outside air, approximately 300 K. What is the maximum thermal efficiency of this steam engine?

SOLUTION

$$e_C = 1 - \frac{T_c}{T_h}$$
$$= 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.4, \text{ or } 40\%$$

PROBLEM 7 The highest theoretical efficiency of a certain engine is 30%.

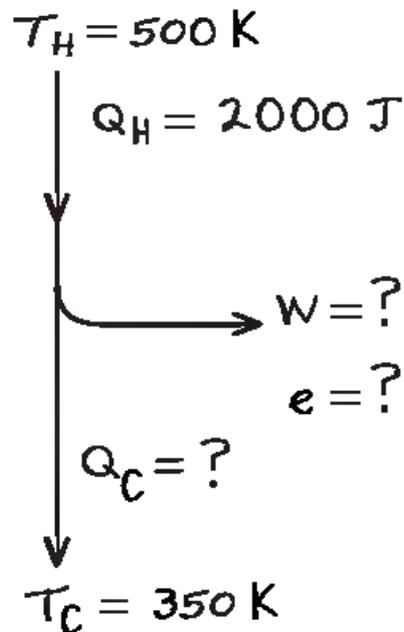
If this engine uses the atmosphere, which has a temperature of 300 K, as its cold reservoir, what is the temperature of its hot reservoir?

SOLUTION

$$\begin{aligned}e_C &= 1 - \frac{T_c}{T_h} \\T_h &= \frac{T_c}{1 - e_C} \\&= \frac{300 \text{ K}}{1 - 0.30} = 430 \text{ K}\end{aligned}$$

PROBLEM 8 A Carnot engine takes 2000 J of heat from a reservoir at 500 K, does some work, and discards some heat to a reservoir at 350 K. How much work does it do, how much heat is discarded, and what is the efficiency ?

SOLUTION



$$Q_C = -Q_H \frac{T_C}{T_H} = -(2000 \text{ J}) \frac{350 \text{ K}}{500 \text{ K}} \\ = -1400 \text{ J}$$

($Q_C < 0$: heat flows out of the engine and into the cold reservoir.)

$$W = Q_H + Q_C = 2000 \text{ J} + (-1400 \text{ J}) \\ = 600 \text{ J}$$

$$e = 1 - \frac{T_C}{T_H} = 1 - \frac{350 \text{ K}}{500 \text{ K}} = 0.30 = 30\%$$

PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (a) Find the pressure and volume at each of points a, b, c, and d in the P V-diagram of the figure.

SOLUTION

$$V_a = \frac{nRT_H}{P_a} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})}{10.0 \times 10^5 \text{ Pa}}$$

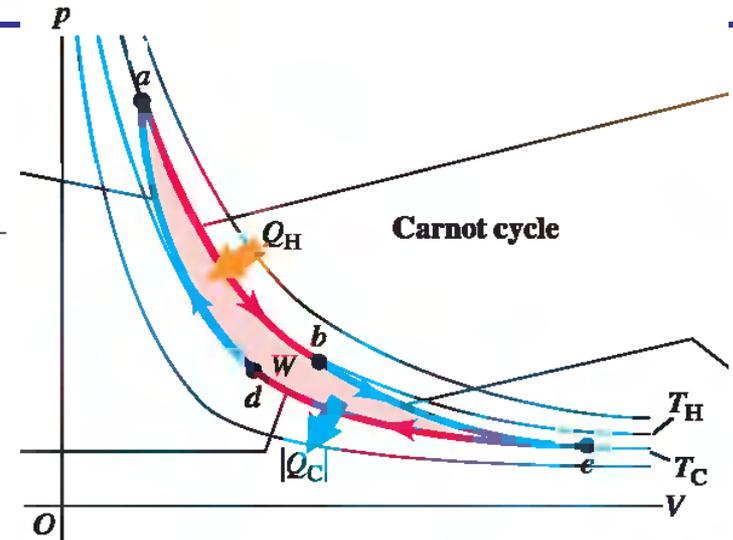
$$= 8.31 \times 10^{-4} \text{ m}^3$$

$$V_b = 2V_a = 2(8.31 \times 10^{-4} \text{ m}^3)$$

$$= 16.6 \times 10^{-4} \text{ m}^3$$

$$P_b = \frac{P_a V_a}{V_b} = 5.00 \times 10^5 \text{ Pa}$$

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}, V_c = V_b \left(\frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (16.6 \times 10^{-4} \text{ m}^3) \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} = 59.6 \times 10^{-4} \text{ m}^3$$



PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (a) Find the pressure and volume at each of points a, b, c, and d in the P V-diagram of the figure.

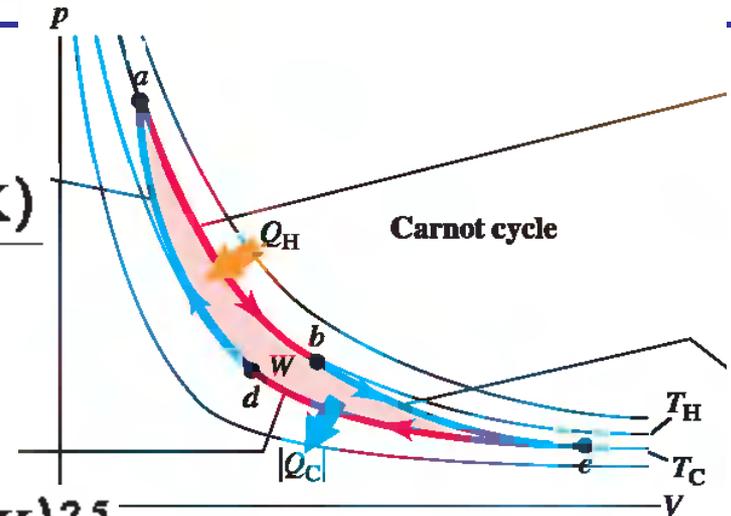
SOLUTION

$$P_c = \frac{nRT_C}{V_c} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{59.6 \times 10^{-4} \text{ m}^3} = 0.837 \times 10^5 \text{ Pa}$$

$$T_C V_d^{\gamma-1} = T_H V_a^{\gamma-1},$$

$$V_d = V_a \left(\frac{T_H}{T_C} \right)^{1/(\gamma-1)} = (8.31 \times 10^{-4} \text{ m}^3) \left(\frac{500 \text{ K}}{300 \text{ K}} \right)^{2.5} = 29.8 \times 10^{-4} \text{ m}^3$$

$$P_d = \frac{nRT_C}{V_d} = \frac{(0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K})}{29.8 \times 10^{-4} \text{ m}^3} = 1.67 \times 10^5 \text{ Pa}$$



PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (b) Find Q , W , and ΔU for each step and for the entire cycle.

SOLUTION

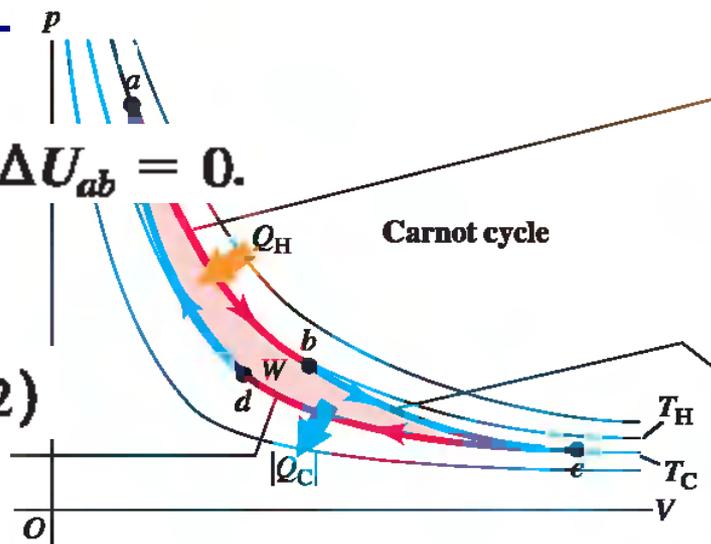
(b) For the isothermal expansion $a \rightarrow b$, $\Delta U_{ab} = 0$.

$$\begin{aligned}
 W_{ab} &= Q_H = nRT_H \ln \frac{V_b}{V_a} \\
 &= (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(500 \text{ K})(\ln 2) \\
 &= 576 \text{ J}
 \end{aligned}$$

For the adiabatic expansion $b \rightarrow c$, $Q_{bc} = 0$.

$$\begin{aligned}
 \Delta U_{bc} &= Q_{bc} - W_{bc} = -W_{bc} \\
 \Delta U &= nC_V \Delta T, \text{ where } \Delta T = T_C - T_H
 \end{aligned}$$

$$\begin{aligned}
 W_{bc} &= -\Delta U_{bc} = -nC_V(T_C - T_H) = nC_V(T_H - T_C) \\
 &= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(500 \text{ K} - 300 \text{ K}) = 832 \text{ J}
 \end{aligned}$$



PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (b) Find Q , W , and ΔU for each step and for the entire cycle.

SOLUTION

For the isothermal compression $c \rightarrow d$, $\Delta U_{cd} = 0$.

$$W_{cd} = Q_C = nRT_C \ln \frac{V_d}{V_c}$$

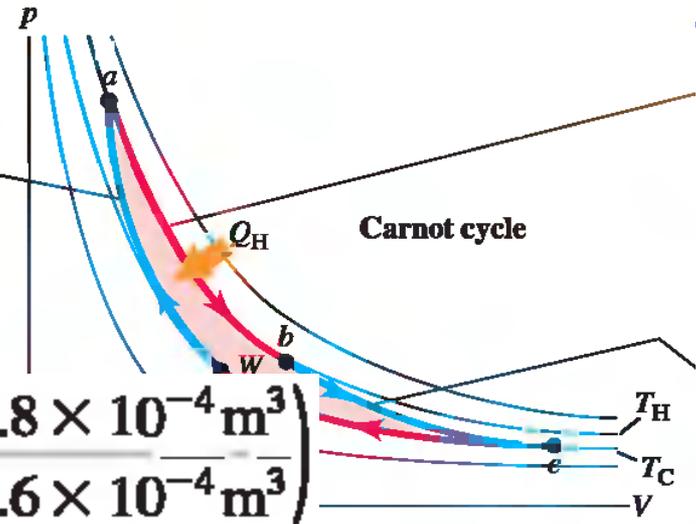
$$= (0.200 \text{ mol})(8.314 \text{ J/mol} \cdot \text{K})(300 \text{ K}) \left(\ln \frac{29.8 \times 10^{-4} \text{ m}^3}{59.6 \times 10^{-4} \text{ m}^3} \right)$$

$$= -346 \text{ J}$$

For the adiabatic compression $d \rightarrow a$, $Q_{da} = 0$.

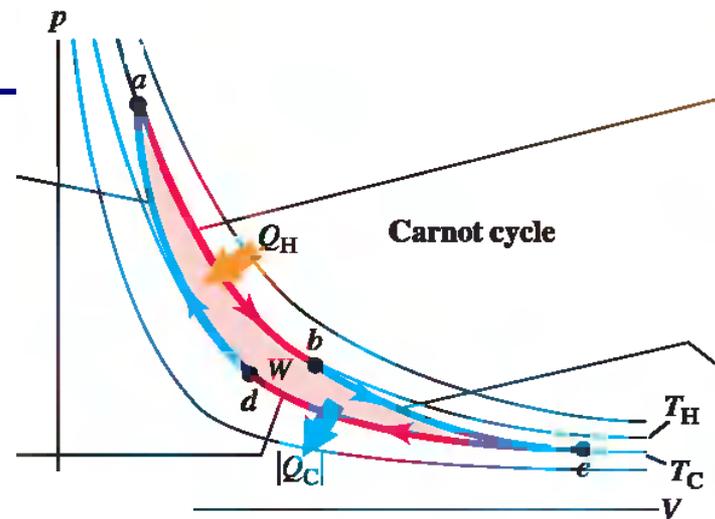
$$W_{da} = -\Delta U_{da} = -nC_V(T_H - T_C) = nC_V(T_C - T_H)$$

$$= (0.200 \text{ mol})(20.8 \text{ J/mol} \cdot \text{K})(300 \text{ K} - 500 \text{ K}) = -832 \text{ J}$$



PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (b) Find Q , W , and ΔU for each step and for the entire cycle.

SOLUTION

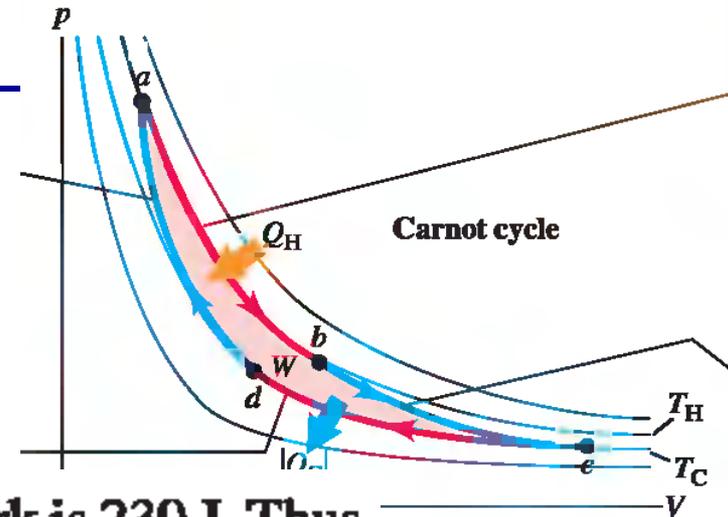


We can tabulate the results as follows:

Process	Q	W	ΔU
$a \rightarrow b$	576 J	576 J	0
$b \rightarrow c$	0	832 J	-832 J
$c \rightarrow d$	-346 J	-346 J	0
$d \rightarrow a$	0	-832 J	832 J
Total	230 J	230 J	0

PROBLEM 9 Suppose 0.200 mol of an ideal diatomic gas ($\gamma = 1.40$) undergoes a Carnot cycle with temperatures 227°C and 27°C . The initial pressure is $P_a = 10.0 \times 10^5 \text{ Pa}$, and during the isothermal expansion at the higher temperature the volume doubles. (c) Determine the efficiency directly from the results of part (b).

SOLUTION



(c) From the table, $Q_H = 576 \text{ J}$ and the total work is 230 J . Thus

$$e = \frac{W}{Q_H} = \frac{230 \text{ J}}{576 \text{ J}} = 0.40 = 40\%$$

We can compare this with the result

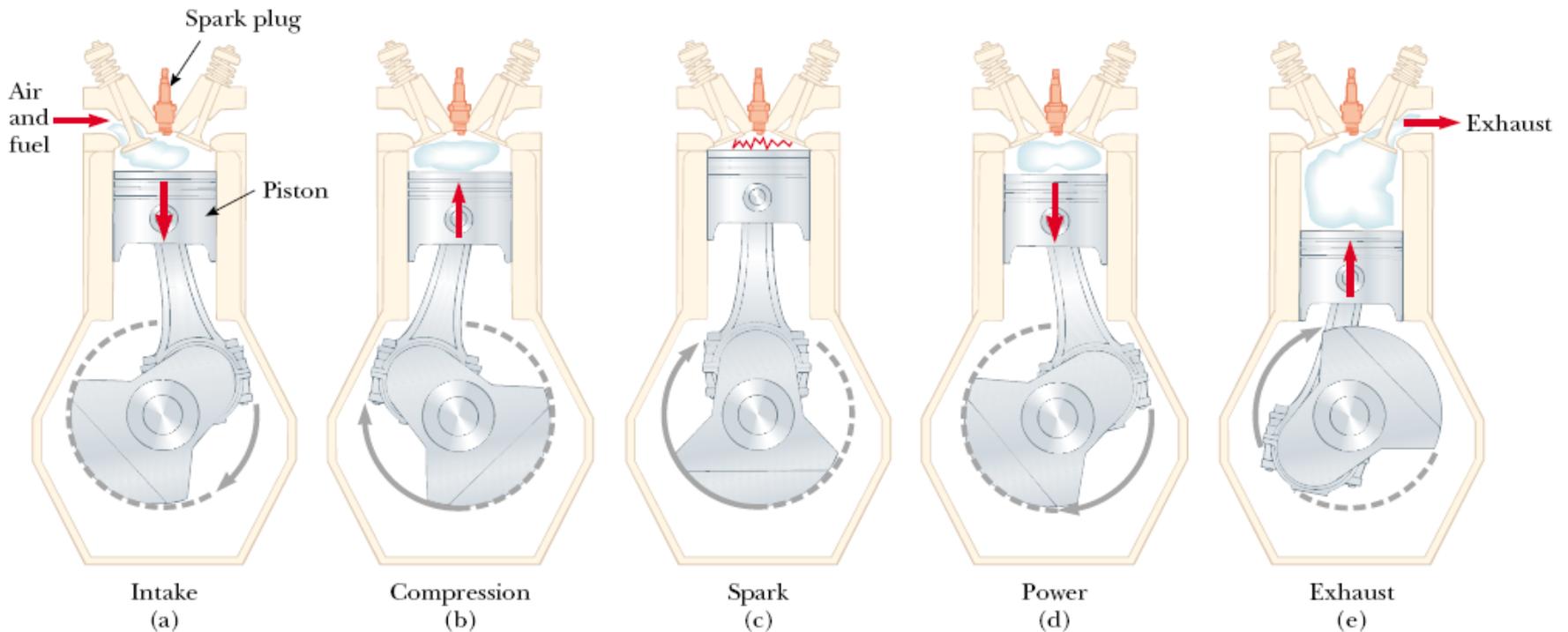
$$e = \frac{T_H - T_C}{T_H} = \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} = 0.40 = 40\%$$

4 Internal-Combustion Engines

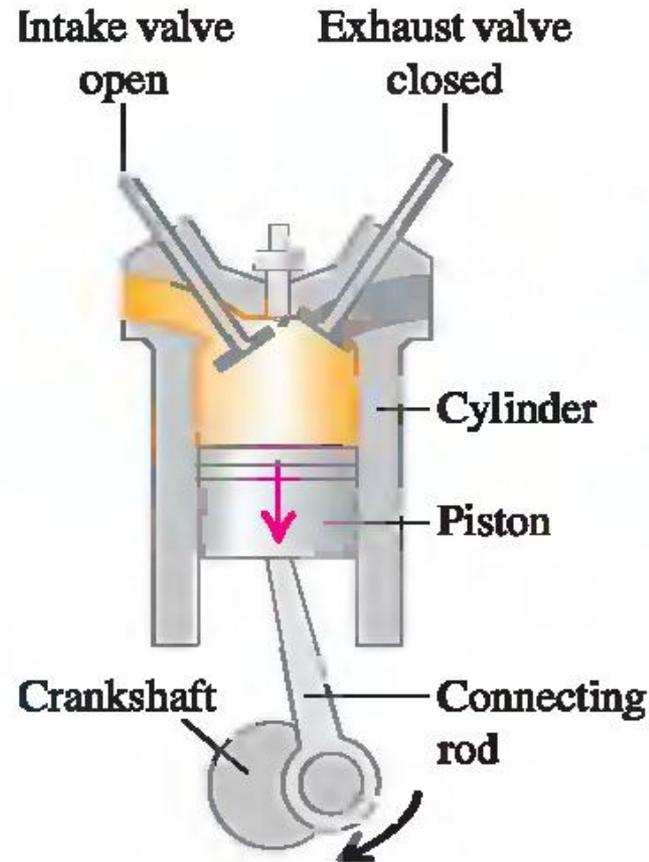
- Gasoline and Diesel Engines

(used in automobiles and many other types of machinery) are familiar examples of a heat engine.

a. Gasoline Engines : In a gasoline engine, six processes occur in each cycle

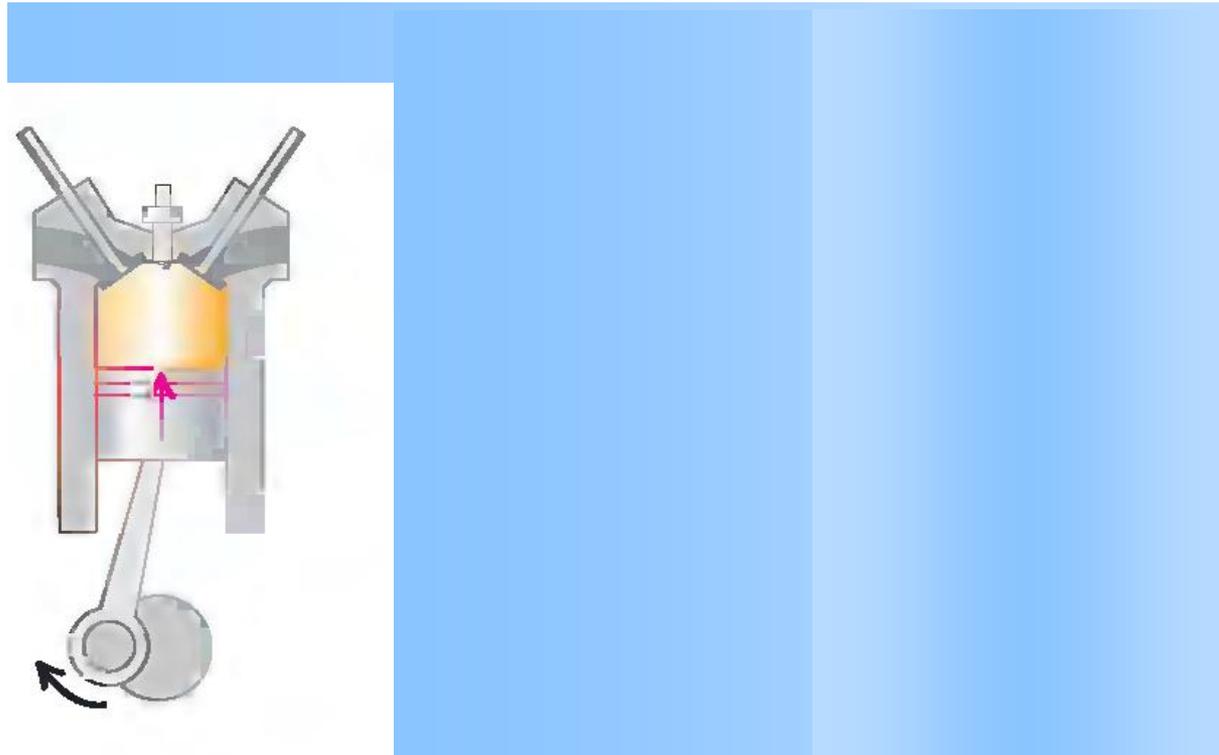


Cycle of a four-stroke internal-combustion engine.



Intake stroke: Piston moves down, causing a partial vacuum in cylinder; gasoline-air mixture enters through intake valve.

Cycle of a four-stroke internal-combustion engine.

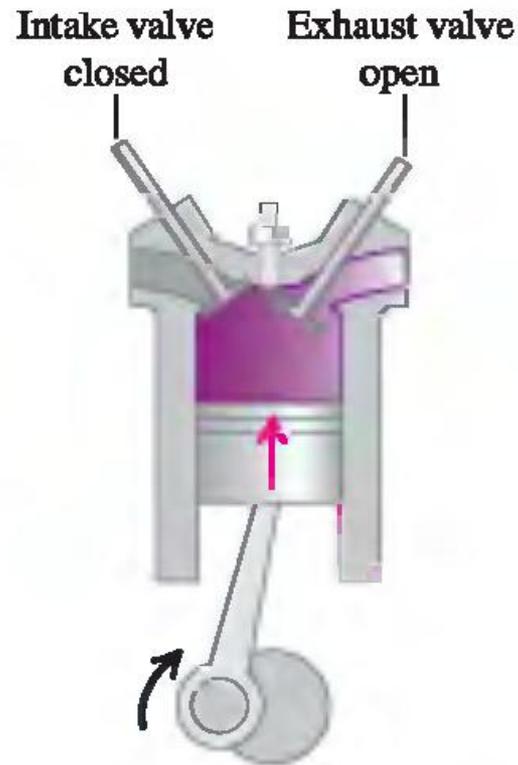


Compression stroke: Intake valve closes; mixture is compressed as piston moves up.

Ignition: Spark plug ignites mixture.

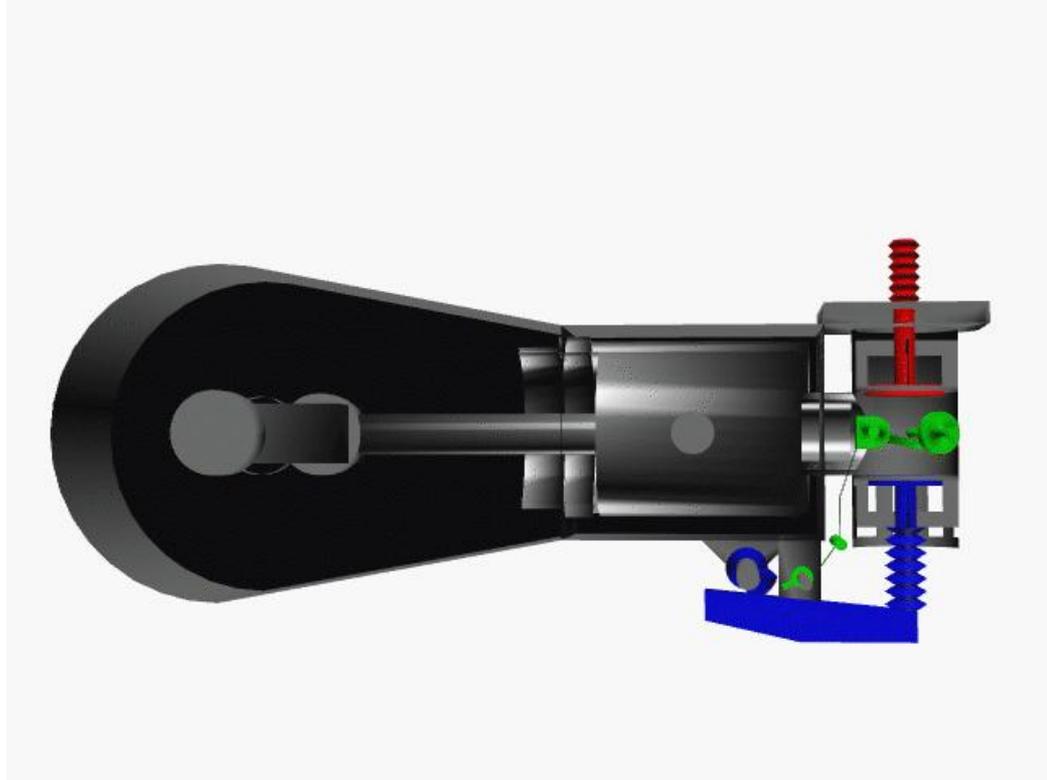
Power stroke: Hot burned mixture expands, pushing piston down.

Cycle of a four-stroke internal-combustion engine.



Exhaust stroke: Exhaust valve opens; piston moves up, expelling exhaust and leaving cylinder ready for next intake stroke.

Cycle of a four-stroke internal-combustion engine.



The Otto cycle

The Otto cycle is an idealized model of the thermodynamic processes in a gasoline engine

If the air–fuel mixture is assumed to be an ideal gas, then the efficiency of the Otto cycle is

$$e = 1 - \frac{1}{(V_1 / V_2)^{\gamma-1}}$$

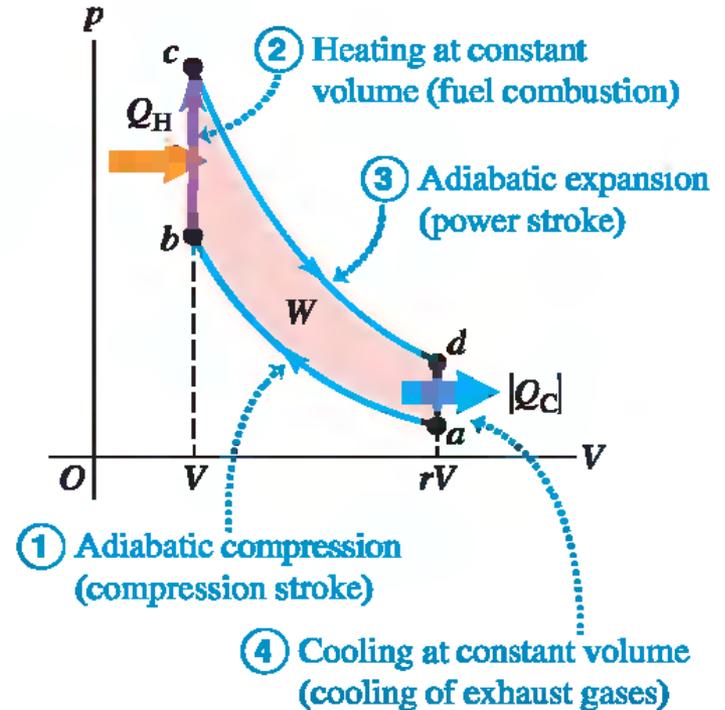
where γ is the ratio of the **molar specific heats** :

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

and V_1/V_2 is the **compression ratio**

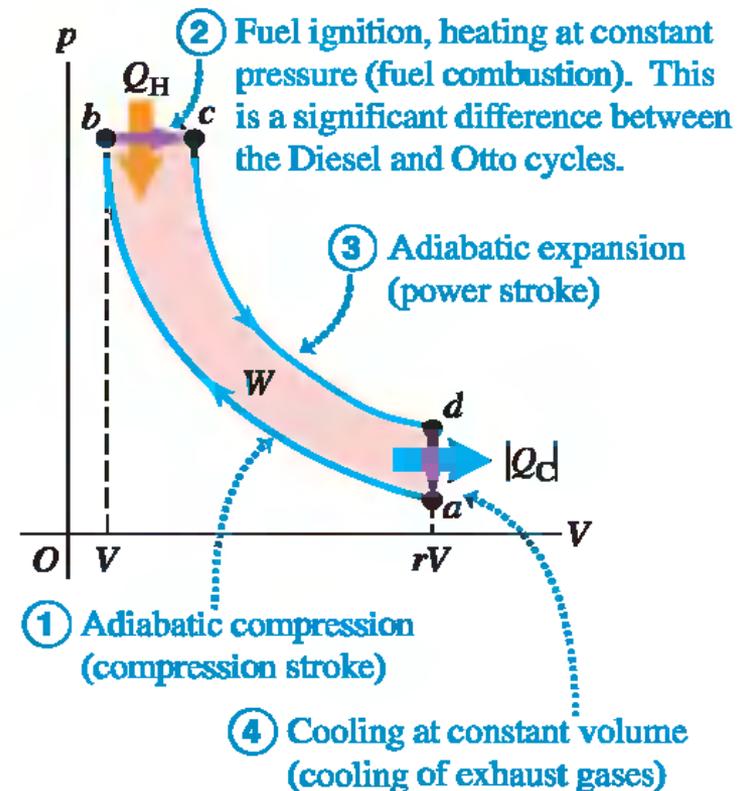
NOTES : • For a typical compression ratio of 8 and with $\gamma = 1.4$, we predict a theoretical efficiency of 56%

• Efficiencies of real gasoline engines are typically around 35%



b. The Diesel Cycle

- Diesel engines operate on a cycle **similar to the Otto** cycle but do not employ a spark plug. There is **no fuel** in the cylinder at the beginning of the compression stroke.
- The compression ratio for a diesel engine is much greater than that for a gasoline engine
- Diesel engines are **more efficient** than gasoline engines because of their greater compression ratios and resulting higher combustion temperatures.



PROBLEM 10 What compression ratio r must an Otto cycle have to achieve an ideal efficiency of 65.0% if $\gamma = 1.40$?

SOLUTION

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

$$\frac{1}{r^{\gamma-1}} = 1 - e = 0.350$$

$$r^{0.40} = \frac{1}{0.350}$$

$$r = 13.8.$$

NOTES : e increases when r increases.

PROBLEM 11 (a) Calculate the theoretical efficiency for an Otto cycle engine with $\gamma = 1.40$ and $r = 9.50$.

(b) If this engine takes in 10,000 J of heat from burning its fuel, how much heat does it discard to the outside air ?

SOLUTION

(a)

$$e = 1 - \frac{1}{r^{\gamma-1}} = 1 - \frac{1}{9.50^{0.40}} = 0.594 = 59.4\%.$$

(b)

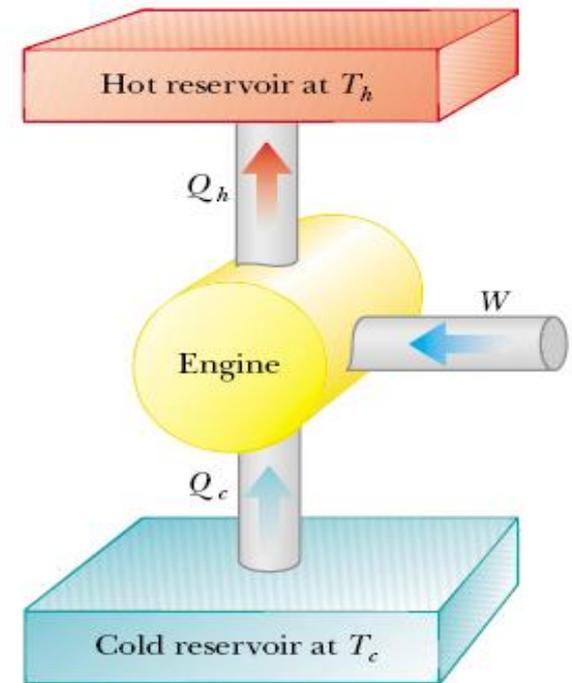
$$e = 1 - \frac{|Q_C|}{|Q_H|}.$$

$$|Q_C| = |Q_H|(1 - e) = (10,000 \text{ J})(1 - 0.594) = 4060 \text{ J}.$$

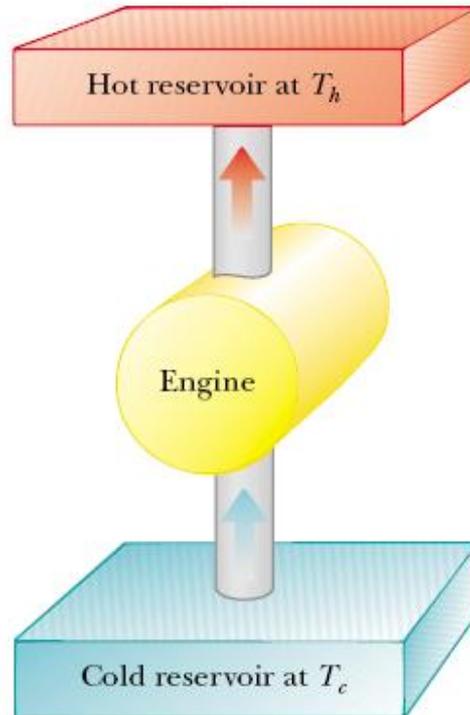
5 Heat Pumps and Refrigerato

- In a refrigerator or heat pump, the engine **absorbs energy Q_c from a cold reservoir** and expels energy Q_h to a hot reservoir

→ some work must be done *on* the engine

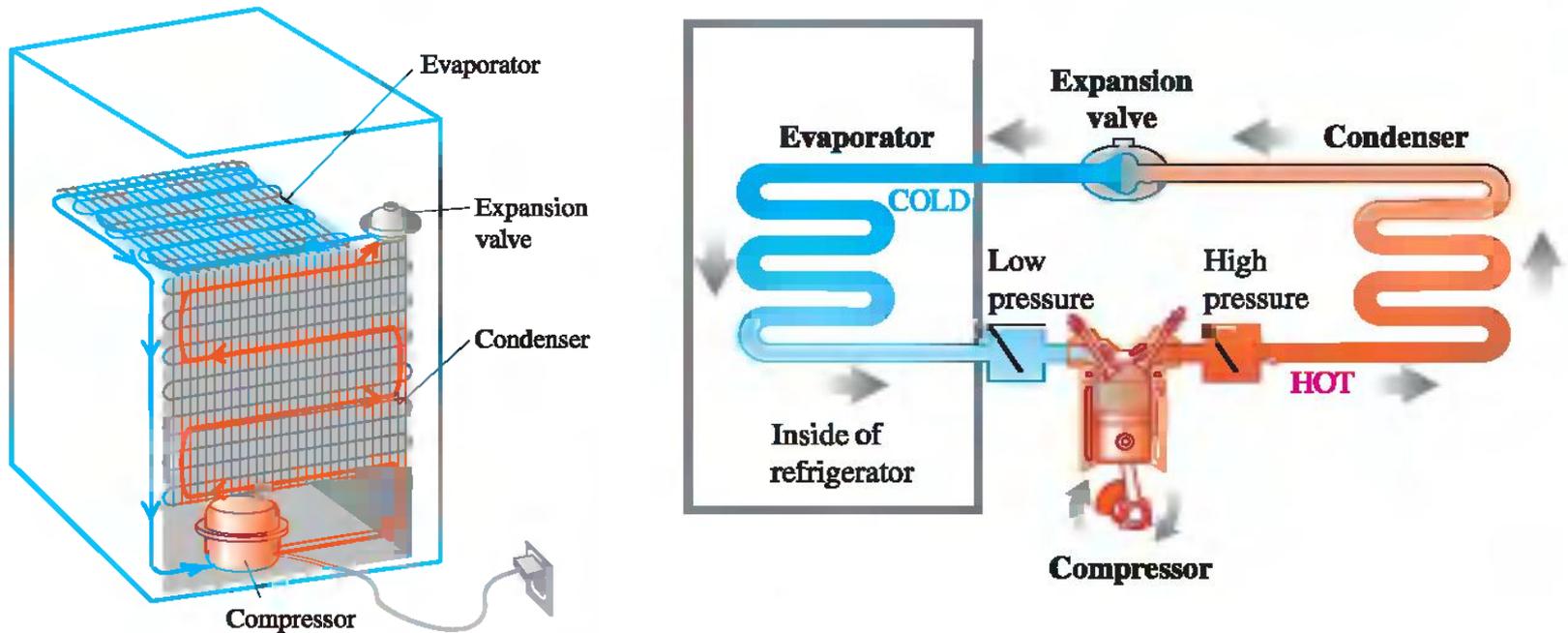


Refrigerator



Impossible refrigerator

• The principles of the common refrigeration cycle



The fluid "circuit" contains a refrigerant fluid (the working substance)

- The compressor takes in fluid, compresses it adiabatically, and delivers it to the condenser coil at high pressure.
- the refrigerant gives off heat Q_H and partially condenses to liquid
- The fluid then expands adiabatically into the evaporator
As the fluid expands, it cools considerably, enough that the fluid in the evaporator coil is colder than its surroundings.

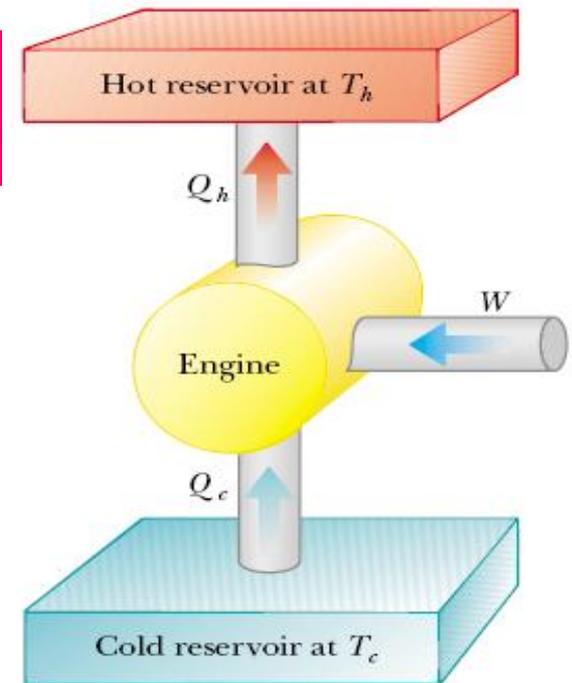
- Effectiveness of a refrigerator:
coefficient of performance (COP)

$$COP = \frac{\text{Energy removed from the cold reservoir}}{\text{Work done by pump}}$$

$$COP = \frac{Q_c}{W}$$

$$Q_c > W \rightarrow COP > 1$$

→ It is desirable for the COP to be as high as possible



Refrigerator

To compare with the thermal efficiency of a Heat Engine:

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

PROBLEM 12 A refrigerator has a coefficient of performance of 2.10. In each cycle it absorbs 3.40×10^4 J of heat from the cold reservoir.

(a) How much mechanical energy is required each cycle to operate the refrigerator?

(b) During each cycle, how much heat is discarded to the high-temperature reservoir?

SOLUTION

$$|W| = Q_C / K = 3.40 \times 10^4 \text{ J} / 2.10 = 1.62 \times 10^4 \text{ J}$$

$$W = Q_C + Q_H$$

$$Q_H = W - Q_C$$

$$Q_H = -1.62 \times 10^4 \text{ J} - 3.40 \times 10^4 \text{ J} = -5.02 \times 10^4 \text{ J}$$

(negative because heat goes out of the system)

6 Entropy

- Pressure and volume are state properties, properties that depend only on the state of the gas and not on how it reached that state. Other state properties are temperature and energy.
- Another state property: its **entropy**.
- **Entropy S** of the system is defined by :

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

J/K

(The change in entropy of a system during an arbitrary process between an initial state i and a final state f)

- To find the entropy change for an irreversible process occurring in a closed system, replace that process with any reversible process that connects the same initial and final states.

The isothermal expansion:

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}$$

To keep the temperature T of the gas constant during the isothermal expansion: heat Q must have been energy transferred from the reservoir to the gas

→ Q is positive and the entropy of the gas increases during the isothermal process and during the free expansion

- Entropy as state function

To make the process reversible, it is done slowly in a series of small steps, with the gas in an equilibrium state at the end of each step. For each small step, the energy transferred as heat to or from the gas is dQ , the work done by the gas is dW , and the change in internal energy is dE_{int} .

The first law of thermodynamics:

$$dE_{\text{int}} = dQ - dW ; \quad nC_V dT = dQ - p dV$$

$$\frac{dQ}{T} = \frac{nC_V dT}{T} + nR \frac{dV}{V}$$

$$\int_i^f \frac{dQ}{T} = \int_i^f \frac{nC_V dT}{T} + \int_i^f nR \frac{dV}{V}$$

$$\Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

- **The second law of thermodynamics :**

“The total entropy of an isolated system that undergoes a change can never decrease”

$$\Delta S \geq 0$$

→ The entropy of the Universe increases in all real processes

- Entropy provides a quantitative **measure of disorder.**

Example

Consider the changes in entropy that occur in a Carnot heat engine operating between the temperatures T_c and T_h .

$$\begin{aligned}\Delta S &= \int_i^f dS = \int_i^f \frac{dQ}{T} \\ &= \frac{Q_h}{T_h} - \frac{Q_c}{T_c}\end{aligned}$$

But for Carnot cycle :

$$\frac{Q_h}{T_h} - \frac{Q_c}{T_c}$$

$$\longrightarrow \Delta S = 0$$

- Consider a system taken through an arbitrary (non-Carnot) **reversible cycle**

Entropy S is a state function $\rightarrow S$ depends only on the properties of a given equilibrium state $\rightarrow \Delta S = 0$

$$\Delta S = \oint dS = \oint \frac{dQ_r}{T} = 0$$

- When a system is in a particular **macroscopic state**, the particles that make up the system may be in any of w possible **microscopic states**.

From a microscopic viewpoint, entropy is defined as :

$$S = k \ln W$$

k : Boltzmann's constant;

W : the number of microstates available to the system

PROBLEM 13 One kilogram of ice at 0°C is melted and converted to water at 0°C . Compute its change in entropy, assuming that the melting is done reversibly. The heat of fusion of water is $L_f = 3.34 \times 10^5 \text{ J/kg}$.

SOLUTION

The heat needed to melt the ice :

$$Q = mL_f = 3.34 \times 10^5 \text{ J}$$

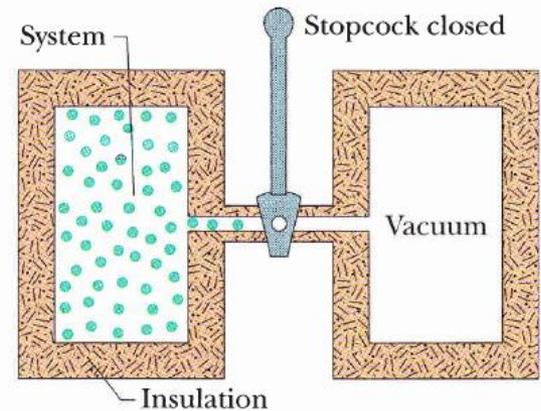
$$\Delta S = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{273 \text{ K}} = 1.22 \times 10^3 \text{ J / K}$$

PROBLEM 14 Suppose 1.0 mol of nitrogen gas is confined to the left side of the container. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

SOLUTION

The entropy change for the irreversible process by calculating it for a reversible process that provides the same change in volume. The temperature of the gas does not change → isothermal expansion

$$\Delta S = \frac{Q}{T} = \frac{nRT \ln(V_f / V_i)}{T} = nRT \ln(V_f / V_i)$$
$$\Delta S = (1 \text{ mol})(8.31)(\ln 2) = +5.76 \text{ J / K}$$



PROBLEM 15 One kilogram of water at 0°C is heated to 100°C. Compute its change in entropy. Specific heat of water is 4190 J/kg.K

SOLUTION

$$\begin{aligned}\Delta S = S_2 - S_1 &= \int_1^2 \frac{dQ}{T} = \int_{T_1}^{T_2} mc \frac{dT}{T} = mc \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \left(\ln \frac{373 \text{ K}}{273 \text{ K}} \right) \\ &= 1.31 \times 10^3 \text{ J/K}\end{aligned}$$

PROBLEM 16 Suppose 1.00 kg of water at 100°C is placed in thermal contact with 1.00 kg of water at 0°C. What is the total change in entropy? Assume that the specific heat of water is constant at 4190 J/kg.K over this temperature range.

SOLUTION

$$\begin{aligned}\Delta S_{\text{hot}} &= mc \int_{T_1}^{T_2} \frac{dT}{T} = (1.00 \text{ kg})(4190 \text{ J/kg} \cdot \text{K}) \int_{373\text{K}}^{323\text{K}} \frac{dT}{T} \\ &= (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{373 \text{ K}} \right) = -603 \text{ J/K}\end{aligned}$$

The entropy change of the cold water is

$$\Delta S_{\text{cold}} = (4190 \text{ J/K}) \left(\ln \frac{323 \text{ K}}{273 \text{ K}} \right) = +705 \text{ J/K}$$

The *total* entropy change of the system is

$$\Delta S_{\text{total}} = \Delta S_{\text{hot}} + \Delta S_{\text{cold}} = (-603 \text{ J/K}) + 705 \text{ J/K} = +102 \text{ J/K}$$

4 Microscopic Interpretation of Entropy

4.1 Macroscopic and microscopic states

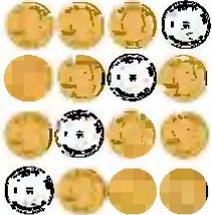
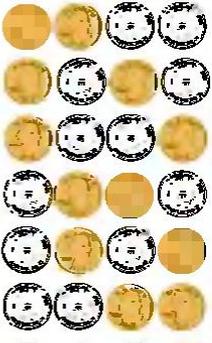
- Toss 4 identical coins on the floor:



There can be many microscopic states that correspond to the same macroscopic description.

- N coins that are all heads constitute a completely ordered macroscopic state (macrostate)
- The macroscopic description "half heads, half tails" : the system is disordered
- The state "half heads, half tails" has a much greater number of possible microscopic states (microstates), much greater disorder :

It is the most probable

Macroscopic state	Corresponding microscopic states
Four heads	
Three heads, one tails	
Two heads, two tails	
One head, three tails	
Four tails	

4.2 Microscopic expression for entropy

- If entropy is a quantitative measure of disorder



For any system, the most probable macrostate is the one with the greatest number of corresponding microstates, which is also the macrostate with the greatest disorder and the greatest entropy.

- Let w represent the number of possible microscopic states (or **multiplicity**) for a given macrostate.

→ **the entropy** of a macroscopic state :

$$S = k \ln w$$

- Consider a system that undergoes a thermodynamic process that takes it from macrostate 1, for which there are w_1 possible microstates (multiplicity w_1), to macroscopic state 2, with w_2 associated microstates (multiplicity w_2) .

The change in entropy in this process is

$$\Delta S = S_2 - S_1 = k \ln w_2 - k \ln w_1$$

$$\Delta S = k \ln \frac{w_2}{w_1}$$

→ The difference in entropy between the two macrostates depends on the ratio of the numbers of possible microstates.

- For a system of N molecules that may be distributed between the two halves of a box.
 n_1 : the number of molecules in one half of the box and
 n_2 : the number in the other half.

The multiplicity:

$$W = \frac{N!}{n_1!n_2!}$$

When N is very large (the usual case):

$$\ln N! \approx N(\ln N) - N$$

(Stirling's approximation)

PROBLEM 17 Suppose that there are 1-00 indistinguishable molecules in the box.

How many microstates are associated with the configuration $(n_1 = 50; n_2 = 50)$, and with the configuration $(n_1 = 100; n_2 = 0)$?

SOLUTION

- Configuration $(n_1 = 50; n_2 = 50)$

The multiplicity: $w = \frac{N!}{n_1!n_2!} = \frac{100!}{50!50!} = 1.01 \times 10^{29}$

- Configuration $(n_1 = 100; n_2 = 0)$

The multiplicity: $w = \frac{N!}{n_1!n_2!} = \frac{100!}{100!0!} = 1$

PROBLEM 18 A thermally insulated box is divided by a partition into two compartments, each having volume V . Initially, one compartment contains n moles of an ideal gas at temperature T , and the other compartment is evacuated. We then break the partition, and the gas expands to fill both compartments. What is the entropy change in this free-expansion process?

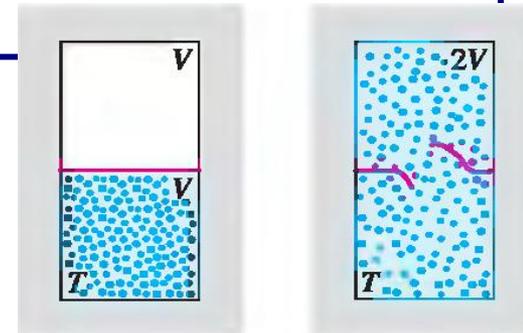
SOLUTION

NB: Use of the equation $w = \frac{N!}{n_1!n_2!}$

- Initial configuration ($n_1 = 100$; $n_2 = 0$)

Initial multiplicity: $w = \frac{N!}{n_1!n_2!} = \frac{100!}{100!0!} = 1$

Initial entropy: $S_i = k \ln w_1 = k \ln 1 = 0$



PROBLEM 18 A thermally insulated box is divided by a partition into two compartments, each having volume V . Initially, one compartment contains n moles of an ideal gas at temperature T , and the other compartment is evacuated. We then break the partition, and the gas expands to fill both compartments. What is the entropy change in this free-expansion process?

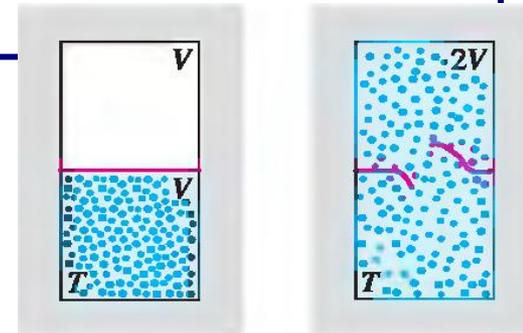
SOLUTION

- Final configuration ($n_1 = N/2$; $n_2 = N/2$)

$$\text{Final multiplicity: } w_f = \frac{N!}{(N/2)!(N/2)!}$$

$$\begin{aligned} \text{Final entropy: } S_f &= k \ln w_f = k \ln(N!) - 2k \ln[(N/2)!] \\ &= k [N(\ln N) - N] - 2k [(N/2) \ln(N/2) - (N/2)] \\ &= Nk \ln 2 = nR \ln 2 \end{aligned}$$

The change in entropy: $\Delta S = S_f - S_i = nR \ln 2$



PROBLEM 18 A thermally insulated box is divided by a partition into two compartments, each having volume V . Initially, one compartment contains n moles of an ideal gas at temperature T , and the other compartment is evacuated. We then break the partition, and the gas expands to fill both compartments. What is the entropy change in this free-expansion process?

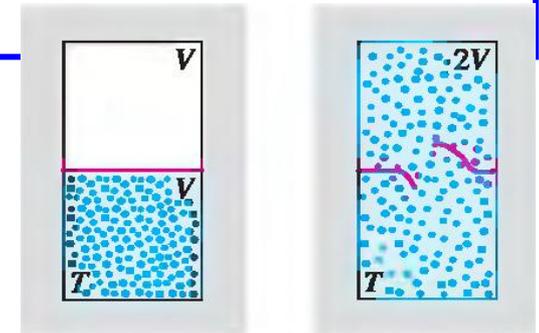
SOLUTION

When the partition is broken, each molecule now has twice as much volume in which it can move and hence has **twice the number of possible positions**.

Let w_1 be the number of microscopic states of the system as a whole when the gas occupies volume V

The number w_2 of microscopic states when the gas occupies volume $2V$ is greater by a factor of 2^N : $w_2 = 2^N w_1$

$$\Delta S = k \ln \frac{w_2}{w_1} = k \ln \frac{2^N w_1}{w_1} = Nk \ln 2 = nN_A k \ln 2 = nR \ln 2$$



PROBLEM 19 Two moles of an ideal gas occupy a volume V . The gas expands isothermally and reversibly to a volume $3V$. (a) Is the velocity distribution changed by the isothermal expansion? (b) Calculate the change in entropy of the gas.

SOLUTION

(a) The velocity distribution depends only on T , so in an isothermal process it does not change.

(b) The number of possible positions available to each molecule is altered by a factor of 3 (becomes larger).

Hence the number of microscopic states the gas occupies at volume $3V$ is $w_2 = (3)^N w_1$, where N is the number of molecules and w_1 is the number of possible microscopic states at the start of the process.

$$\Delta S = k \ln(w_2 / w_1) = k \ln(3)^N = Nk \ln(3) = nN_A k \ln(3) = nR \ln(3)$$

$$\Delta S = (2.00 \text{ mol})(8.3145 \text{ J/mol} \cdot \text{K}) \ln(3) = +18.3 \text{ J/K}$$