Lecture 47

(CH14:1)

The Laws of Thermodynamics

Chapter 14 Opener

Review

T [K]

$P.V = nRT$

$P.V = N k_B T$, $N = n.N_A$, $N_A = 6.023 \times 10^{23}$

$\bar{K} = \frac{3}{2} k_B T$ (one molecule)

$\overset{\circ}{E}_{th} = N.\frac{3}{2} k_B T$, $\overset{\circ-\circ}{E} = N \frac{5}{2} k_B T$

$E^1_{th} \xrightarrow{Q} E^2_{th}$; Q [J], [cal]

1 cal = 4.18 J

$Q = m c_m \Delta T$

$\left.\begin{array}{l} Q = n c_v \Delta T \\ Q = n c_p \Delta T \end{array}\right]$, $\overset{\circ}{c}_v = 3 \times \frac{1}{2} R$; degrees of freedom

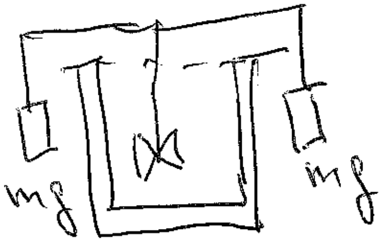
$\overset{\circ-\circ}{C}_v = 5 \times \frac{1}{2} R$

$Q = m L_{f,v}$, $\Delta T = 0$

$$\frac{Q}{t} = K.A.\frac{\Delta T}{\Delta x}$$

and $\Delta T \leftarrow W_{mechanical}$

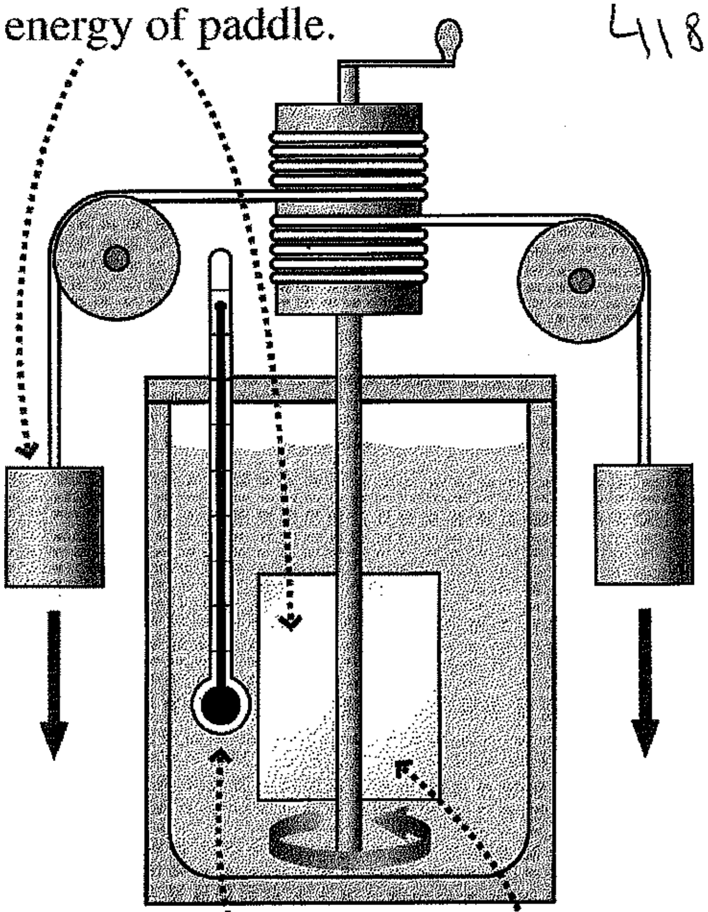
$\nwarrow Q$



Mechanical equivalent of heat

Figure 13.1

4186 J raise 1kg H_2O by 1°C



Potential energy of falling weights becomes kinetic energy of paddle.

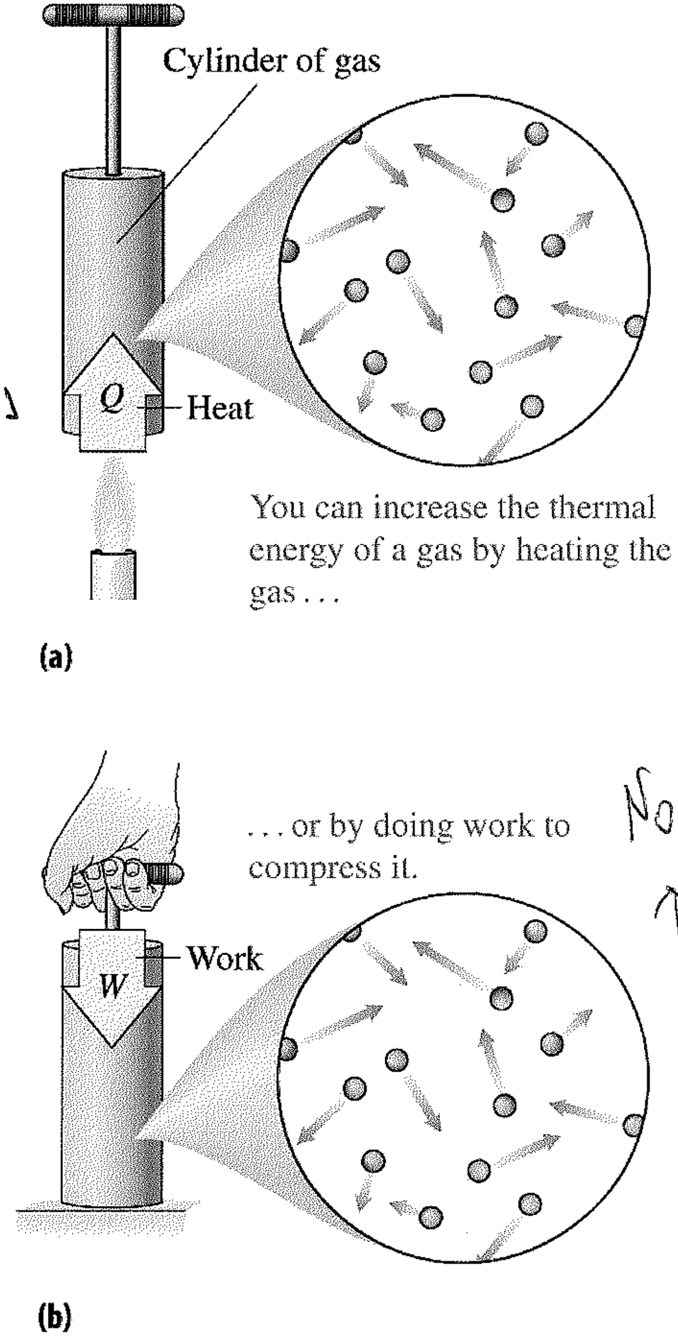
The paddle's kinetic energy in turn becomes internal energy of the water, indicated by rising temperature.

Laws of Thermodynamics

Figure 14.1

U - internal energy

$U \leftarrow E_{th} + \text{energy of bonds}$



You can increase the thermal energy of a gas by heating the gas . . .

. . . or by doing work to compress it.

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1st Law

$$\boxed{\Delta U = Q + W}$$

Monoatomic gas

$$\Delta U = \Delta E_{th} = \frac{3}{2} N k_B \Delta T$$

No interaction, i.e. ideal gas

Diatomic gas

$$\Delta U = \Delta E_{th} = \frac{5}{2} N k_B \Delta T$$

Degrees of freedom

1.25 ℓ He → ΔT = 100°C ; ΔU = ?

27. ORGANIZE AND PLAN Helium is a monatomic gas so the internal energy difference when warmed is $\Delta U = \frac{3}{2} N k_B \Delta T$. The number of atoms in 1.25 L is given by the ideal gas law.

Known: $V = 1.25\ \text{L};\ \Delta T = 100°\text{C}$.

SOLVE From the ideal gas law $PV = Nk_BT$ we find that internal energy increases by:

$$\xrightarrow{} \quad Nk_B = \frac{PV}{T}$$

$$\Delta U = \frac{3}{2} N k_B \Delta T = \frac{3}{2} PV \frac{\Delta T}{T}$$

1 ℓ = 10^{-3} m³

1 atm = 1.013×10^5 Pa

≈ 101 kPa

Insert known values:

$$\Delta U = \frac{3}{2}(1\ \text{atm})(1.25\ \text{L})\frac{(100°\text{C})}{(20°\text{C})} = \frac{3}{2}(101\ \text{kPa})(1.25 \times 10^{-3}\ \text{m}^3)\frac{(373\ \text{K})}{(293\ \text{K})} = 64.8\ \text{J}$$

REFLECT We will assume room temperature and atmospheric pressure unless stated otherwise (or unless such an assumption appears obviously erroneous). Note that it's important to convert the room temperature to Kelvin because it's not a temperature difference.

80 kcal per km = ΔU

~330kJ

$Q = ?$ (lost) if 120g H_2O lost

$W = ?$

53. ORGANIZE AND PLAN The heat lost is the heat of vaporization of 120 g of perspiration, which we can approximate with 120 g of water. The heat of vaporization of water is listed in Table 13.3. The work done is the internal energy change minus the heat lost.

Known: $\Delta U = 80$ kcal; $m = 120$ g; $L_v = 2.26 \times 10^6$ J/kg.

SOLVE (a) The heat lost is given by Equation 13.6:

$$Q = mL_v = (120\text{ g})(2.26 \times 10^6\text{ J/kg}) = 271\text{ kJ}$$

(b) The work done by the runner is:

$\Delta U = Q + W$

1 cal = 4.18 J

$$W = \Delta U - Q = \underset{330\text{kJ}}{(80\text{ kcal})} - (271\text{ kJ}) = 64\text{ kJ}$$

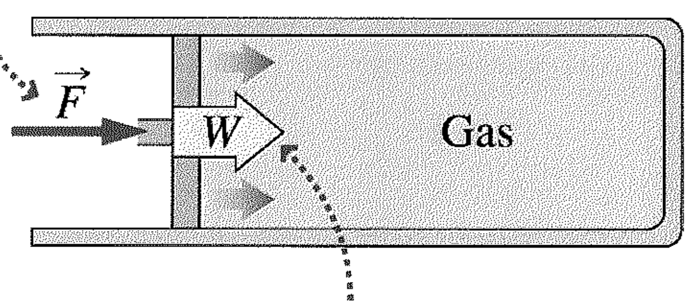
REFLECT The heat of vaporization for water has a slight dependency on temperature. The value in Table 13.3 is the heat of vaporization at the boiling point. At body temperature, the heat of vaporization of water is slightly larger, 2.4×10^6 J/kg, but the value used above is an acceptable approximation.

1st Law $\boxed{\Delta U = Q + W}$

Figure 14.2

(sign rule)

Piston compresses the gas.

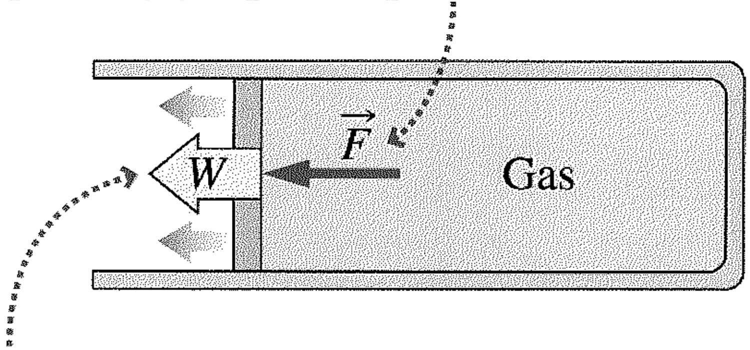


Force and displacement are in the same direction, so the piston does positive work on the gas.

$W > 0$

(a) Gas is compressed: work is positive

Expanding gas pushes piston out.



Because the gas does positive work on the piston, the work done *on the gas* is *negative*.

$W < 0$

(b) Gas expands: work is negative

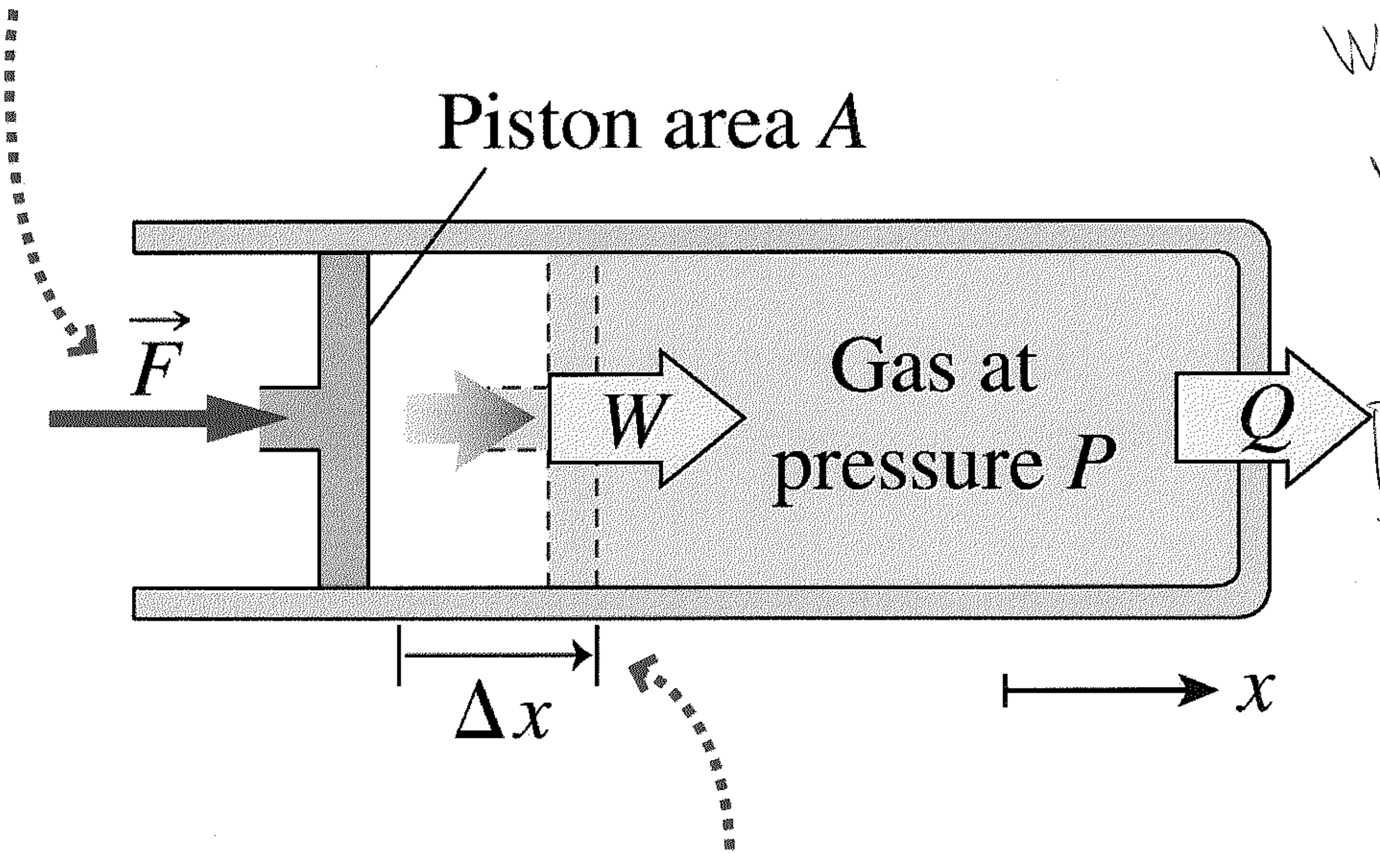
P= const. (Isobaric process)

$P =$ 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

$\Delta V = V_f - V_i$

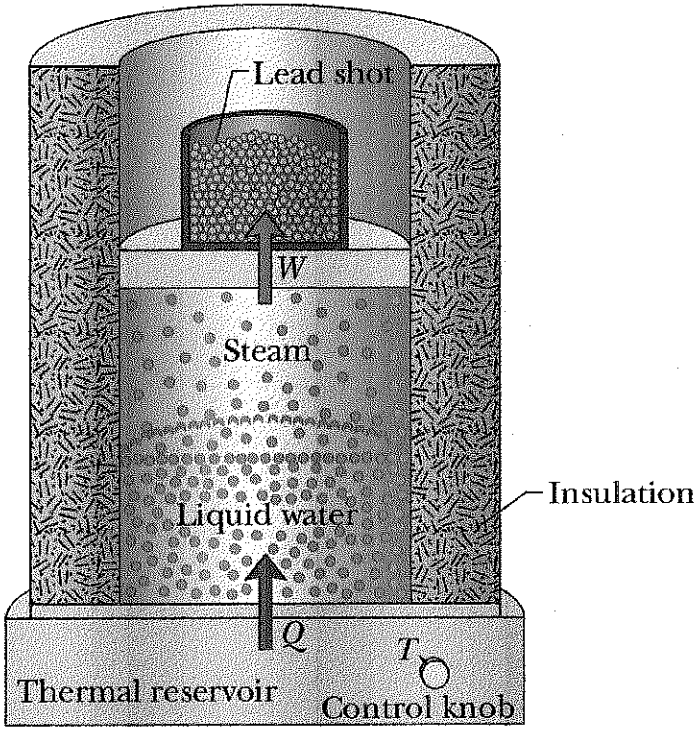
$\Delta V < 0$

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

so $W > 0$ on the gas

Sample Problem 18-5

Let 1.0 kg of liquid water at 100°C be converted to steam at 100°C by boiling at standard atmospheric pressure (which is 1.0 atm or 1.01×10^5 Pa) in the arrangement of the figure, The volume of the water changes from an initial value of 1.0×10^{-3} m^3 as a liquid to 1.672 m^3 as steam.



(a) How much work is done by the system?

$$W = -p(\underbrace{V_f - V_i}_{\Delta V})$$

$$= -(1.01\times10^5\ Pa)(1.67\,m^3 - 1.0\times10^{-3}\ m^3)$$

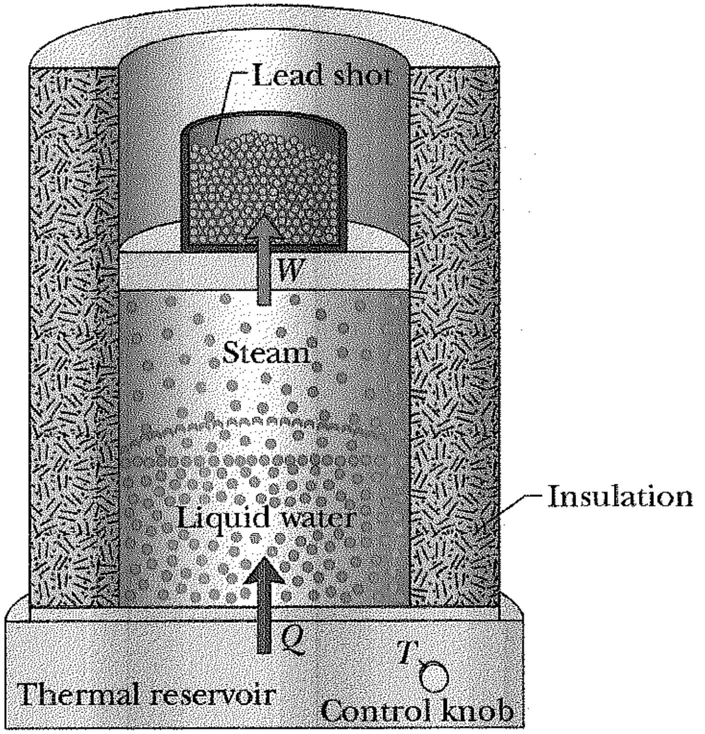
$$= -1.69\times10^5\ J = -169\ kJ$$

Sample Problem 18-5 (cont)

(b) How much energy is transferred as heat during the process? to the system

$Q = L_V m = (2256\ \text{kJ/kg})(1.0\ \text{kg})$

$= 2{,}256\ \text{kJ}$



(c) What is the change in the system's internal energy?

$\Delta U = Q + W$, but $W = -169\ \text{kJ}$

$\Delta U = Q + W = 2256\ \text{kJ} - 169\ \text{kJ}$

$= 2{,}087\ \text{kJ}$

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).

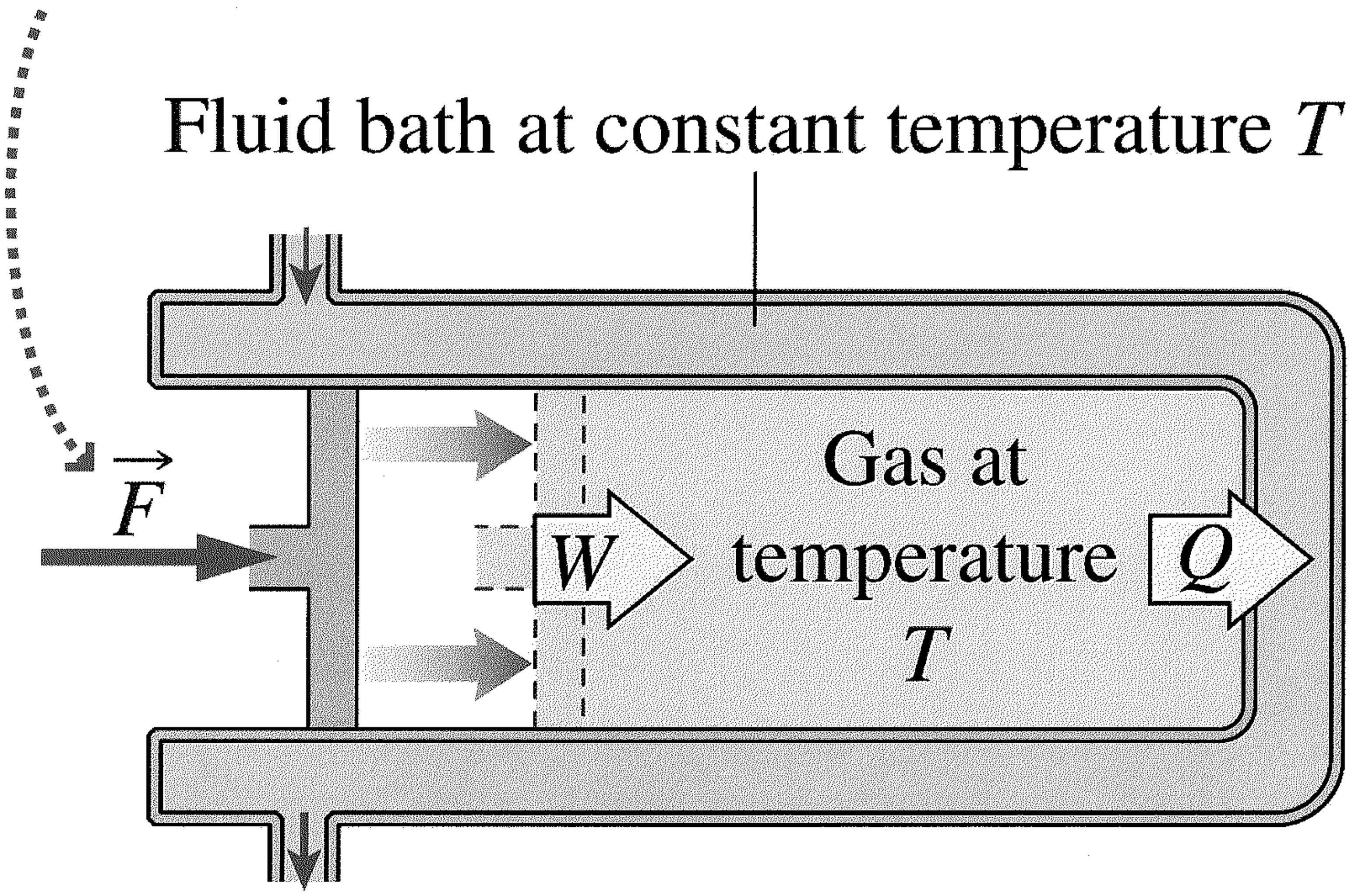
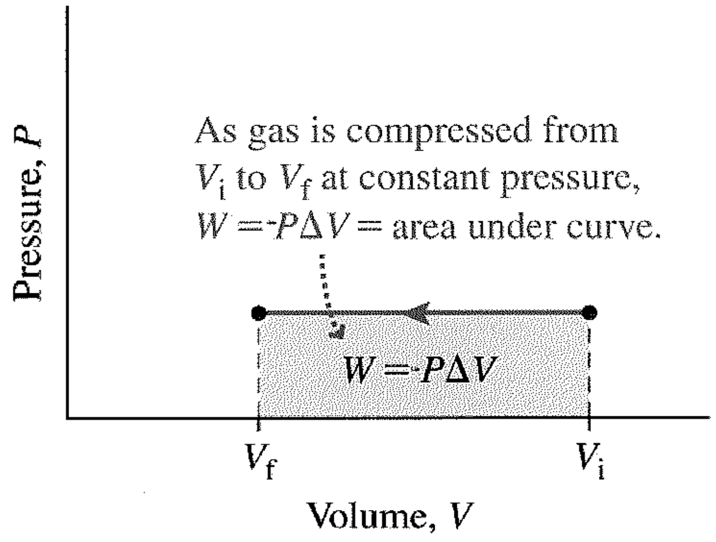


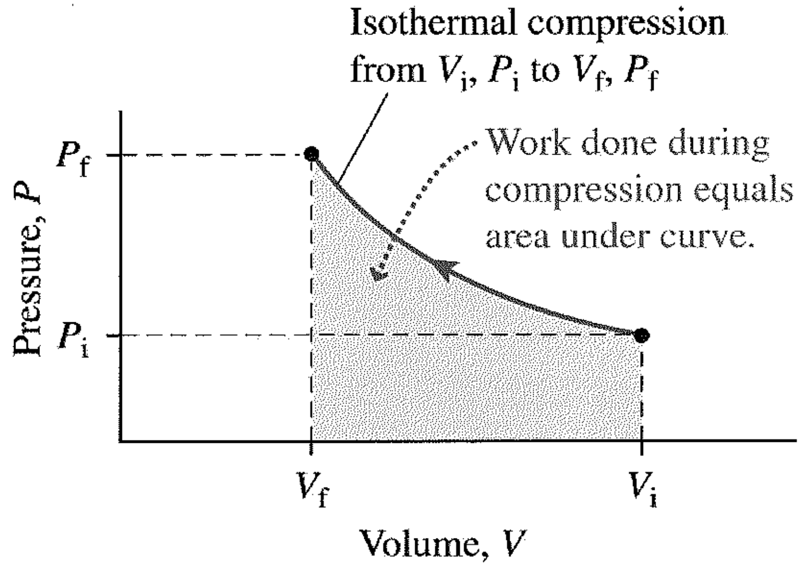
Figure 14.5



(a) Compression at constant pressure

For $P = \text{const}$

$W = -P \cdot \Delta V$



(b) Isothermal compression

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

$$\boxed{\begin{gathered} P \cdot V = nRT \\ P = \frac{nRT}{V} \end{gathered}}$$

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

on the gas

Sample Problem 19-2

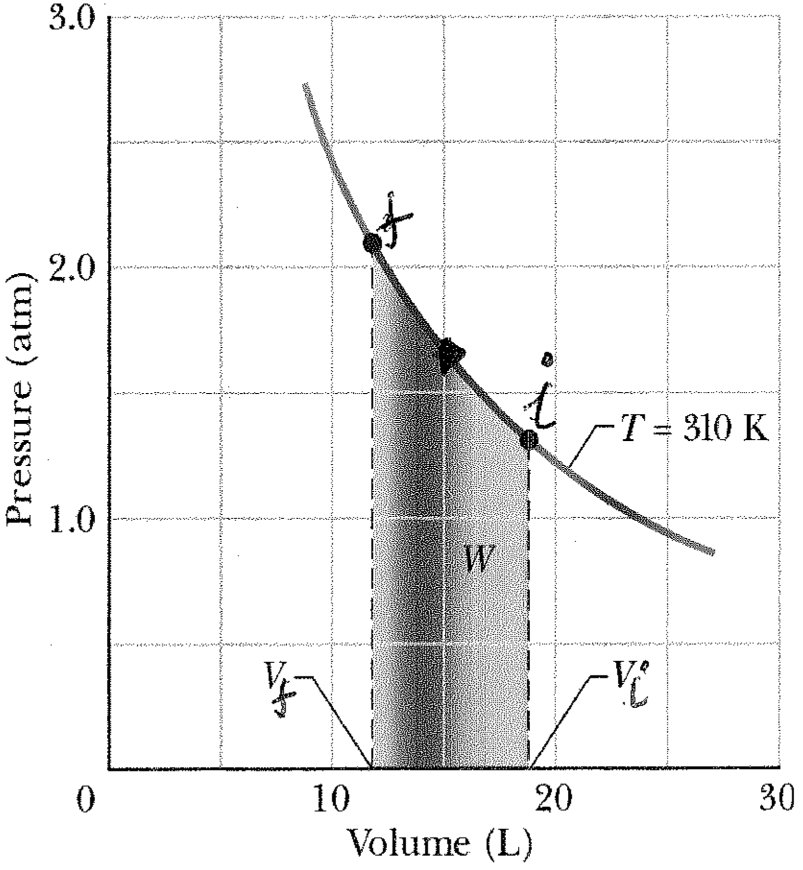
One mole of oxygen (assume to be an ideal gas) shrinks at a constant temperature T of 310 K from an initial volume V_i of 12 L to a final volume V_f of 19 L. How much work is done on the gas during the expansion?

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

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

$$= 1183\ J$$

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



0.1 mol gas at 300K , $V\uparrow$ at $T=$ const

$Q=?$ so $V_f = 3V_i$

42.ORGANIZE AND PLAN The work done on an expanding gas is negative. The sum of the work done to and the heat added to an isothermal system is zero. To calculate a precise value we use the formula for work done on an isothermal system.

Known: $n = 0.10\text{ mol}$; $T = 300\text{ K}$; $V_f = 3V_i$.

SOLVE (a) When the gas is expanding the work done on the gas is negative, so the heat added is positive, i.e., heat flows into the gas.

(b) The work done on an isothermal system is:

$0 = \Delta U \sim E_{th} = Q + W$

W is (−w) so $Q > 0$

for $T=$ const

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

↘ by the gas

and $W + Q = 0$, so the required heat is:

$Q = -W$

$$Q = -W = -nRT\ln\left(\frac{V_i}{V_f}\right) = -(0.10\text{ mol})(8.31\text{ J/(mol}\cdot\text{K)})(300\text{ K})\ln\left(\frac{1}{3}\right) = 0.27\text{ kJ}$$

REFLECT It is straightforward to see that the answer is reasonable, because $\ln(3) \approx 1$.

0.3mol He  $V_f = 5V_i$ at 300 K | $W_{gas} = ?$

38. **ORGANIZE AND PLAN** We will use the formula for work done by the gas in an isothermal process.

Known: $n = 0.30$ mol; $T = 300$ K; $V_f = 5V_i$.

SOLVE The work done on the gas is:

$$W = nRT\ln\left(\frac{V_i}{V_f}\right) = (0.30\text{ mol})(8.31\text{ J/(mol}\cdot\text{K)})(300\text{ K})\ln\left(\frac{1}{5}\right) = -1.2\text{ kJ}$$

The work done by the gas is positive 1.2 kJ.

REFLECT It does not matter in an isothermal process whether the gas is monatomic or diatomic.

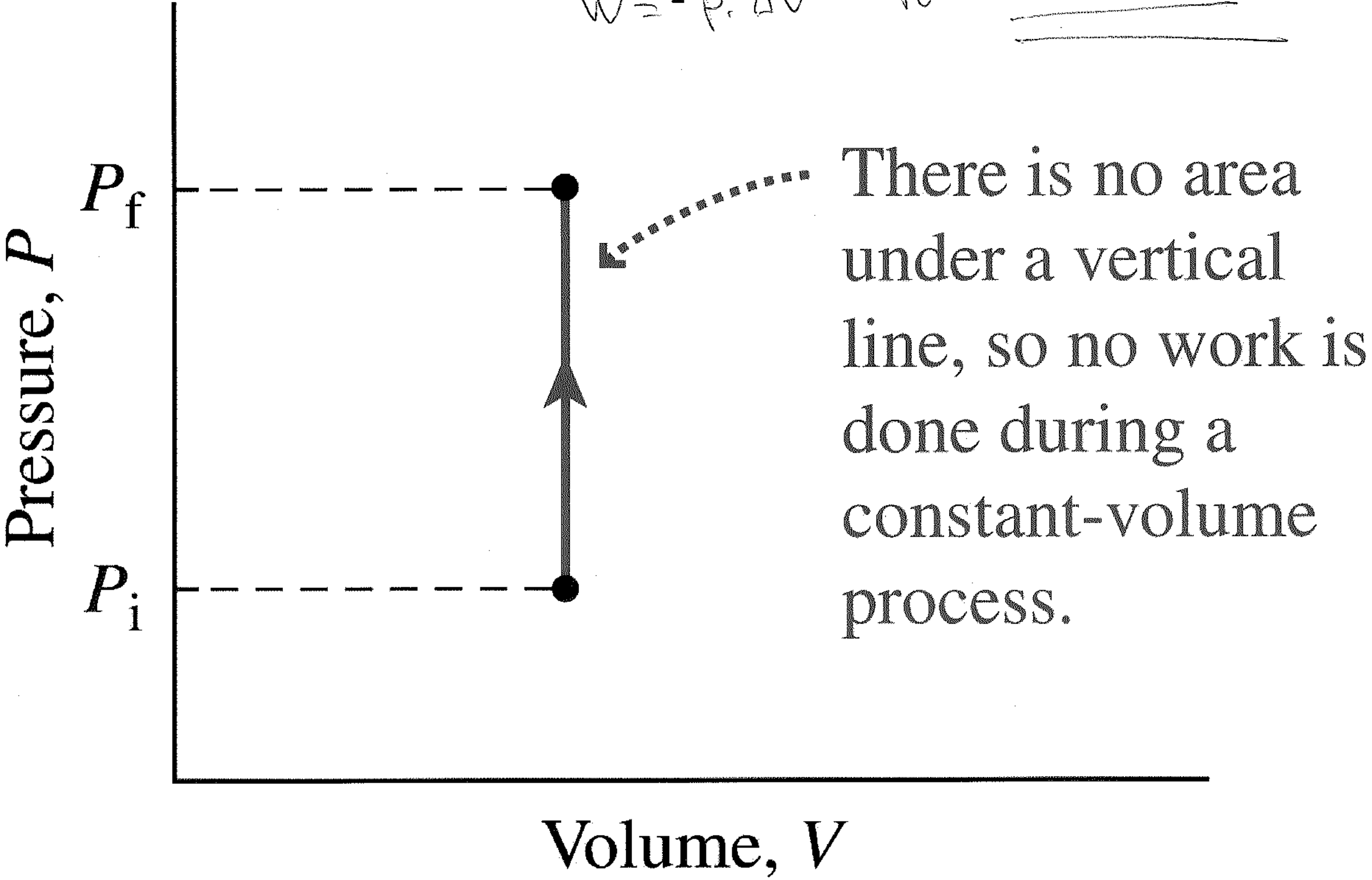
Figure 14.7

Constant Volume

$W = -P \cdot \Delta V \quad 0$

$\Delta U = Q$

$W = 0$



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

Figure 14.8

Adiabatic Process

$Q = 0$

$\Delta U = -W$

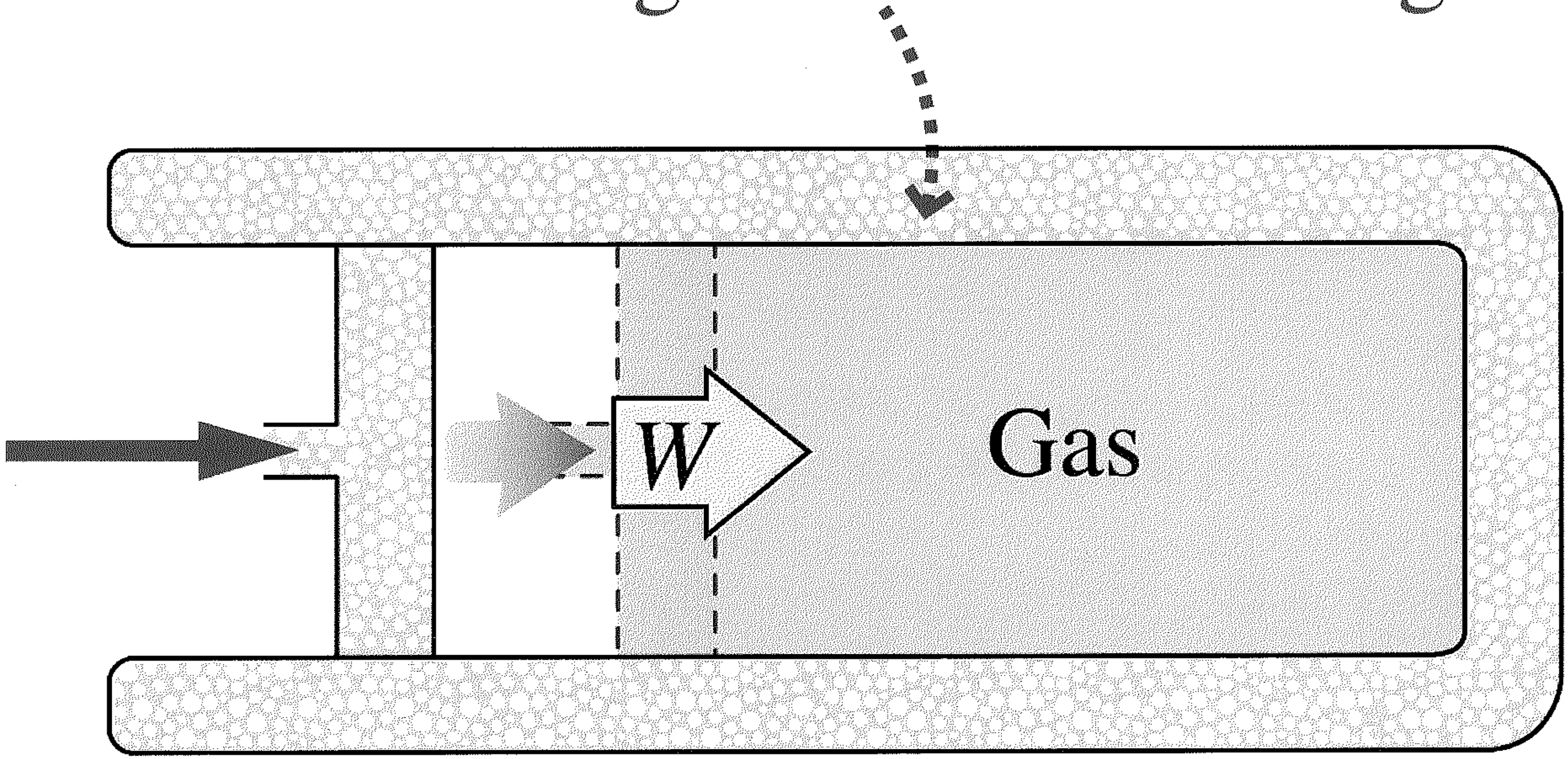
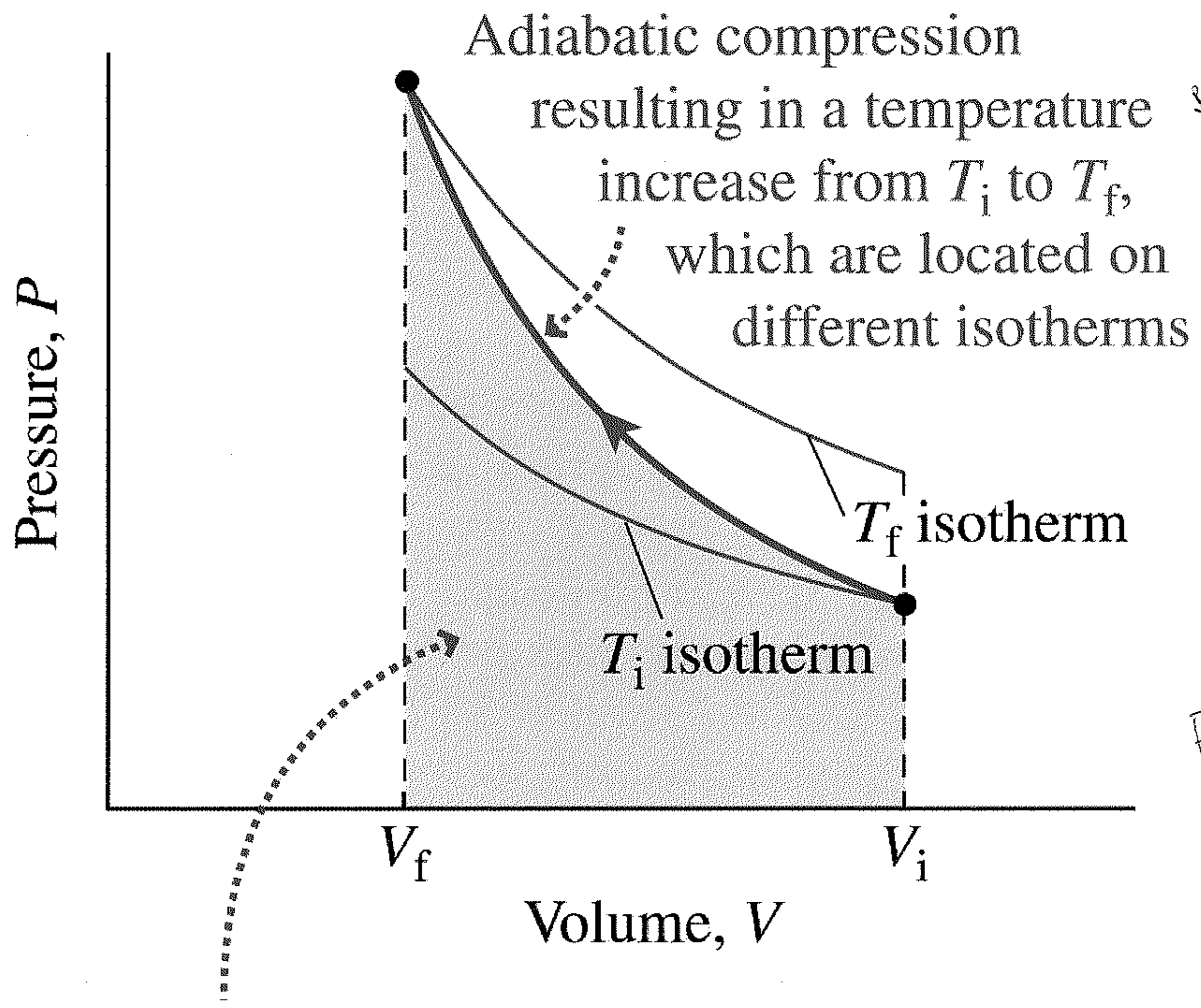

Insulation prevents heat flow between gas and surroundings.

Figure 14.9



Adiabatic compression resulting in a temperature increase from T_i to T_f, which are located on different isotherms

Area under adiabatic curve is greater than area under T_i isotherm, so adiabatic compression requires more work than equivalent isothermal compression.

$Q = 0$

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) The gas does positive work. This means the work done on the gas is negative, and from our argument above that means the final temperature is less than the initial temperature, so the gas temperature 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:

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

$P_i V_i = nRT_i$

$P_f V_f = nRT_f$

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

Solve for the temperature difference and insert know values:

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

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.

Reviewing New Concepts: The First Law of Thermodynamics in 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)	$W = nRT \ln\left(\frac{V_i}{V_f}\right)$	$\Delta U = 0$ $Q = -W = -nRT \ln\left(\frac{V_i}{V_f}\right)$
Constant volume	$W = 0$	$\Delta U = Q$
Adiabatic ($Q = 0$)	$W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$	$\Delta U = W = \frac{P_f V_f - P_i V_i}{\gamma - 1}$

$\downarrow P.V^{\gamma} = \text{Const}$

$\Delta S = \frac{Q}{T}$

↑ $45W = \frac{\Delta U}{\Delta t}$ ← ΔU↑ , W rate 165 W | $\frac{\Delta Q}{\Delta t} = ?$

29. ORGANIZE AND PLAN Heat, internal energy, and work are related through the first law of thermodynamics. We will divide the quantities in this law by time to get powers and heat flow rates.

Known: $\Delta U/\Delta t = 45\text{ W}$; $P = -165\text{ W}$.

SOLVE The first law of thermodynamics divided by time is:

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

← $\Delta U = \Delta Q + W / \Delta t$

which we can rewrite to get an expression for the heat flow into the system:

and

$\frac{W}{\Delta t} = P$

$$\frac{\Delta Q}{\Delta t} = \frac{\Delta U}{\Delta t} - P = (45\text{ W}) - (-165\text{ W}) = 210\text{ W}$$

REFLECT The power is negative because the system is doing work.

$P[W]$

$[W] = \frac{J}{s}$