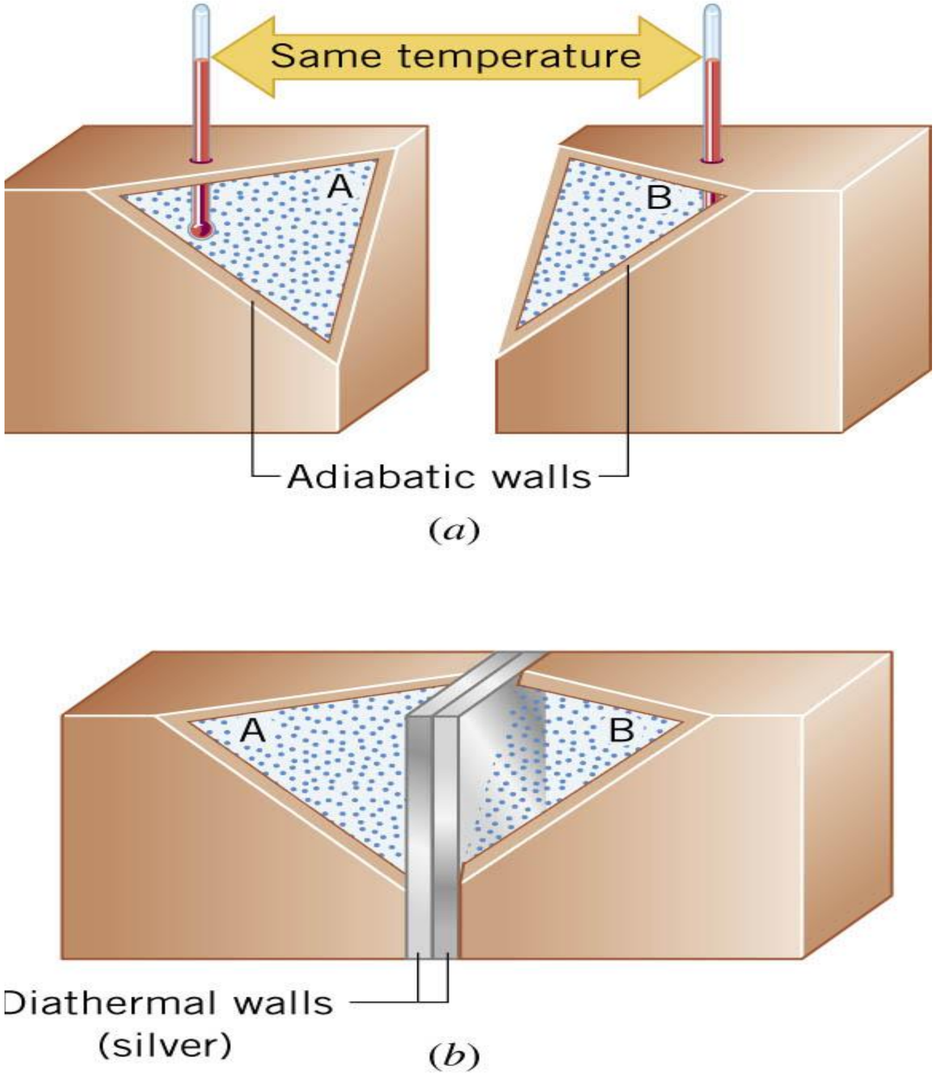
Ch15. Thermodynamics

Thermodynamics **is the branch of physics that is built upon the fundamental laws that heat and work obey.**

In thermodynamics the collection of objects on which attention is being focused is called the *system*, while everything else in the environment is called the *surroundings*. The system and its surroundings are separated by walls of some kind. Walls that permit heat to flow through them, such as those of the engine block, are called *diathermal walls*. Perfectly insulating walls that do not permit heat to flow between the system and its surroundings are known as *adiabatic walls*.

The Zeroth Law of Thermodynamics



Thermal equilibrium: **Two systems are said to be in thermal equilibrium if there is no net flow of heat between them when they are brought into thermal contact.**

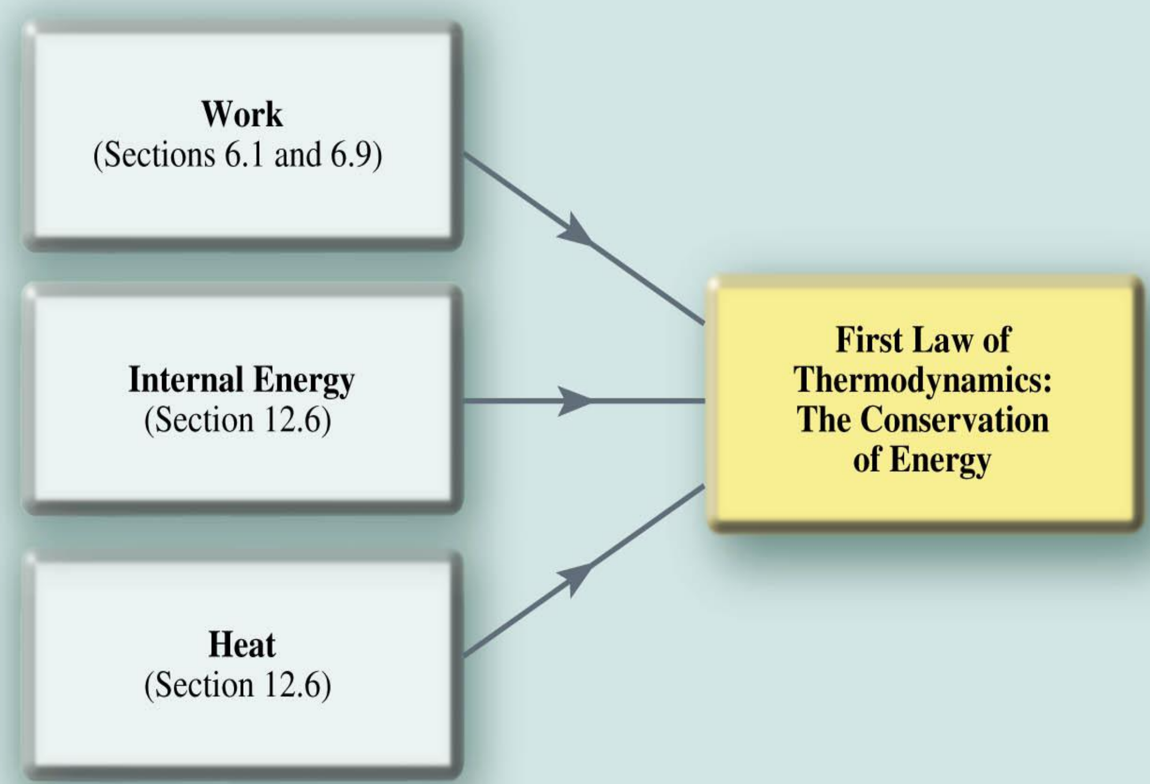
Temperature is the indicator of thermal equilibrium in the sense that there is no net flow of heat between two systems in thermal contact that have the same temperature.

THE ZEROTH LAW OF THERMODYNAMICS

Two systems individually in thermal equilibrium with a third system* are in thermal equilibrium with each other.

The First Law of Thermodynamics

CONCEPTS AT A GLANCE



Work
(Sections 6.1 and 6.9)

Internal Energy
(Section 12.6)

Heat
(Section 12.6)

First Law of Thermodynamics: The Conservation of Energy

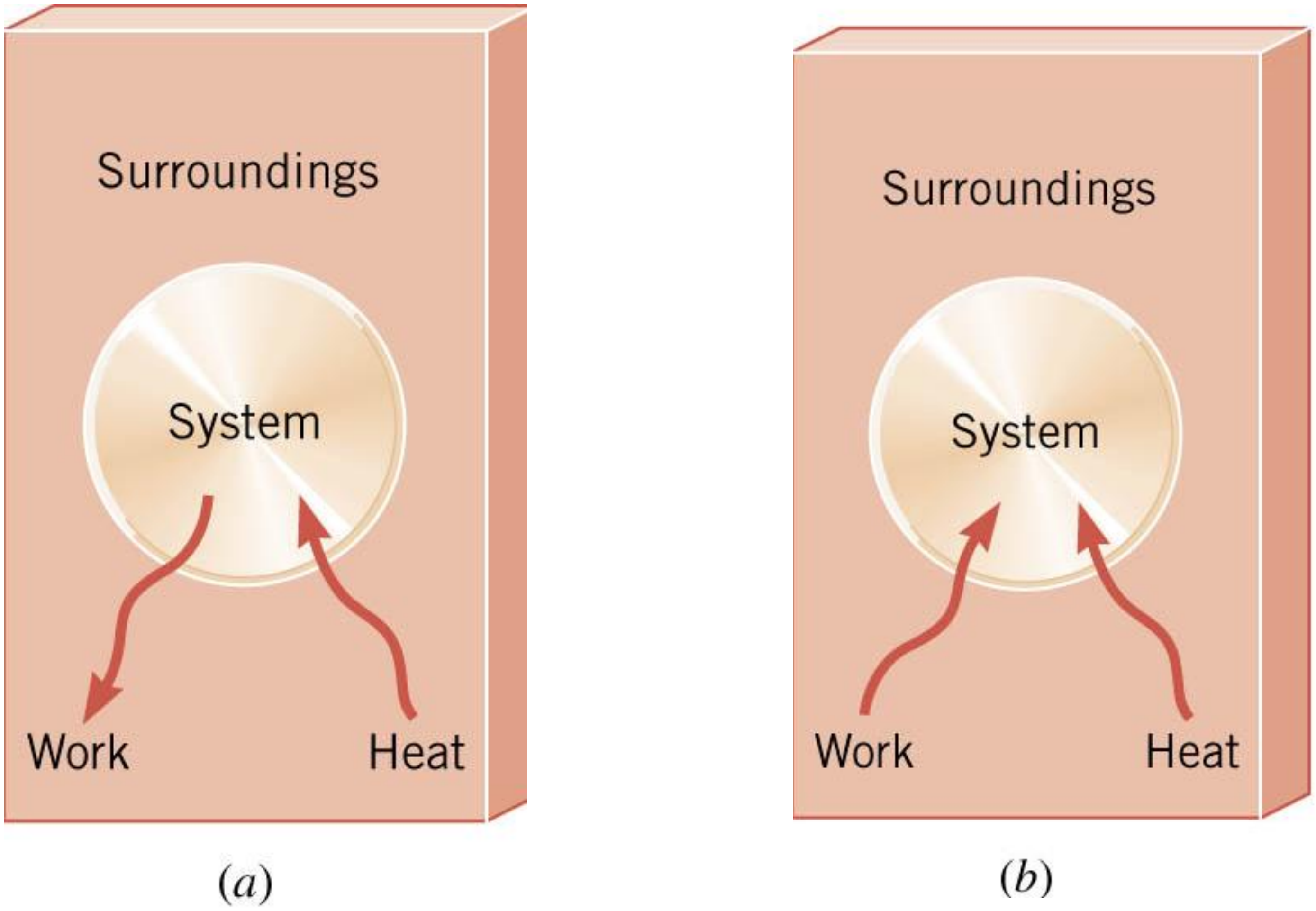
THE FIRST LAW OF THERMODYNAMICS

The internal energy of a system changes from an initial value U_i to a final value of U_f due to heat Q and work.

$$\Delta U = U_f - U_i = Q - W$$

Q **is positive when the system gains heat and negative when it loses heat.** ***W*** **is positive when work is done by the system and negative when work is done on the system.**

Example 1.
Positive and Negative Work



The figure illustrates a system and its surroundings. In part *a*, the system gains 1500 J of heat from its surroundings, and 2200 J of work is done *by* the system on the surroundings. In part *b*, the system also gains 1500 J of heat, but 2200 J of work is done *on* the system by the surroundings. In each case, determine the change in the internal energy of the system.

(a)

$$\Delta U = Q - W = (+1500\,\mathrm{J}) - (+2200\,\mathrm{J}) = \boxed{-700\,\mathrm{J}}$$

(b)

$$\Delta U = Q - W = (+1500\,\mathrm{J}) - (-2200\,\mathrm{J}) = \boxed{+3700\,\mathrm{J}}$$

Example 2. An Ideal Gas

The temperature of three moles of a monatomic ideal gas is reduced from T_i = 540 K to T_f = 350 K by two different methods. In the first method 5500 J of heat flows into the gas, while in the second, 1500 J of heat flows into it. In each case find (a) the change in the internal energy and (b) the work done by the gas.

(a)

$$\Delta U = \tfrac{3}{2} nR(T_f - T_i) = \tfrac{3}{2}(3.0\,\text{mol})\,[8.31\,\text{J}/(\text{mol}\cdot\text{K})]\,(350\,\text{K} - 540\,\text{K}) = \boxed{-7100\,\text{J}}$$

(b)

1st method $W = Q - \Delta U = 5500\,\text{J} - (-7100\,\text{J}) = \boxed{12\,600\,\text{J}}$

2nd method $W = Q - \Delta U = 1500\,\text{J} - (-7100\,\text{J}) = \boxed{8600\,\text{J}}$

Check Your Understanding 1

A gas is enclosed within a chamber that is fitted with a frictionless piston. The piston is then pushed in, thereby compressing the gas. Which statement below regarding this process is consistent with the first law of thermodynamics?

a. The internal energy of the gas will increase.

b. The internal energy of the gas will decrease.

c. The internal energy of the gas will not change.

d. The internal energy of the gas may increase, decrease, or remain the same, depending on the amount of heat that the gas gains or loses.

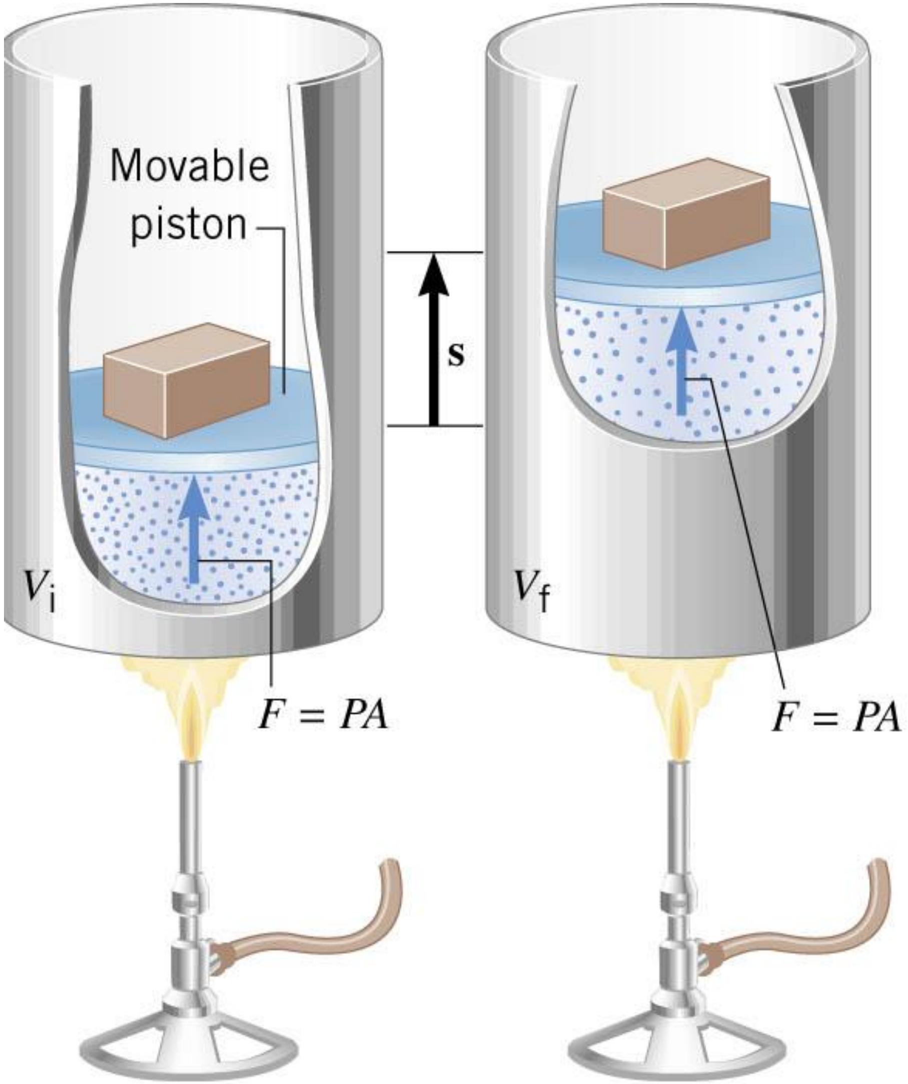
(d)

Thermal Processes

quasi-static **means that it occurs slowly enough that a uniform pressure and temperature exist throughout all regions of the system at all times.**

An isobaric process is one that occurs at constant pressure.

$$\textbf{\textit{Isobaric process}} \quad W = P\Delta V = P(V_f - V_i)$$



The substance in the chamber is expanding isobarically because the pressure is held constant by the external atmosphere and the weight of the piston and the block.

Example 3.
Isobaric Expansion of Water

One gram of water is placed in the cylinder in above figure, and the pressure is maintained at 2.0 × 10^5 Pa. The temperature of the water is raised by 31 C° . In one case, the water is in the liquid phase and expands by the small amount of 1.0 × 10^{-8} m^3. In another case, the water is in the gas phase and expands by the much greater amount of 7.1 × 10^{-5} m^3. For the water in each case, find (a) the work done and (b) the change in the internal energy.

$$c = 4186\ \mathrm{J/(kg\cdot C^\circ)}$$

$$c_P = 2020\ \mathrm{J/(kg\cdot C^\circ)}.$$

(a)

$$W_{\text{liquid}} = P\Delta V = (2.0 \times 10^5\ \text{Pa})(1.0 \times 10^{-8}\ \text{m}^3) = \boxed{0.0020\ \text{J}}$$

$$W_{\text{gas}} = P\Delta V = (2.0 \times 10^5\ \text{Pa})(7.1 \times 10^{-5}\ \text{m}^3) = \boxed{14\ \text{J}}$$

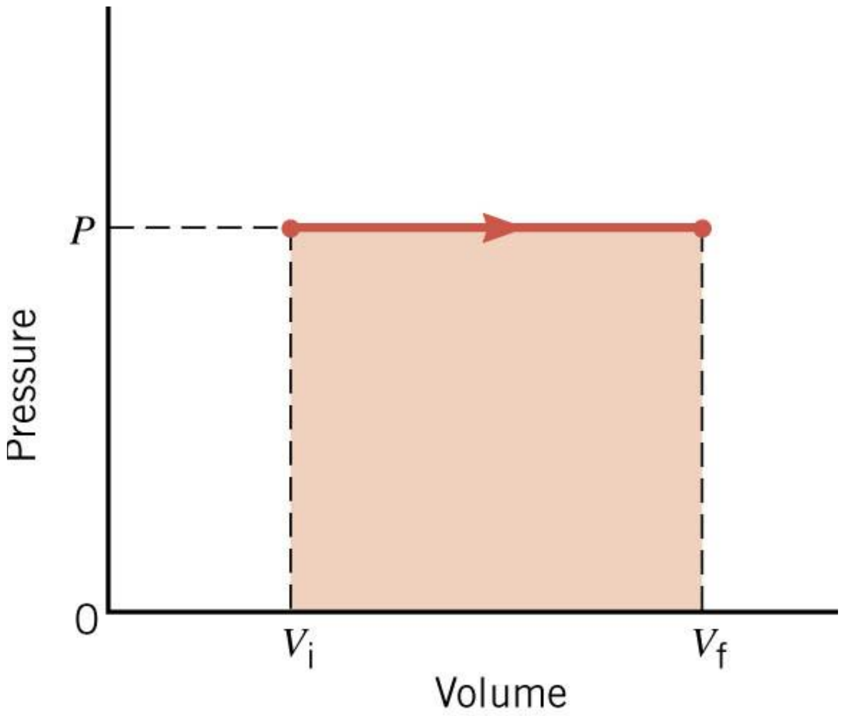
(b)

$$\Delta U_{\text{liquid}} = [4186\ \text{J}/(\text{kg}\cdot\text{C}^\circ)](0.0010\ \text{kg})(31\ \text{C}^\circ) - 0.0020\ \text{J}$$

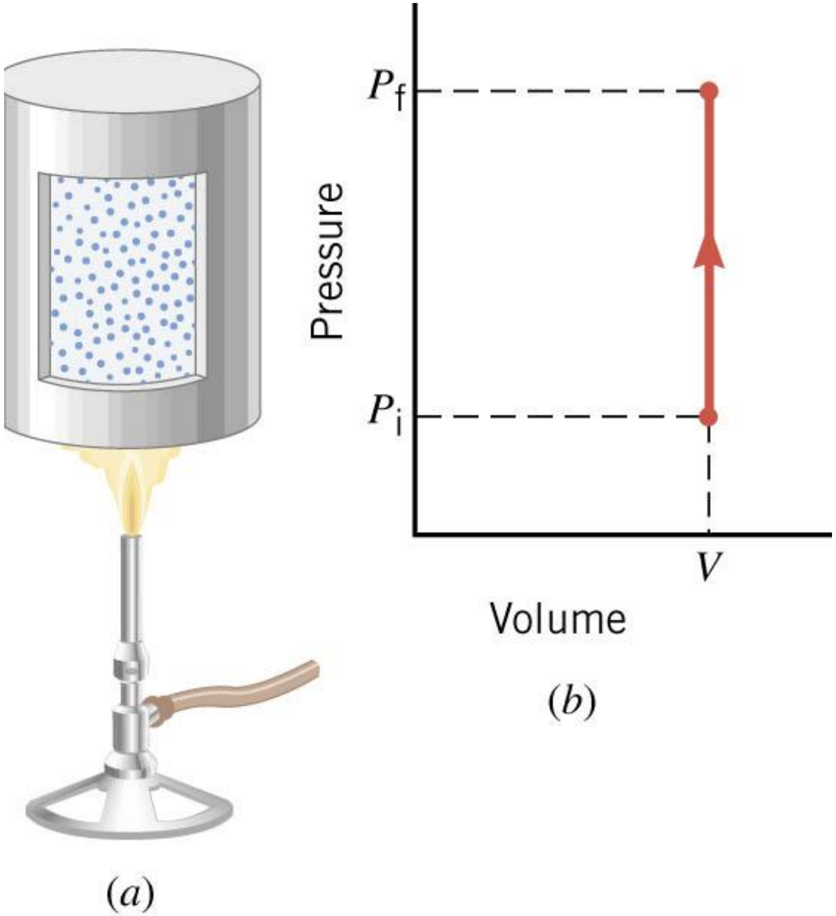
$$= 130\ \text{J} - 0.0020\ \text{J} = \boxed{130\ \text{J}}$$

$$\Delta U_{\text{gas}} = [2020\ \text{J}/(\text{kg}\cdot\text{C}^\circ)](0.0010\ \text{kg})(31\ \text{C}^\circ) - 14\ \text{J}$$

$$= 63\ \text{J} - 14\ \text{J} = \boxed{49\ \text{J}}$$



For an isobaric process, a pressure-versus-volume plot is a horizontal straight line, and the work done [$W = P(V_f - V_i)$] is the colored rectangular area under the graph.



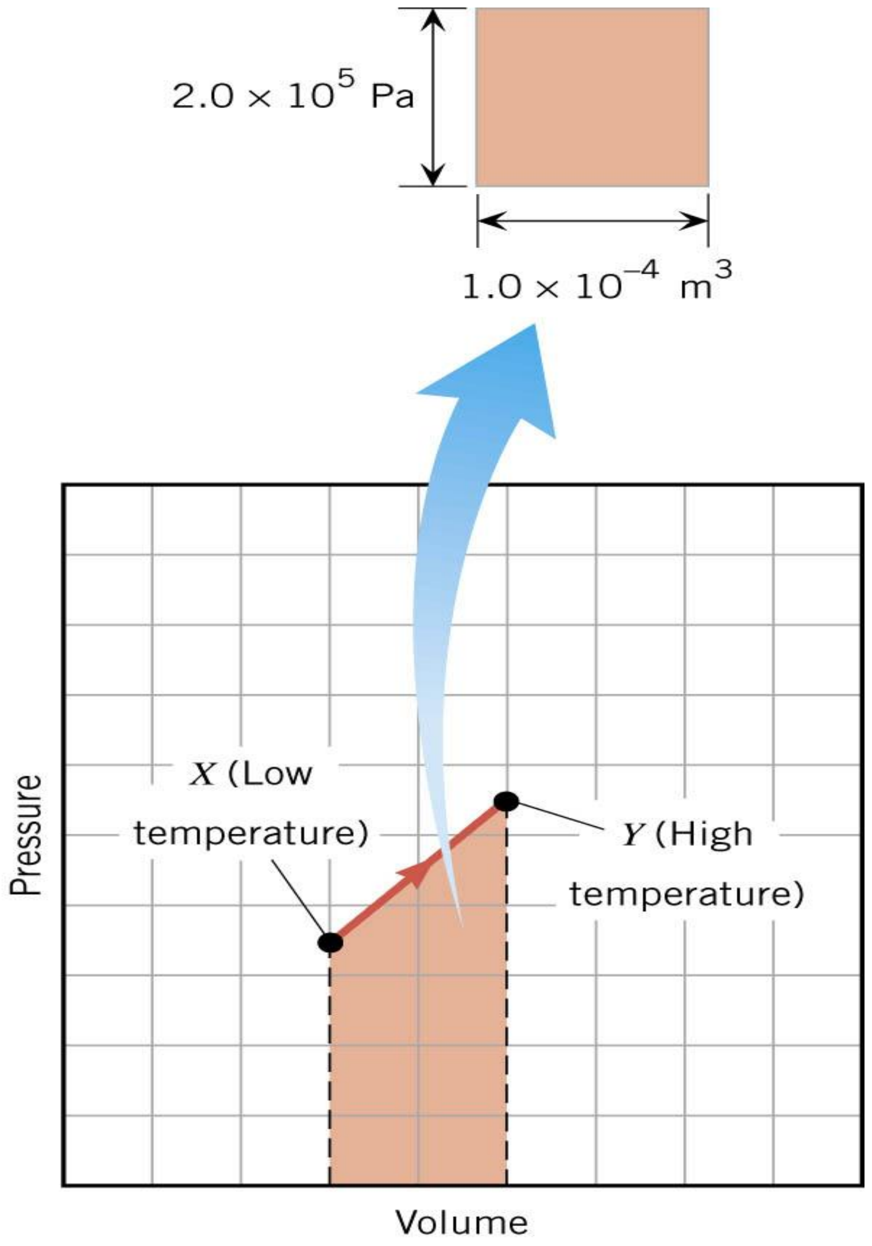
(a) The substance in the chamber is being heated isochorically because the rigid chamber keeps the volume constant.

(b) The pressure-volume plot for an isochoric process is a vertical straight line. The area under the graph is zero, indicating that no work is done.

isochoric process, one that occurs at constant volume.

***isothermal process*, one that takes place at constant temperature.** **(when the system is an ideal gas.)**

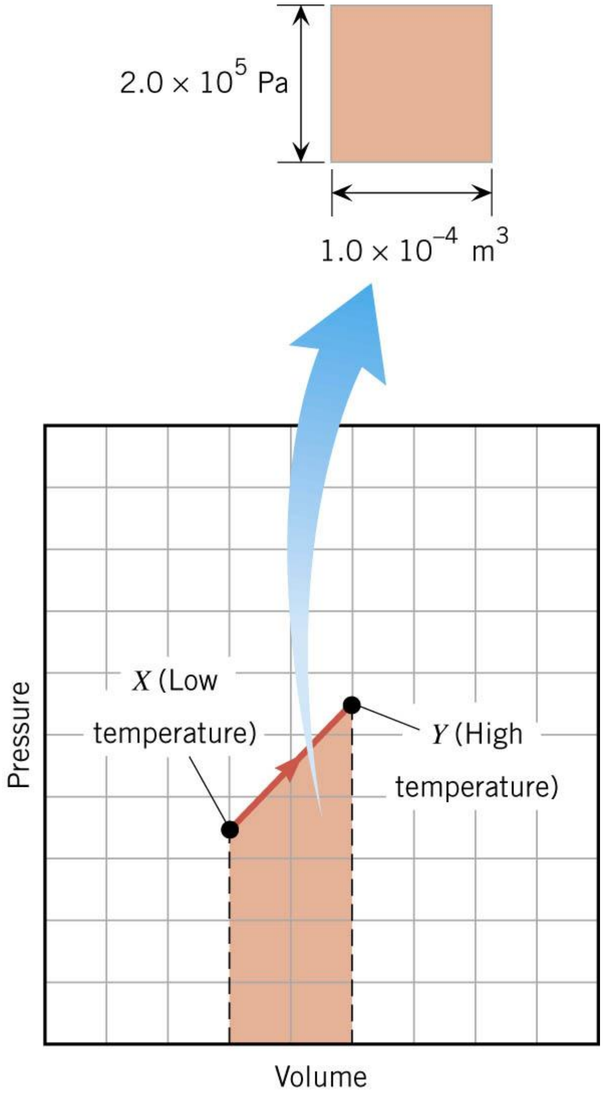
***There is adiabatic process*, *one that occurs without the transfer of heat* . Since there is no heat transfer, Q equals zero, and the first law indicates that $\Delta U = Q - W = -W$. Thus, when work is done by a system adiabatically, W is positive and the internal energy of the system decreases by exactly the amount of the work done. When work is done on a system adiabatically, W is negative and the internal energy increases correspondingly.**



The area under a pressure-volume graph is the work for any kind of process.

The colored area gives the work done by the gas for the process from *X* to *Y*.

Example 4. Work and the Area Under a Pressure-Volume Graph

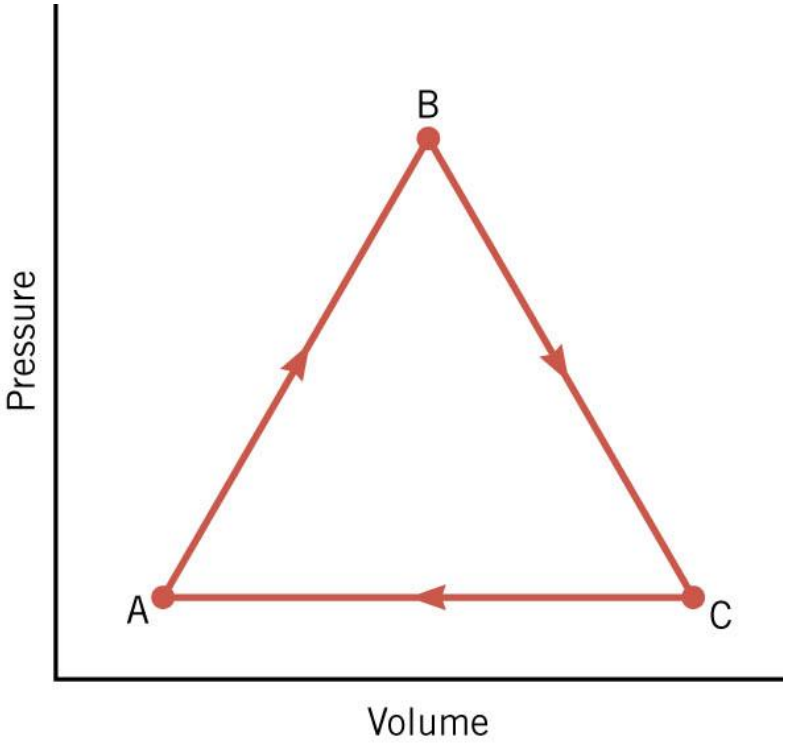


Determine the work for the process in which the pressure, volume, and temperature of a gas are changed along the straight line from *X* to *Y* in the figure.

$$W = +(8.9\ \text{squares})(2.0 \times 10^{1}\ \text{J}/\text{square})$$

$$= +180\ \text{J}$$

Check Your Understanding 2

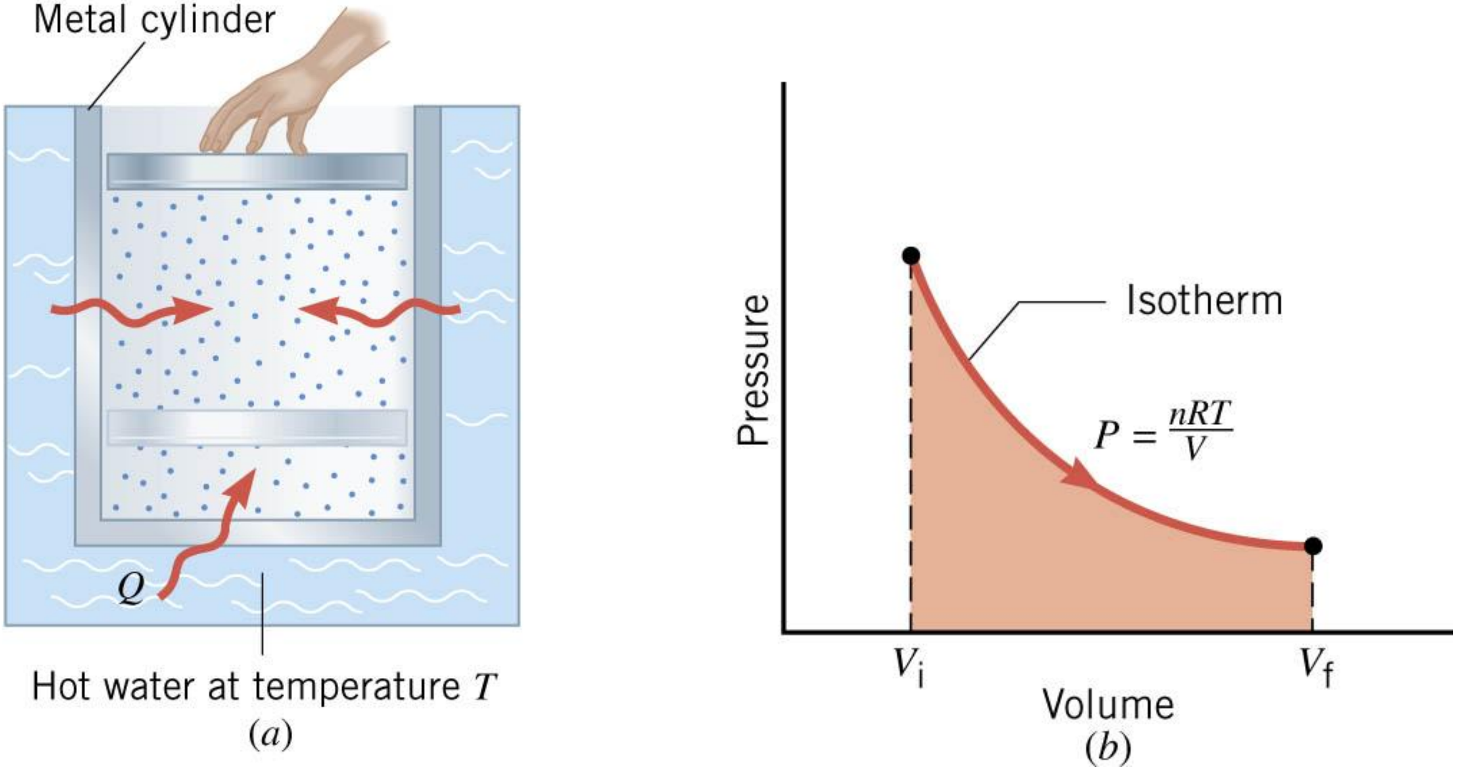


The drawing shows a pressure-versus-volume plot for a three-step process: A to B, B to C, and C to A. For each step, the work can be positive, negative, or zero. Which answer below correctly describes the work for the three steps?

	A → B	B → C	C → A
a.	Positive	Negative	Negative
b.	Positive	Positive	Negative
c.	Negative	Negative	Positive
d.	Positive	Negative	Zero
e.	Negative	Positive	Zero

(b)

Thermal Processes Using an Ideal Gas



ISOTHERMAL EXPANSION OR COMPRESSION

$$P = nRT/V$$

$$W = P\,\Delta V = P(V_f - V_i)$$

Isothermal expansion or compression of an ideal gas

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

Example 5.
Isothermal Expansion of an Ideal Gas

Two moles of the monatomic gas argon expand isothermally at 298 K, from an initial volume of V_i = 0.025 m^3 to a final volume of V_f = 0.050 m^3. Assuming that argon is an ideal gas, find (a) the work done by the gas, (b) the change in the internal energy of the gas, and (c) the heat supplied to the gas.

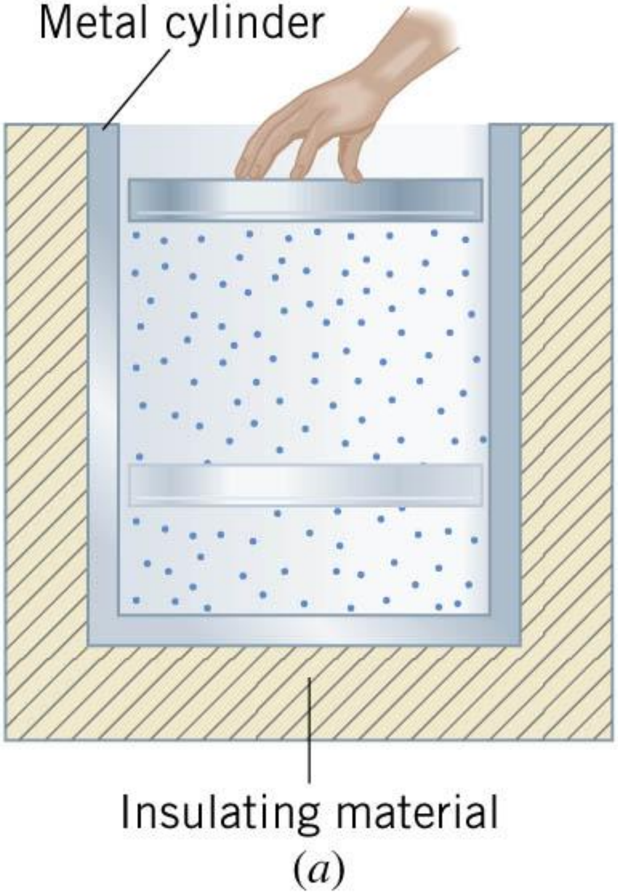
(a)

$$W = nRT\ln\left(\frac{V_\mathrm{f}}{V_\mathrm{i}}\right) = (2.0\,\mathrm{mol})\,[8.31\,\mathrm{J}/(\mathrm{mol}\cdot\mathrm{K})]\,(298\,\mathrm{K})\ln\left(\frac{0.050\,\mathrm{m}^3}{0.025\,\mathrm{m}^3}\right) = \boxed{+3400\,\mathrm{J}}$$

(b) $\boxed{\Delta U = 0\,\mathrm{J}}$

(c) $Q = \Delta U + W = 0\,\mathrm{J} + 3400\,\mathrm{J} = \boxed{+3400\,\mathrm{J}}$

ADIABATIC EXPANSION OR COMPRESSION



$$U = \frac{3}{2} nRT$$

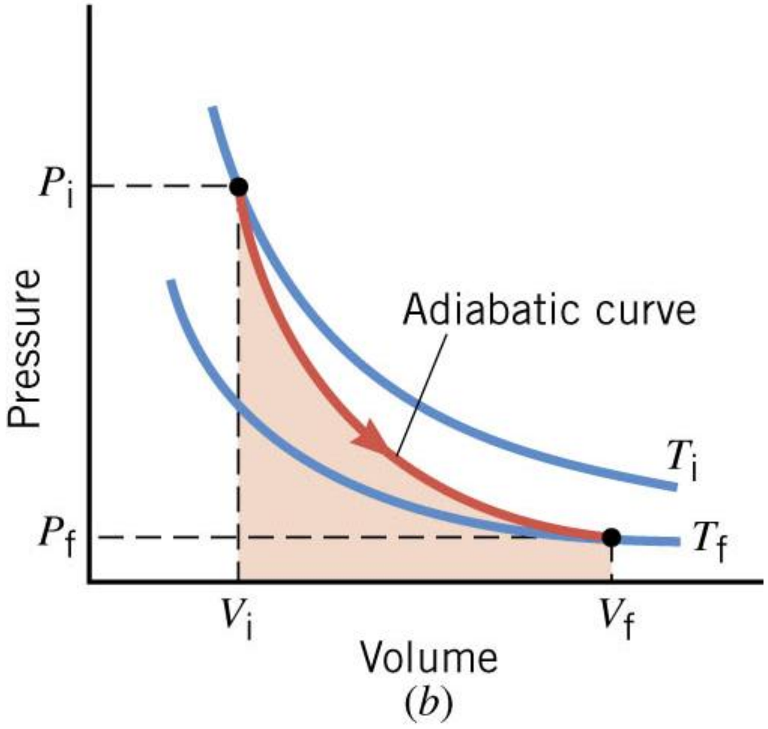
$$\Delta U = U_f - U_i = \frac{3}{2} nR(T_f - T_i)$$

Adiabatic expansion or compression of a monatomic ideal gas

$$W = \frac{3}{2} nR(T_i - T_f)$$

$[T_i = P_i V_i/(nR)]$

$[T_f = P_f V_f/(nR)]$.



(*b*)

Adiabatic expansion or compression of an ideal gas

$$P_i V_i^{\gamma} = P_f V_f^{\gamma}$$

Type of Thermal Process	**Work** Done	First Law of **Thermodynamics** ($\Delta U = Q - W$)
Isobaric (constant pressure)	$W = P(V_f - V_i)$	$\Delta U = Q - \underbrace{P(V_f - V_i)}_{W}$
Isochoric (constant volume)	$W = 0\ \text{J}$	$\Delta U = Q - \underbrace{0\ \text{J}}_{W}$
Isothermal (constant temperature)	$W = nRT\ln\left(\frac{V_f}{V_i}\right)$ (for an ideal gas)	$\underbrace{0\ \text{J}}_{\Delta U \text{ for an ideal gas}} = Q - \underbrace{nRT\ln\left(\frac{V_f}{V_i}\right)}_{W}$
Adiabatic (no **heat** flow)	$W = \frac{3}{2}nR(T_f - T_i)$ (for a monatomic ideal gas)	$\Delta U = \underbrace{0\ \text{J}}_{Q} - \underbrace{\frac{3}{2}nR(T_i - T_f)}_{W}$

Specific Heat Capacities

$$Q = Cn\,\Delta T$$

where the capital letter *C* refers to the ***molar specific heat capacity*** in units of J/(mol·K).

$$Q = \Delta U + W$$

$$Q_{\text{constant pressure}} = \frac{3}{2}nR(T_{\text{f}} - T_{\text{i}}) + nR(T_{\text{f}} - T_{\text{i}}) = \frac{5}{2}nR(T_{\text{f}} - T_{\text{i}})$$

$$Q_{\text{constant volume}} = \frac{3}{2}nR(T_{\text{f}} - T_{\text{i}}) + 0$$

Constant pressure for a monatomic ideal gas

$$C_P = \frac{Q_{\text{constant pressure}}}{n(T_f - T_i)} = \frac{5}{2}R$$

Constant volume for a monatomic ideal gas

$$C_V = \frac{Q_{\text{constant volume}}}{n(T_f - T_i)} = \frac{3}{2}R$$

Monatomic ideal gas

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}$$

$$C_P - C_V = R$$