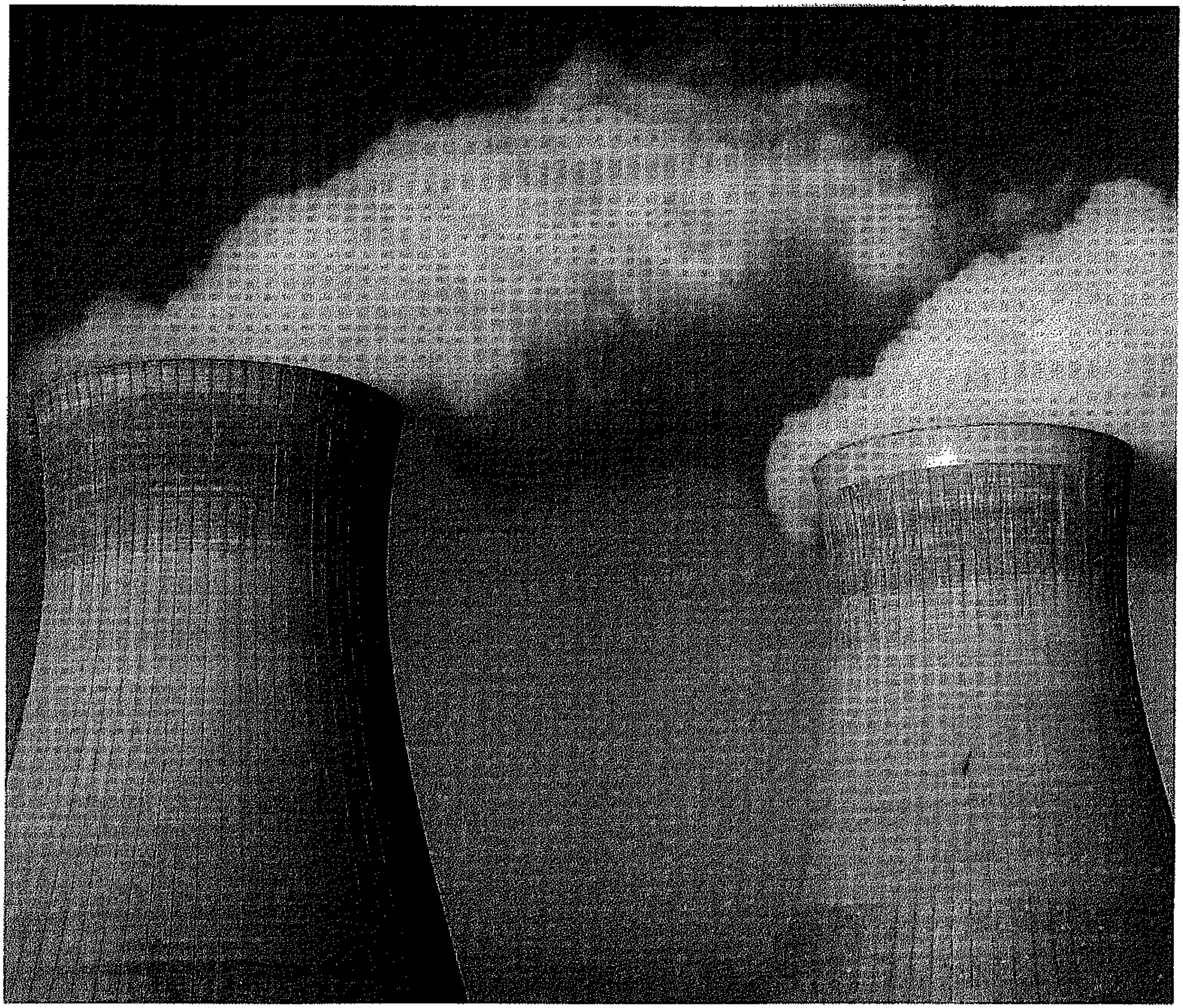
# Lecture 48

# (CH14:2-3)

The Laws of Thermodynamics

Chapter 14 Opener



## TACTIC 14.1 The First Law of Thermodynamics

The first law of thermodynamics states:

$$\Delta U = Q + W$$

Solving first-law problems requires keeping track of which terms in this equation change and which don't. Specifically:

- In an isothermal (constant-temperature) process involving an ideal gas, the internal energy $U$ is constant, so $\Delta U = 0$.
- In a constant-volume process, the work done is zero ($W = 0$).
- In an adiabatic process, the heat flow is zero ($Q = 0$).
- In other processes, the quantities in $\Delta U = Q + W$ can all change simultaneously.
- The work done depends on the type of process but is always equal to the area under the pressure-volume graph. Work is positive for compression and negative for expansion.

Metabolic processes

$$\Delta U = W + Q$$

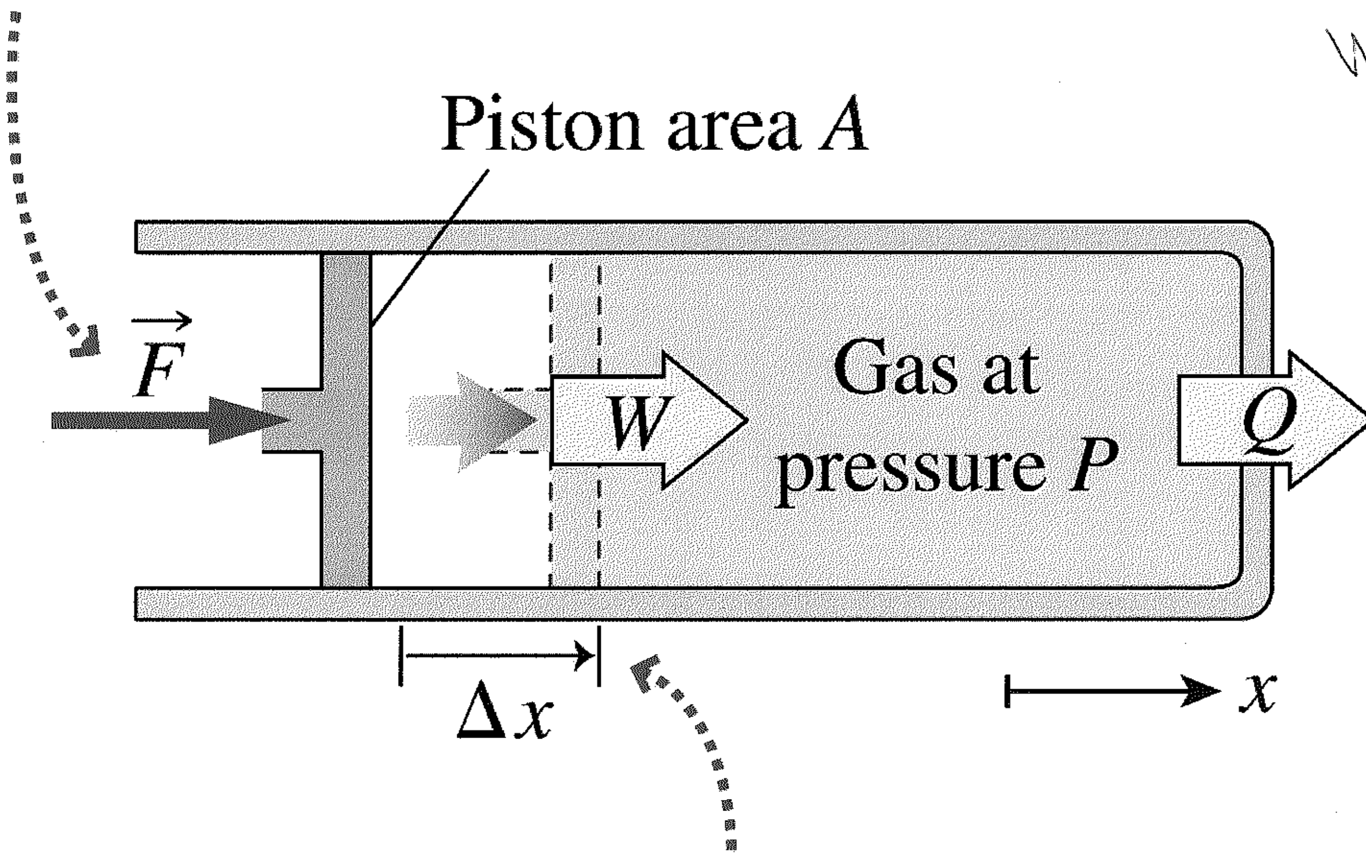
$$\underset{\text{food}}{\downarrow} \quad (-) + (-)$$

P= const. (Isobaric process) $\qquad$ P= const

Figure 14.3

A constant force is applied and heat is allowed to escape, so the pressure remains constant as the gas is compressed.

$P = \frac{F}{A} \rightarrow F = P \cdot A$




$W = F_x \cdot \Delta x = P \cdot A \cdot \Delta x$

$V = A \cdot x$

$\Delta V = - A \cdot \Delta x$

$\boxed{W = -P \cdot \Delta V}$

where

$\Delta V = V_f - V_i$

$\Delta V < 0$

The piston moves through displacement $\Delta x$, resulting in work $W = F_x \Delta x = PA\Delta x$.

so $W > 0$ on the gas

Example: A flexible container contains $2.42 \times 10^{-5}$ $m^3$ of fluid at room T. Somebody pushes on the container, maintaining a constant 1-atm pressure, and reduces its volume by 25 %. How much work is done on the fluid ?

Work done on the fluid: $W = -P(V_f - V_i) = 1\text{atm}(0.75V_i - V_i) =$

$= -(1.013\times10^5 \text{ Pa})V_i(-0.25) = (1.013\times10^5 \text{ Pa})(2.42 \times 10^{-5} \text{ m}^3)(0.25) = 0.61 \text{ J}$

T= const. Isothermal process

Figure 14.4

In an isothermal process, the temperature of the gas is held constant while the gas is compressed (or expands).

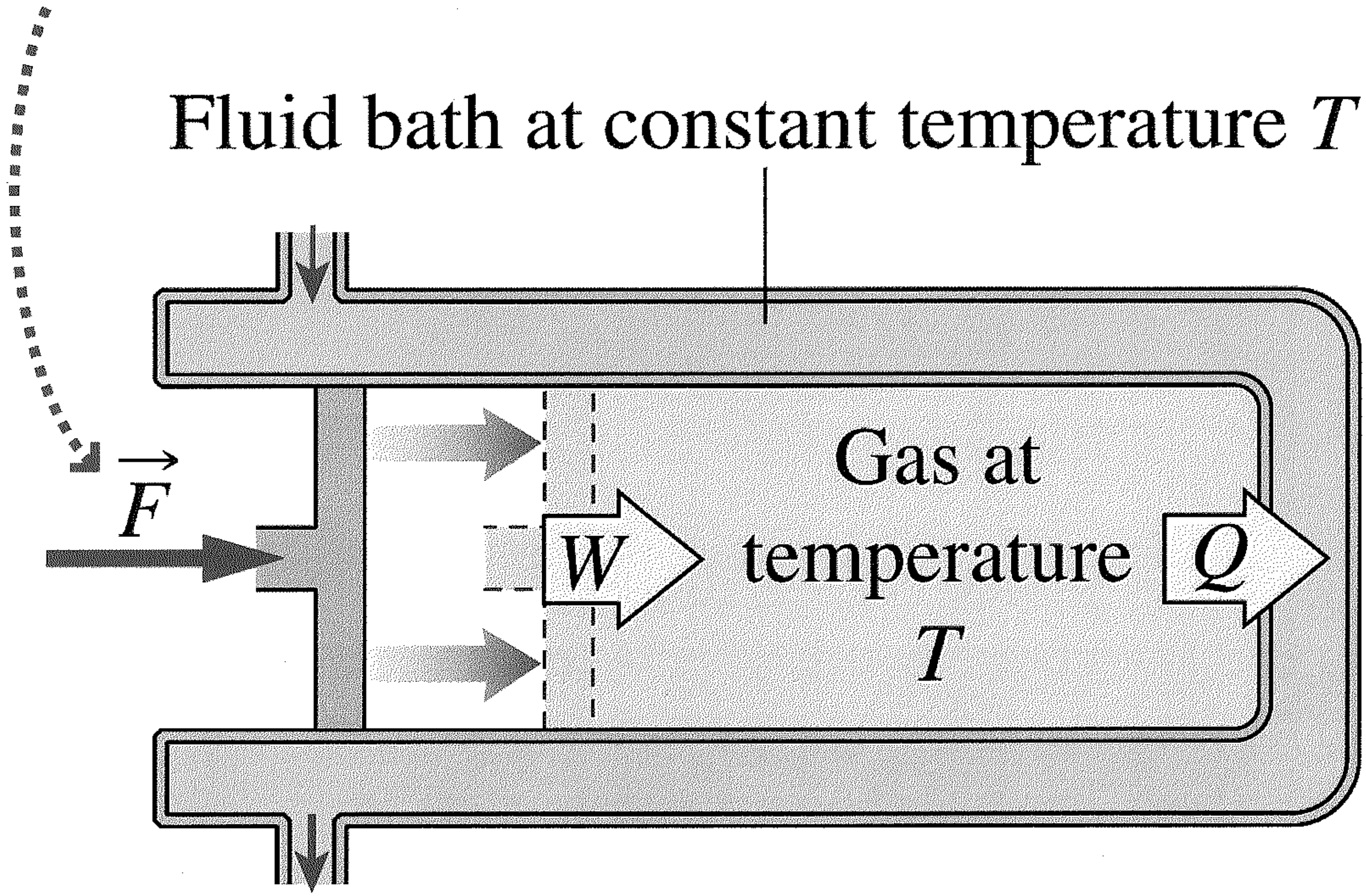
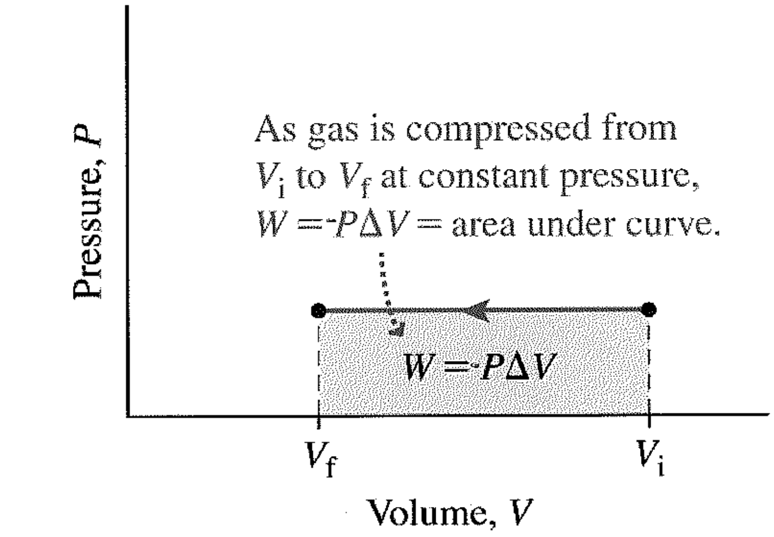
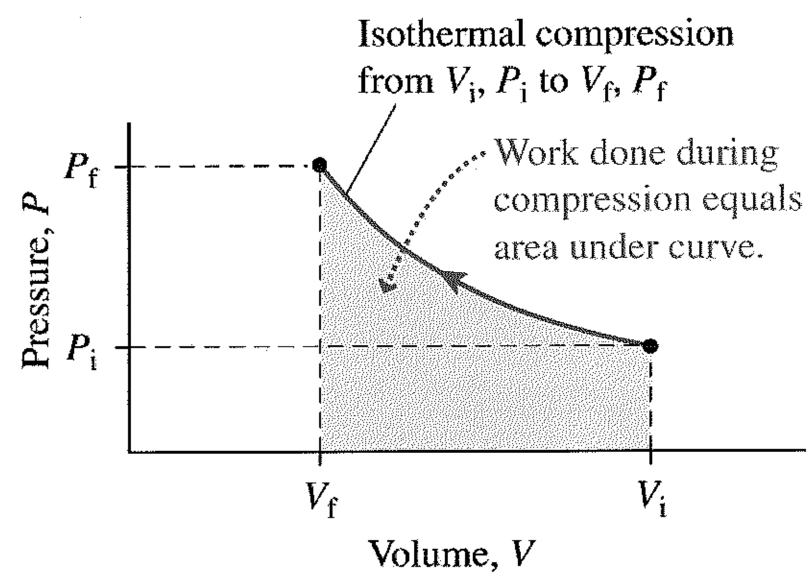


Figure 14.5




**(a)** Compression at constant pressure

For $P =$ const
$W = -P \cdot \Delta V$




**(b)** Isothermal compression



so $P \sim \frac{1}{V}$ when $T =$ const

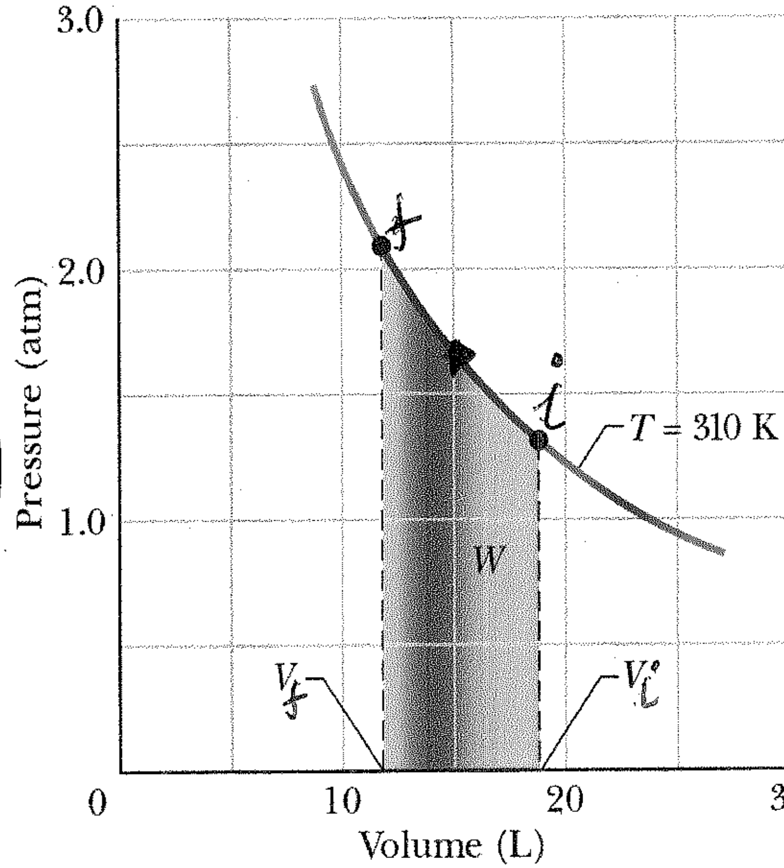
$$\boxed{\begin{aligned} P \cdot \cancel{V} &= nRT \\ P &= \frac{nRT}{V} \end{aligned}}$$

$W = nRT \ln\left(\frac{V_i}{V_f}\right)$

on the gas

# Sample Problem 19-2

One mole of oxygen (assume to be an ideal gas) shrinks at a constant temperature T of 310 K from an initial volume $V_i$ of 12 L to a final volume $V_f$ of 19 L. How much work is done on the gas during the expansion?




$$W = \qquad = nRT\ln\frac{V_i}{V_f}$$

$$= (1\,mol)(8.31\,J/mol\cdot K)(310\,K)\ln\left(\frac{19\,L}{12\,L}\right)$$

$$= 1183\ J$$

$1\,L = 10^{-3}\,m^3$

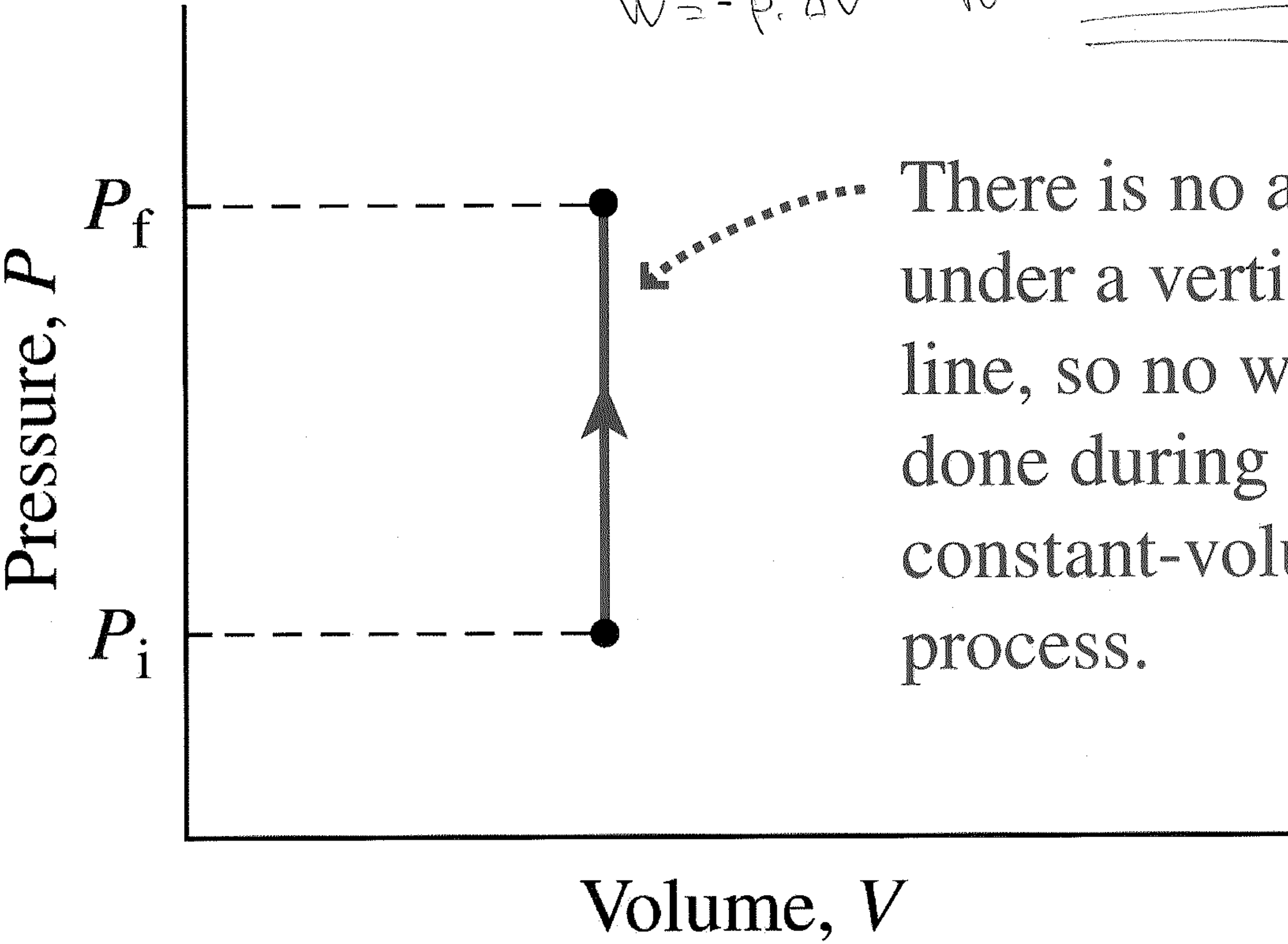
Figure 14.7

Constant Volume

$W = -P \cdot \Delta V$ ≠ 0

$\Delta U = Q$

$W = 0$




There is no area under a vertical line, so no work is done during a constant-volume process.

Figure 14.8

# Adiabatic Process

$Q = 0$

$\Delta U = W$

Insulation prevents heat flow between gas and surroundings.

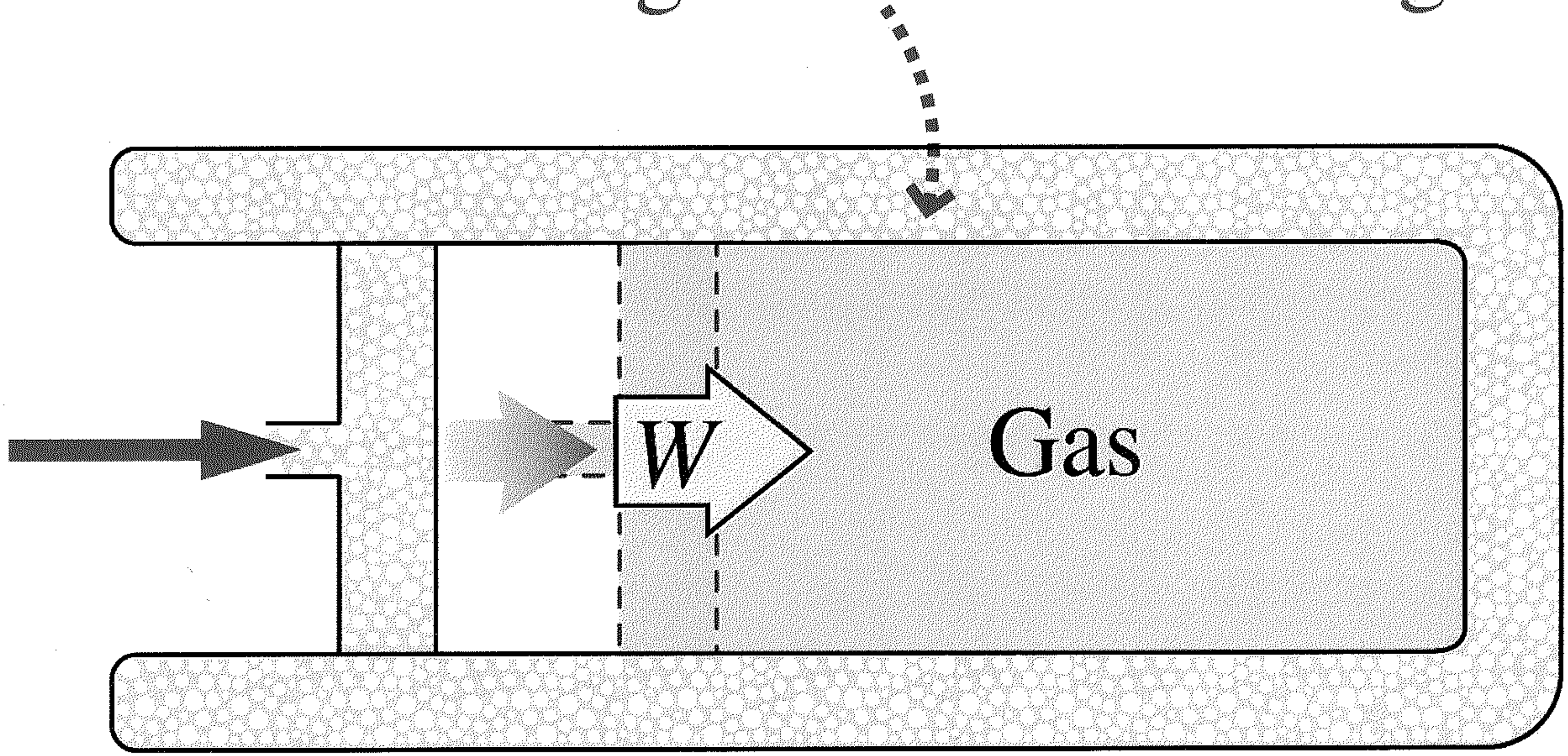
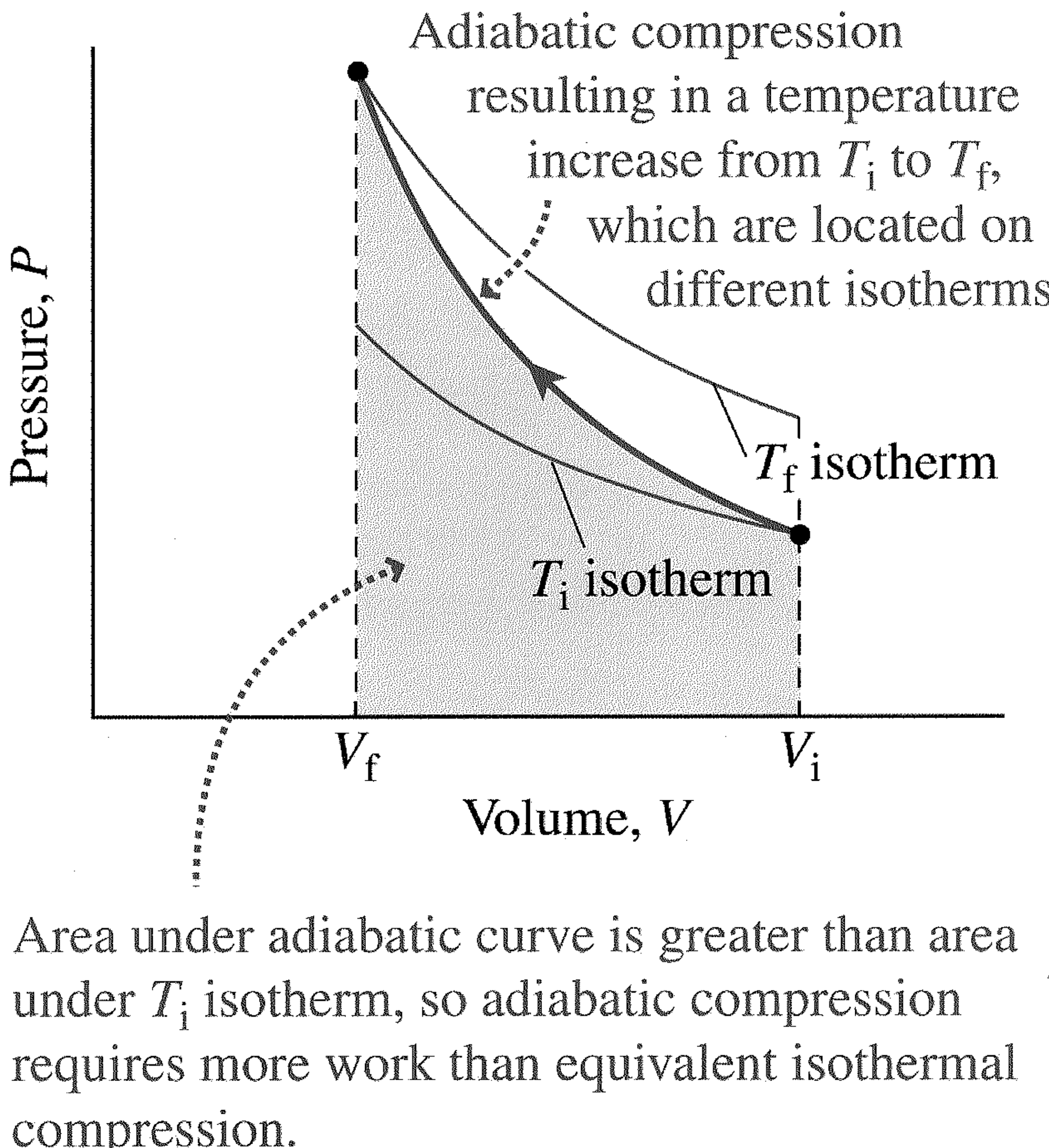


Figure 14.9






$Q = 0$

so from $\Delta U = Q + W$

$\Delta U = W$

But $U \sim E_{th} \sim T$

so if $(+W)$ then $T\uparrow$

$P \cdot V^{\gamma} = \text{const}$

$\gamma = C_p / C_v$

For monoatomic

$C_p = 5R/2$

$C_v = 3R/2$

so $\gamma = 5/3$

For diatomic

$\gamma = 7/5$

$$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

$Q=0$; 2 mols $H_2$ do 750 J of work | $\Delta T = ?$

expansion

**46. ORGANIZE AND PLAN** The work done on the gas in an adiabatic process is proportional to the difference between two products: the final pressure times volume minus the initial pressure times volume. From the ideal gas law this means that the work done on the gas is proportional to the difference between final and initial temperature.

*Known:* $n = 2.0$ mol; $W = -750$ J.

**SOLVE** (a) T

decreases.

The reason for this is that to do work the gas must expend its internal energy, which is proportional to temperature for a diatomic gas.

(b) The work done in an adiabatic process is:

$$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$$

$\gamma = \frac{7}{2}$ for diatomic

Rewrite this expression using the ideal gas law:

$P_i V_i = nRT_i$

$P_f V_f = nRT_f$

$$W = \frac{P_f V_f - P_i V_i}{\gamma - 1} = \frac{nR}{\gamma - 1}(T_f - T_i) = \frac{nR\Delta T}{\gamma - 1}$$

Solve for the temperature difference and insert know values:

$P_f V_f - P_i V_i = nR(T_f - T_i)$

$$\Delta T = \frac{(\gamma - 1)W}{nR} = \frac{\left(\frac{7}{5} - 1\right)(-750\text{ J})}{(2.0\text{ mol})(8.31\text{ J/(mol}\cdot\text{K)})} = -18\text{ K}$$

**REFLECT** The expression we derived here between the work done and the temperature difference holds true for all adiabatic processes if the gas is an ideal gas.

## eviewing New Concepts: The First Law of Thermodynamics n Thermal Processes

| Process | Work $W$ | First law accounting, with $\Delta U = Q + W$ |
|---|---|---|
| Constant pressure | $W = -P\Delta V$ | $\Delta U = Q - P\Delta V$ |
| Constant temperature (isothermal) | $W = nRT \ln\left(\frac{V_i}{V_f}\right)$ | $\Delta U = 0$<br>$Q = -W = -nRT \ln\left(\frac{V_i}{V_f}\right)$ |
| Constant volume | $W = 0$ | $\Delta U = Q$ |
| Adiabatic ($Q = 0$) | $W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$ | $\Delta U = W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$ |

$P.V = nRT$ $\quad$ $P.V^{\gamma} = \text{const}$

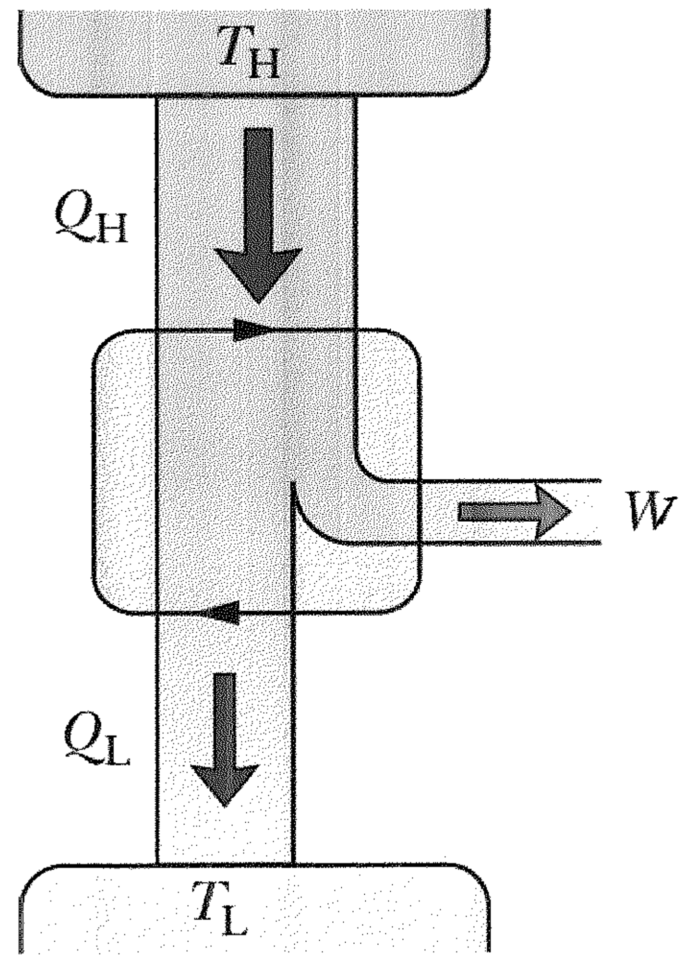
monoatomic $\gamma = 5/3$

$\gamma = 7/5$


Calorimetry reveals that a Milky Way® candy bar contains more energy than a stick of dynamite. The candy bar contains 200 food Calories. That's 200,000 physicist calories or about 840,000 joules! Nearly a megajoule! A megajoule of energy from a candybar can perform enough work to lift an average 70-kilogram human being 1200 meters in the air. That's higher than the cliff face of Yosemite's El Capitan. No stick of dynamite can do that! In fact,an ounce of dynamite produces only one-quarter as many calories when it explodes as an ounce of sugar does when it burns.

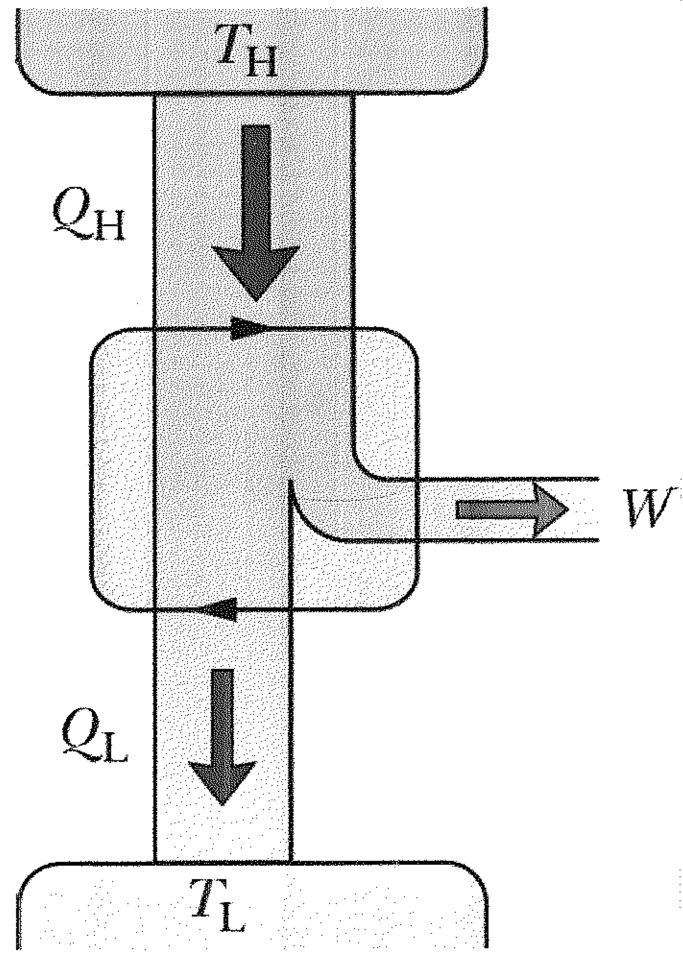
# Heat Engines

- Elements of an engine (                )
  - Heat $Q_H$ is transferred from the hot reservoir of temperature $T_H$ to the working substance
  - Heat $Q_L$ is transferred from the working substance to the cold reservoir $T_L$



- **Thermal efficiency** (or **efficiency**):

$$\varepsilon = \frac{energy\ we\ get}{energy\ we\ pay\ for} = \frac{|W|}{|Q_H|}$$




- Engines work in **cycles**; if reversible

Energy is conserved

$W = Q_H - Q_L$

$$\Delta E_{\text{int}} = 0 = (|Q_H| - |Q_L| - W)$$

$$\varepsilon = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{|Q_H|} = 1 - \frac{|Q_L|}{|Q_H|}$$

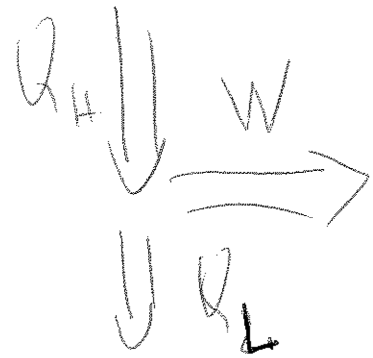
$W = 650\text{ J} \rightarrow Q_L = 1270\text{ J}; \quad \varepsilon = ?$

**63.** . **ORGANIZE AND PLAN** The efficiency is the ratio between work done and heat used.
*Known:* $W = 650\text{ J}$; $Q_H = 1270\text{ J}$.
**SOLVE** The heat engine's efficiency is:

$Q_H = W + Q_L$
$= 1920\text{ J}$

$$e = \frac{W}{Q_H} = \frac{(650\text{ J})}{1920\text{ J}} = 0.338 \approx 34\%$$

P



Carnot Engine

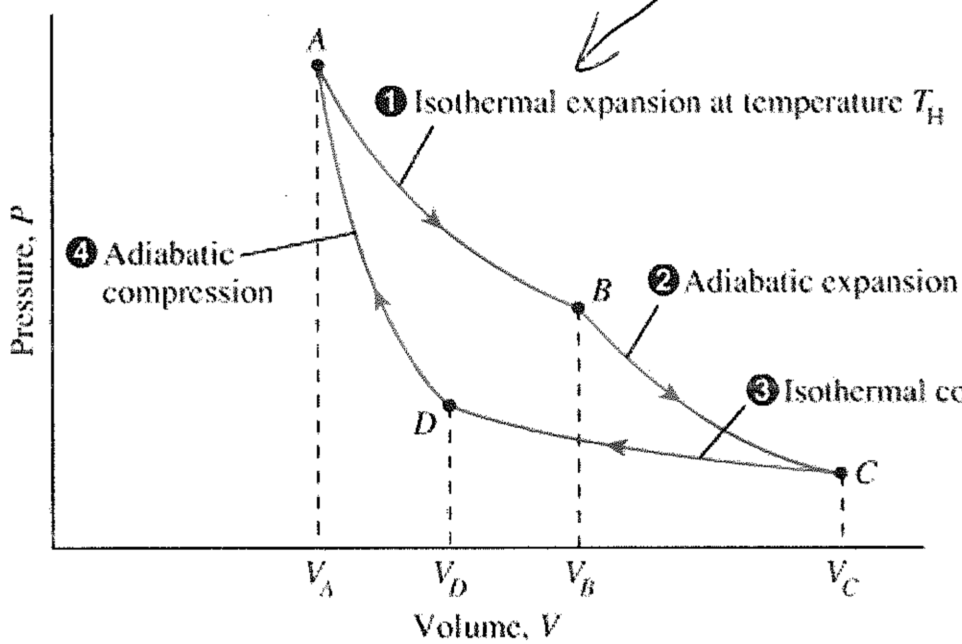
Carnot efficiency.

Operates between $T_H$ and $T_C$ but in cycle

T in [K]

$$e_C = 1 - \frac{T_L}{T_H}$$

T [K]

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Jet engine ; $\varepsilon = ?$

**96. ORGANIZE AND PLAN** The maximum efficiency is that of a Carnot engine, one minus the temperature ratio between the cold and hot reservoirs.

*Known:* $T_H = 1050°\text{C}$; $T_C = 590°\text{C}$.

**SOLVE** The maximum efficiency is:

$$e_{\text{Carnot}} = 1 - \frac{T_C}{T_H} = 1 - \frac{(590°\text{C})}{(1050°\text{C})} = 0.348 \doteq 1 - \frac{(590 + 273)}{(1050 + 273)}$$

**REFLECT** If you could invent a way of operating a jet engine such that the exhaust temperature is that of the surrounding air (typically $-40°\text{C}$ at the cruising height of commercial airliners), you would raise the maximum efficiency to better than 0.8!

# Sample Problem 20-4

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?

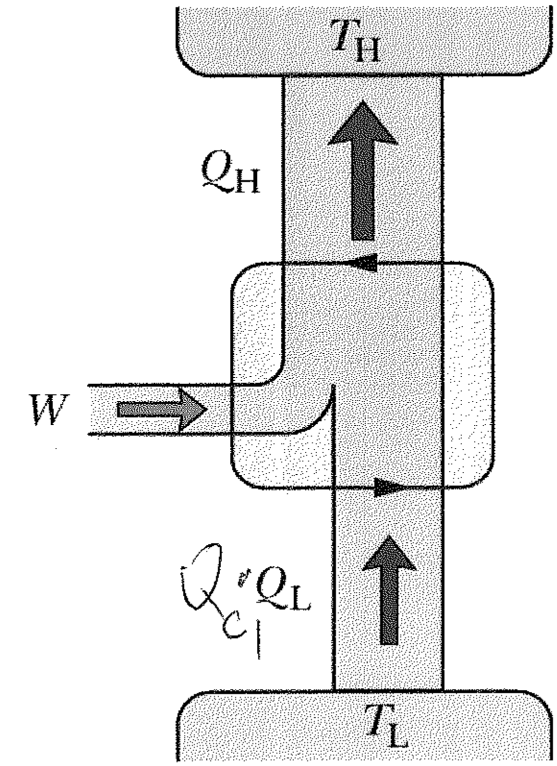
$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300\,K}{850\,K} = 0.647$$

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

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

# Refrigerators

- **Refrigerator:** device that uses work to transfer thermal energy from the low-temperature reservoir to the high-temperature reservoir (Fig 20-13)
- **Ideal refrigerator:** processes involved in the refrigerator's operations are reversible




$W = Q_H - Q_L$

$Q_L + W = Q_H$
conservation

- Coefficient of performance:

$$\mathrm{COP} = K = \frac{\textit{what we want}}{\textit{what we pay for}} = \frac{|Q_L|}{|W|} \begin{matrix} \rightarrow \text{benefit} \\ \rightarrow \text{Energy cost} \end{matrix}$$

$$|W| = |Q_H| - |Q_L| \leftarrow Q_L + W = Q_H$$

$$K = \frac{|Q_L|}{|Q_H| - |Q_L|} = \frac{1}{\frac{Q_H}{Q_L} - 1} \quad (\text{from } 2 \sim 4)$$

- Carnot (ideal) refrigerator:

$$K_C = \frac{T_L}{T_H - T_L}$$

# Problem

$$K = \frac{\textit{what we want}}{\textit{what we pay for}} = \frac{|Q_L|}{|W|}$$

$$|W| = |Q_H| - |Q_L|$$

$$K = \frac{|Q_L|}{|Q_H| - |Q_L|}$$

A Carnot refrigerator does 200 J of work to remove 600 J from its cold compartment. *(a)* What is the refrigerator's coefficient of performance? *(b)* How much energy per cycle is exhausted to the kitchen as heat?

34. (a) We use Eq. 21-12.

$$\frac{Q_L}{Q_H - Q_L} = K = \frac{|Q_L|}{|W|} = \frac{600}{200} = 3 \,.$$

(b) Energy conservation for a refrigeration cycle requires $|Q_L| + |W| = |Q_H|$, so that the result is 800 J.

$$Q_H - Q_L = W$$

$$Q_H = W + Q_L = 200\,J + 600\,J = 800\,J$$

Real Refrigerators

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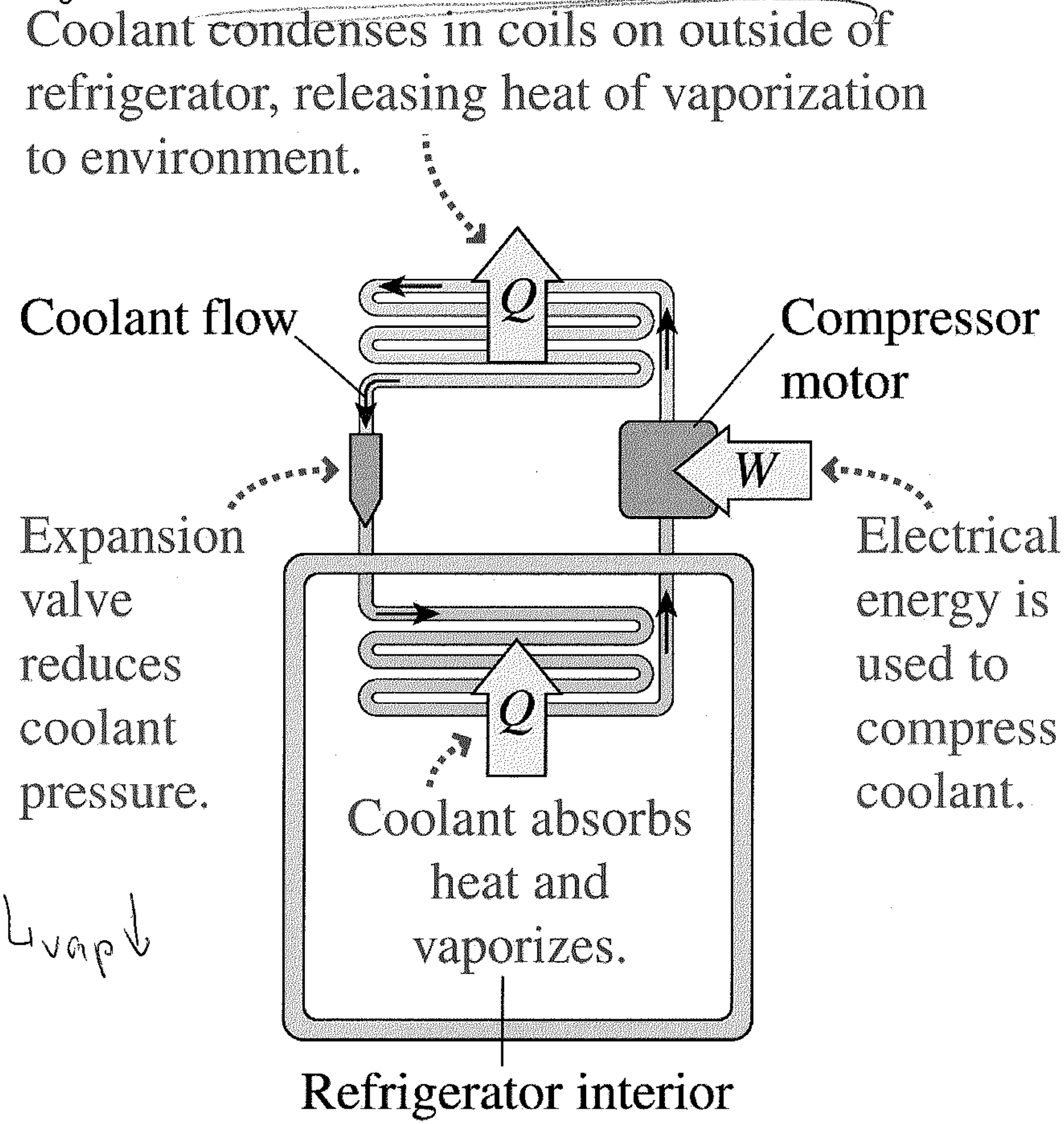


$P\downarrow$ so $L_{vap}\downarrow$