

## The first law of thermodynamics

- Heat and internal energy
- Specific heat
- Latent heat
- Work and heat in thermodynamic processes
- The first law of thermodynamics
- Some applications of the first law of thermodynamics
- Energy transfer mechanisms in thermal processes



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<https://twiki.cern.ch/twiki/bin/view/Main/PhatSrimanobhasTeaching>

# Heat and internal energy

The **caloric theory** is an obsolete scientific theory that heat consists of a self-repellent fluid called caloric that flows from hotter bodies to colder bodies.

Nowadays, in thermodynamics,

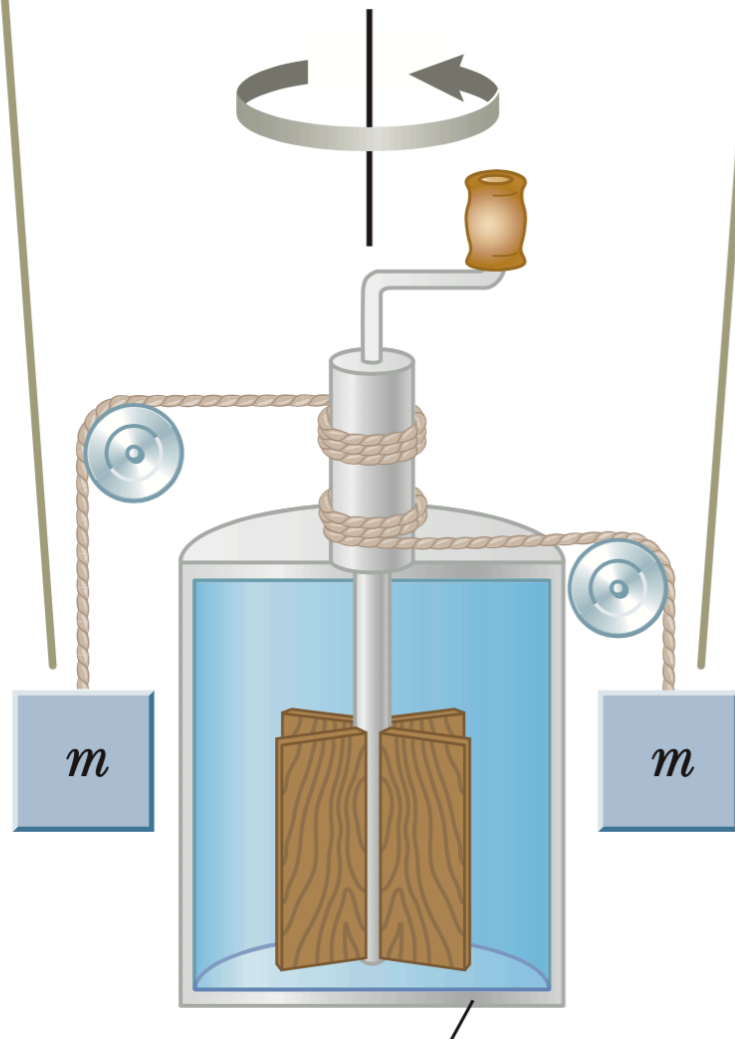
**Heat** is defined as a *process of transferring energy* across the boundary of a system because of a temperature difference between the system and its surroundings. It is also the amount of energy  $Q$  transferred by this process.

**Internal energy** is *all the energy of a system that is associated with its microscopic components* —atoms and molecules—when viewed from a reference frame at rest with respect to the center of mass of the system.



# The Mechanical Equivalent of Heat

The falling blocks rotate the paddles, causing the temperature of the water to increase.



Thermal  
insulator

Joule's experiment

# Specific heat

The **heat capacity**  $C$  of a particular sample is defined as the amount of energy needed to raise the temperature of that sample by  $1^\circ\text{C}$ .

$$C \equiv \frac{Q}{\Delta T}$$

The **specific heat**  $c$  of a substance is the heat capacity per unit mass.

$$c \equiv \frac{Q}{m\Delta T}$$

**Table 20.1** Specific Heats of Some Substances at  $25^\circ\text{C}$  and Atmospheric Pressure

Substance	Specific Heat ( $\text{J}/\text{kg} \cdot ^\circ\text{C}$ )	Substance	Specific Heat ( $\text{J}/\text{kg} \cdot ^\circ\text{C}$ )
<i>Elemental solids</i>		<i>Other solids</i>	
Aluminum	900	Brass	380
Beryllium	1 830	Glass	837
Cadmium	230	Ice ( $-5^\circ\text{C}$ )	2 090
Copper	387	Marble	860
Germanium	322	Wood	1 700
Gold	129	<i>Liquids</i>	
Iron	448	Alcohol (ethyl)	2 400
Lead	128	Mercury	140
Silicon	703	Water ( $15^\circ\text{C}$ )	4 186
Silver	234	<i>Gas</i>	
		Steam ( $100^\circ\text{C}$ )	2 010

*Note:* To convert values to units of  $\text{cal}/\text{g} \cdot ^\circ\text{C}$ , divide by 4 186.

Note:

The heat capacity of most systems is not constant (though it can often be treated as such). It depends on the temperature, pressure, and volume of the system under consideration.

## Example

A 0.05 kg ingot of metal is heated to  $200.0^{\circ}\text{C}$  and then dropped into a calorimeter containing 0.400 kg of water initially at  $20.0^{\circ}\text{C}$ . The final equilibrium temperature of the mixed system is  $22.4^{\circ}\text{C}$ . Find the specific heat of the metal.

# Notes:

## Molar specific heat

In the gas system, we normally use the number of mole instead of the mass of gas. We then define the "molar specific heat" in the same way as the specific heat.

$$c \equiv \frac{Q}{m\Delta T} \rightarrow c_{mol} \equiv \frac{Q}{n\Delta T}$$

## Heat and change of internal energy when the volume is constant

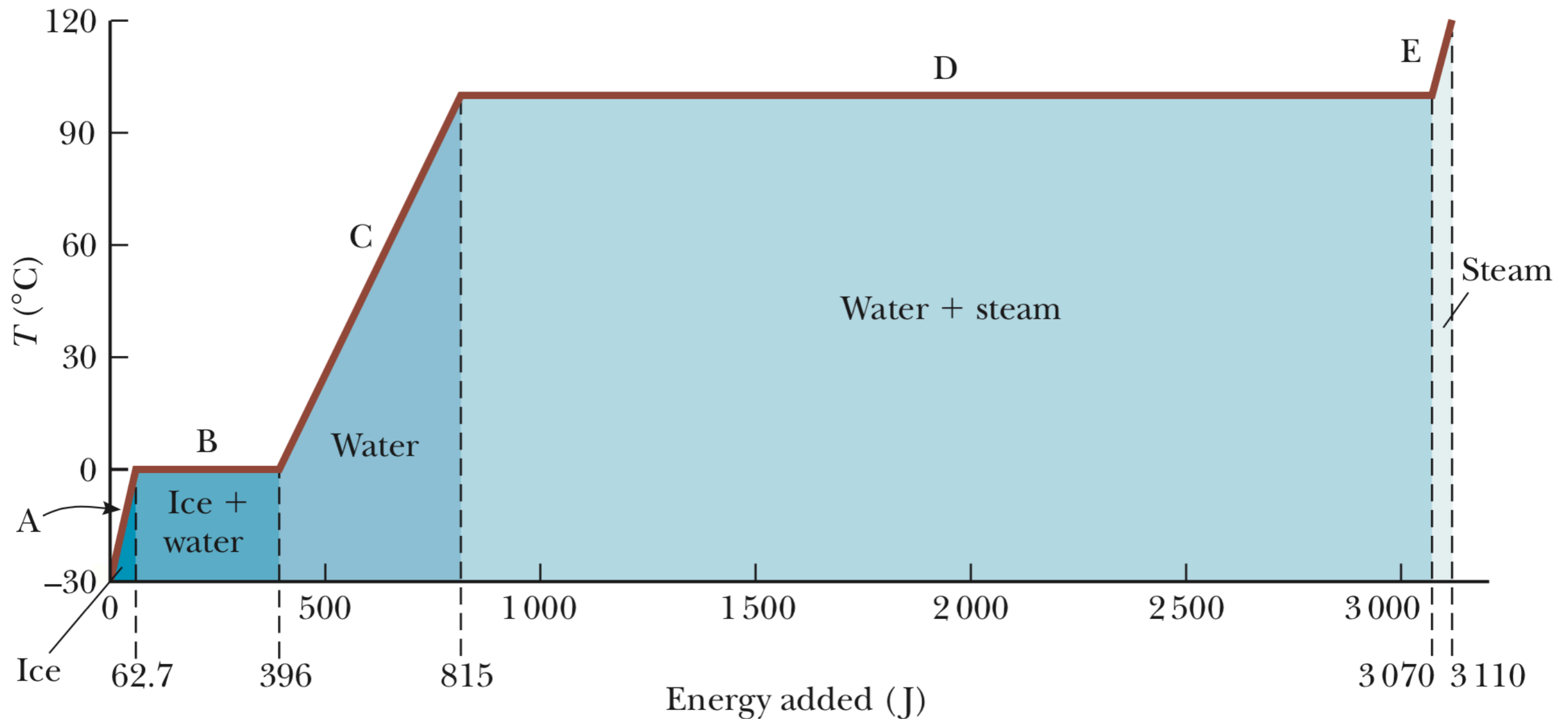
We can identify  $mc\Delta T$  (or  $nc_{mol}\Delta T$ ) as the change in internal energy of the system if we ignore any thermal expansion or contraction of the

$$\text{system} \Rightarrow \Delta E_{int} = Q$$

*We will discuss more on this later.*

# Latent Heat

Latent heat (also known as latent energy or heat of transformation) is energy released or absorbed, by a body or a thermodynamic system, during a constant-temperature process — usually a phase transition.



# Latent Heat

$$Q = mL$$

**Table 20.2**

**Latent Heats of Fusion and Vaporization**

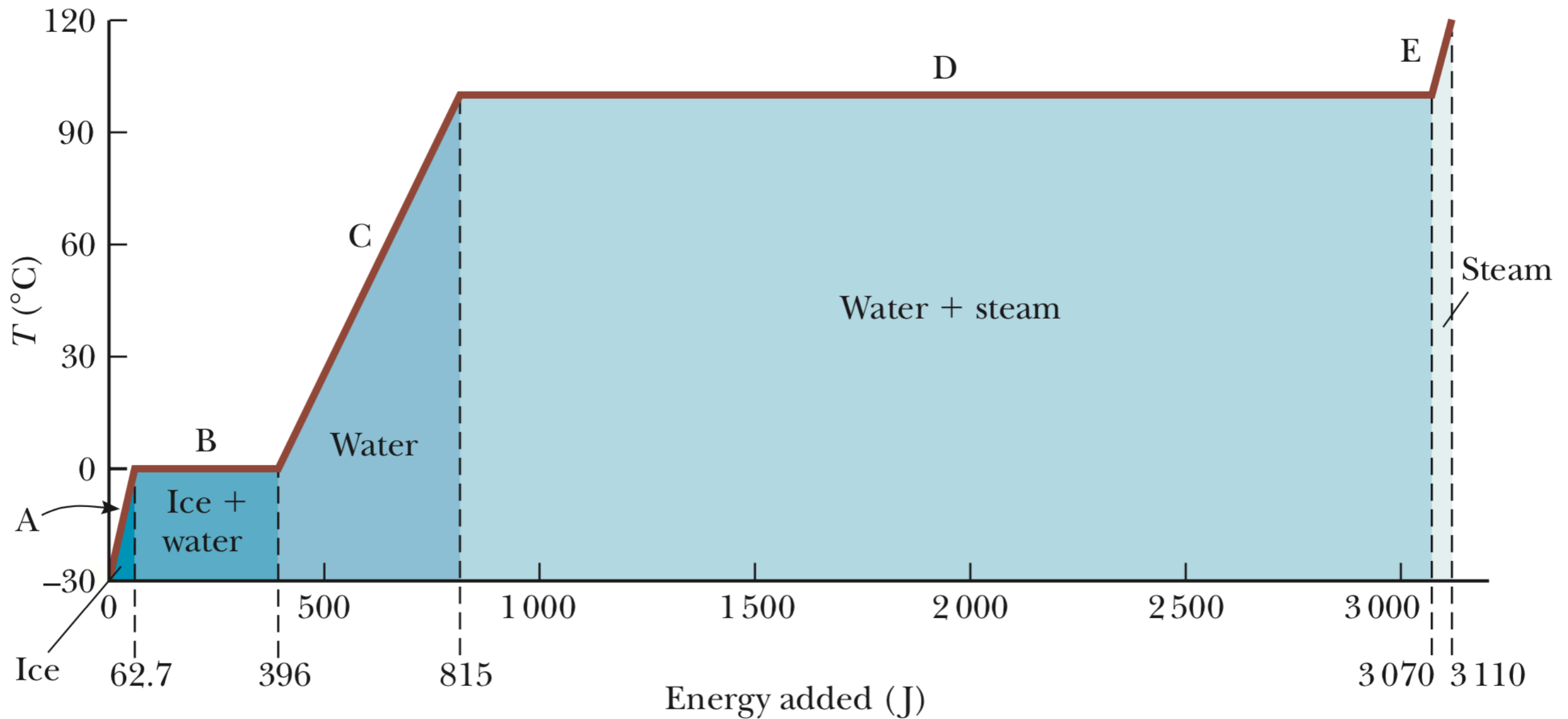
Substance	Melting Point (°C)	Latent Heat of Fusion (J/kg)	Boiling Point (°C)	Latent Heat of Vaporization (J/kg)
Helium <sup>a</sup>	-272.2	$5.23 \times 10^3$	-268.93	$2.09 \times 10^4$
Oxygen	-218.79	$1.38 \times 10^4$	-182.97	$2.13 \times 10^5$
Nitrogen	-209.97	$2.55 \times 10^4$	-195.81	$2.01 \times 10^5$
Ethyl alcohol	-114	$1.04 \times 10^5$	78	$8.54 \times 10^5$
Water	0.00	$3.33 \times 10^5$	100.00	$2.26 \times 10^6$
Sulfur	119	$3.81 \times 10^4$	444.60	$3.26 \times 10^5$
Lead	327.3	$2.45 \times 10^4$	1 750	$8.70 \times 10^5$
Aluminum	660	$3.97 \times 10^5$	2 450	$1.14 \times 10^7$
Silver	960.80	$8.82 \times 10^4$	2 193	$2.33 \times 10^6$
Gold	1 063.00	$6.44 \times 10^4$	2 660	$1.58 \times 10^6$
Copper	1 083	$1.34 \times 10^5$	1 187	$5.06 \times 10^6$

<sup>a</sup>Helium does not solidify at atmospheric pressure. The melting point given here corresponds to a pressure of 2.5 MPa.



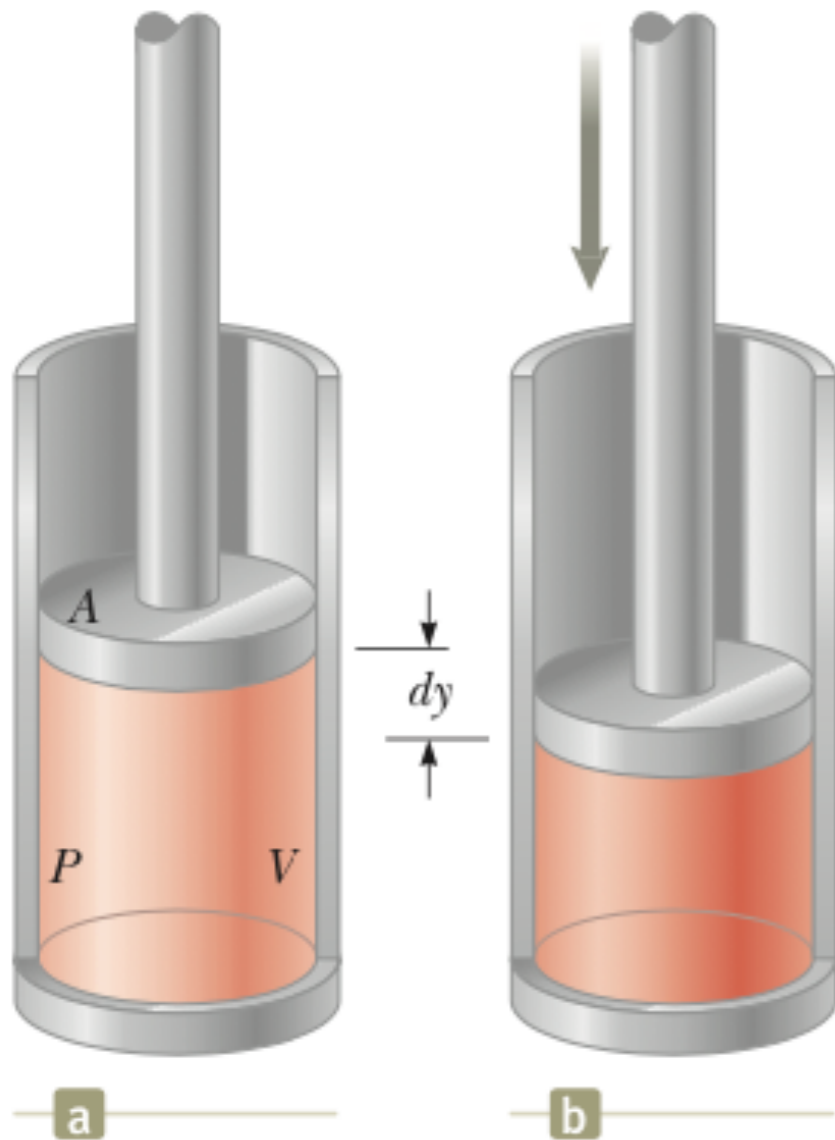
# Example

What is the required energy to convert a system consisting of a 1.00-g cube of ice at  $30.0^{\circ}\text{C}$  to steam at  $120.0^{\circ}\text{C}$ ?



# Work and Heat in Thermodynamic Processes

Consider the state of the system:  $P_i, V_i, T_i \rightarrow P_f, V_f, T_f$

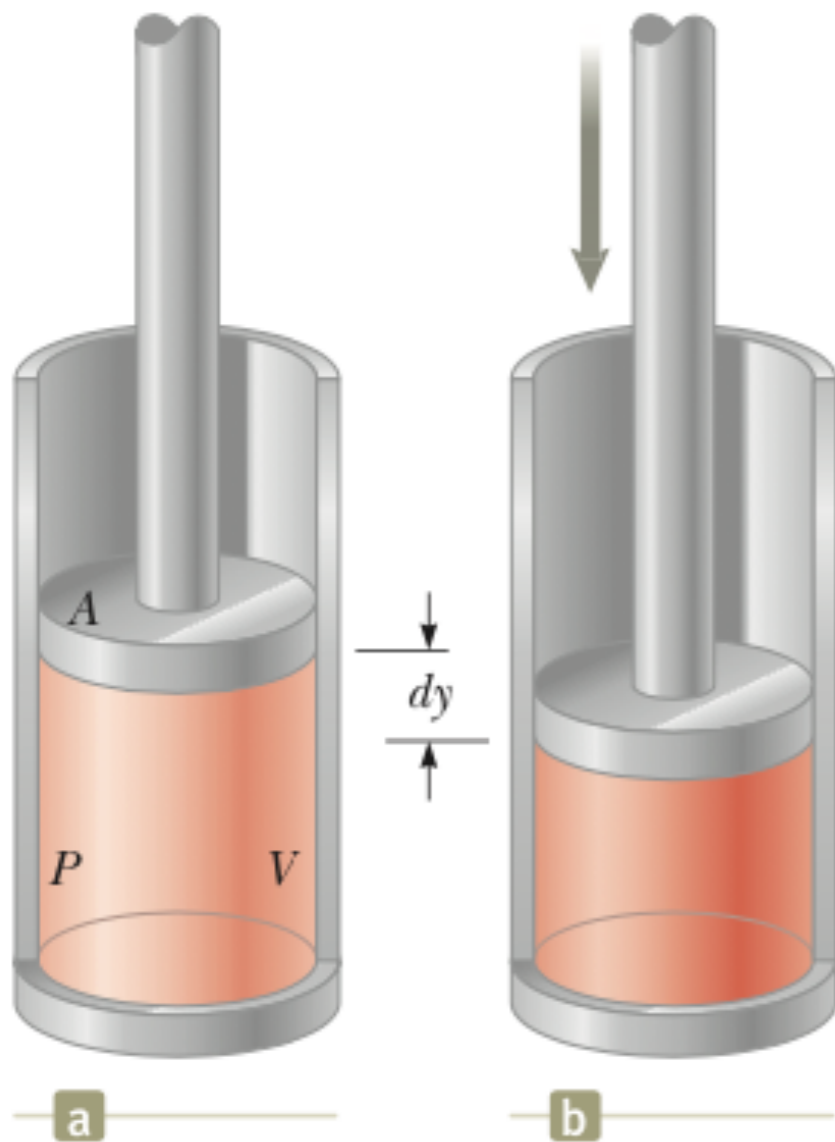


**Consider quasi-static situation. What is it?**

*"A state of a system can be specified only if the system is in thermal equilibrium internally. In the case of a gas in a container, internal thermal equilibrium requires that every part of the gas be at the same pressure and temperature."*

# Work and Heat in Thermodynamic Processes

Consider  $P_i, V_i \rightarrow P_f, V_f$



$$dW =$$

## **Compressing**

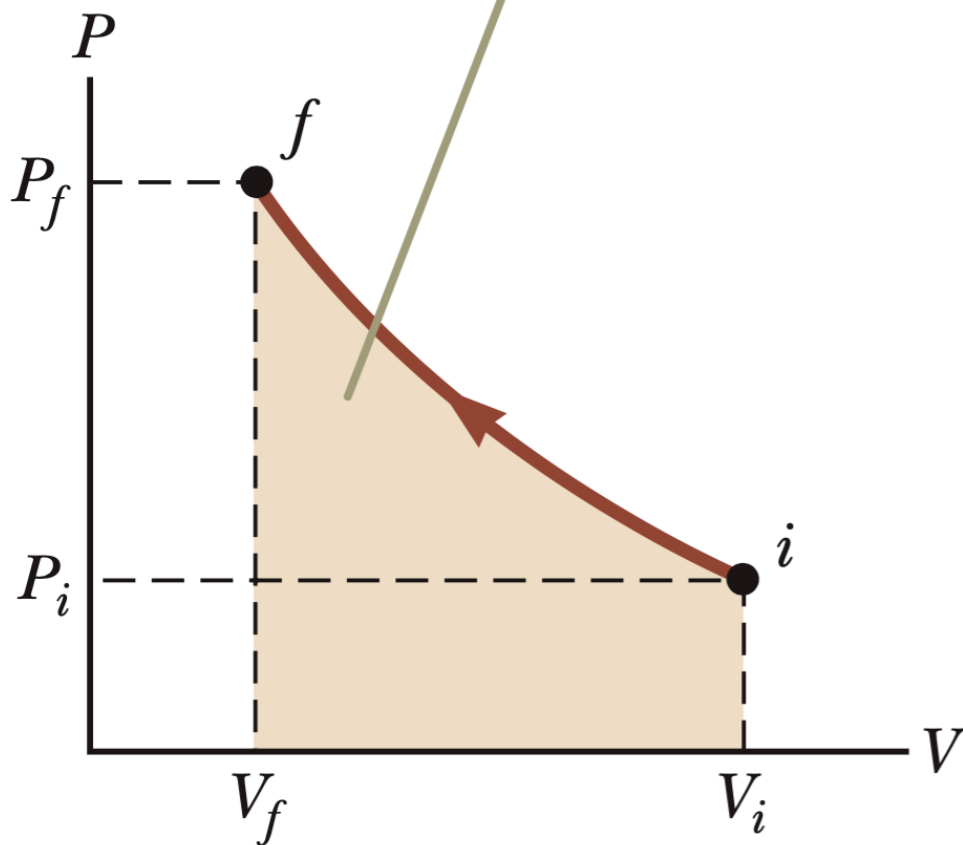
- $dV$  is
- Work done on a gas:
- Work done by a gas:

## **Expanding**

- $dV$  is
- Work done on a gas:
- Work done by a gas:

# Work and Heat in Thermodynamic Processes

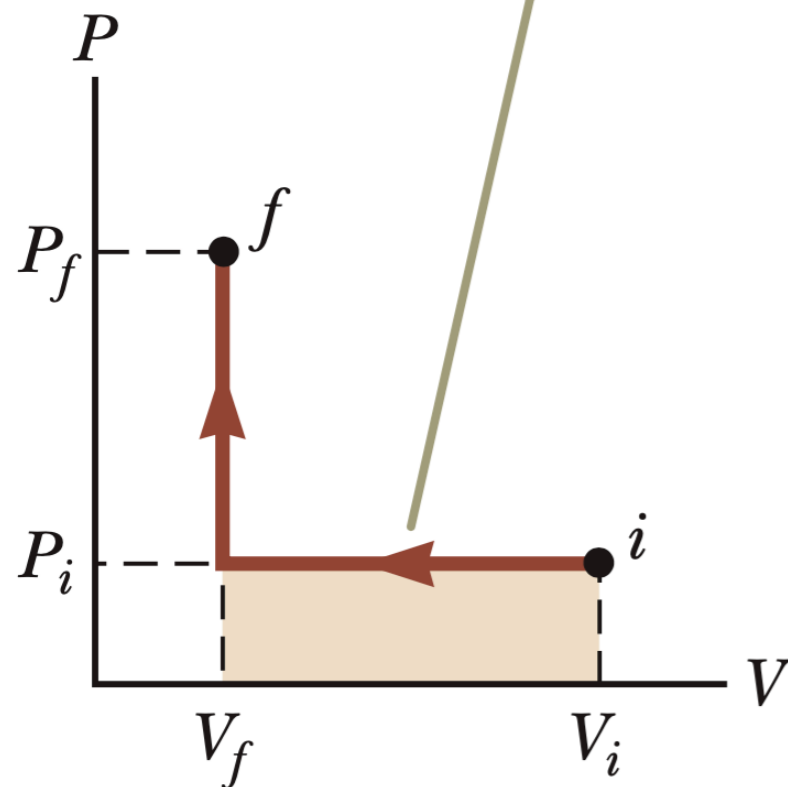
The work done on a gas equals the negative of the area under the  $PV$  curve. The area is negative here because the volume is decreasing, resulting in positive work.



$$W = - \int_{V_i}^{V_f} P dV \quad \text{Work done on a gas (on a system)}$$

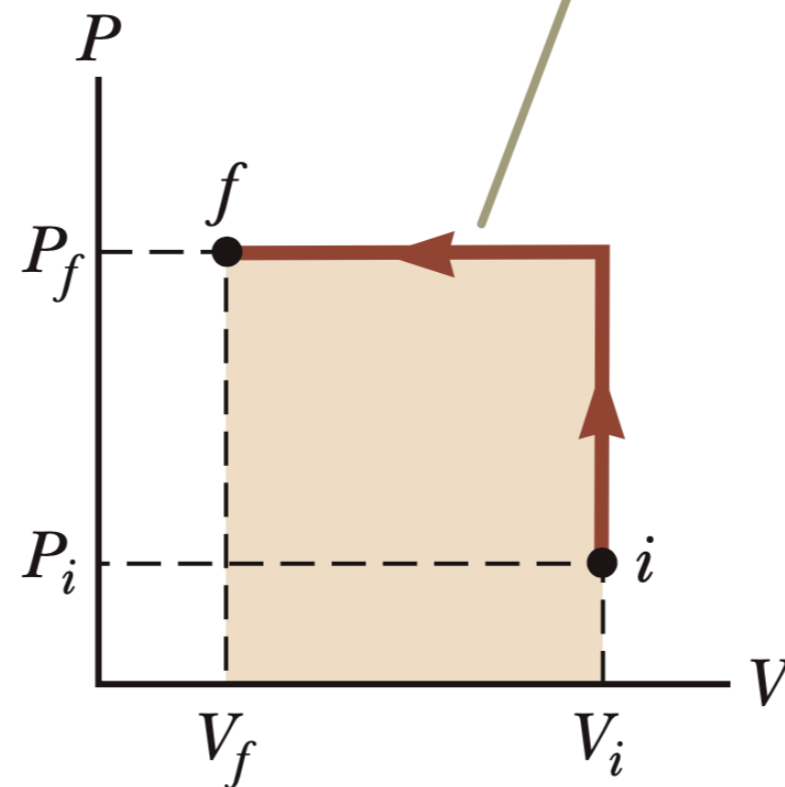
# Work and Heat in Thermodynamic Processes

A constant-pressure compression followed by a constant-volume process



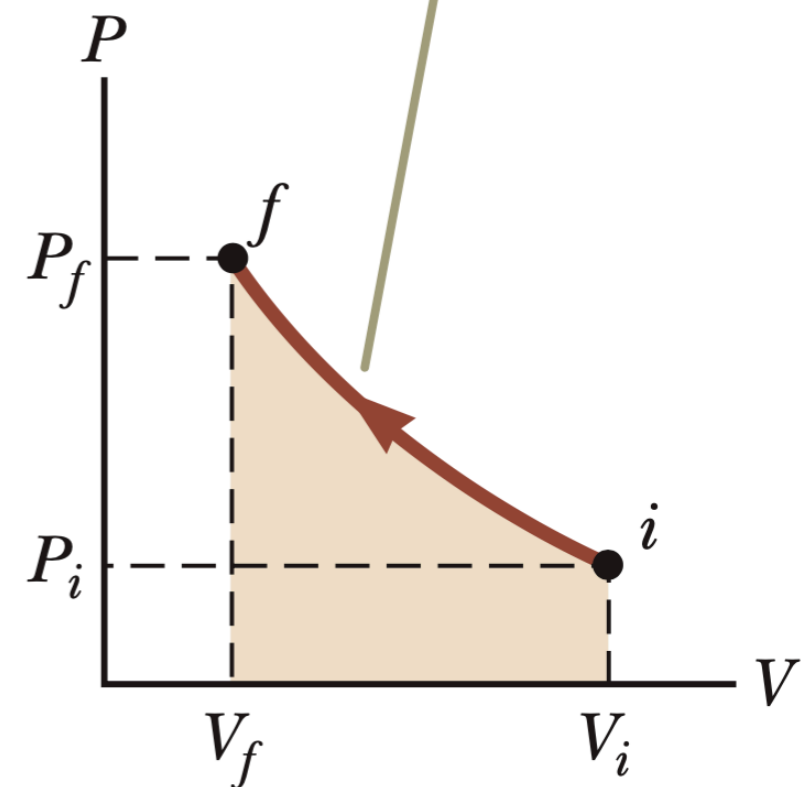
a

A constant-volume process followed by a constant-pressure compression



b

An arbitrary compression

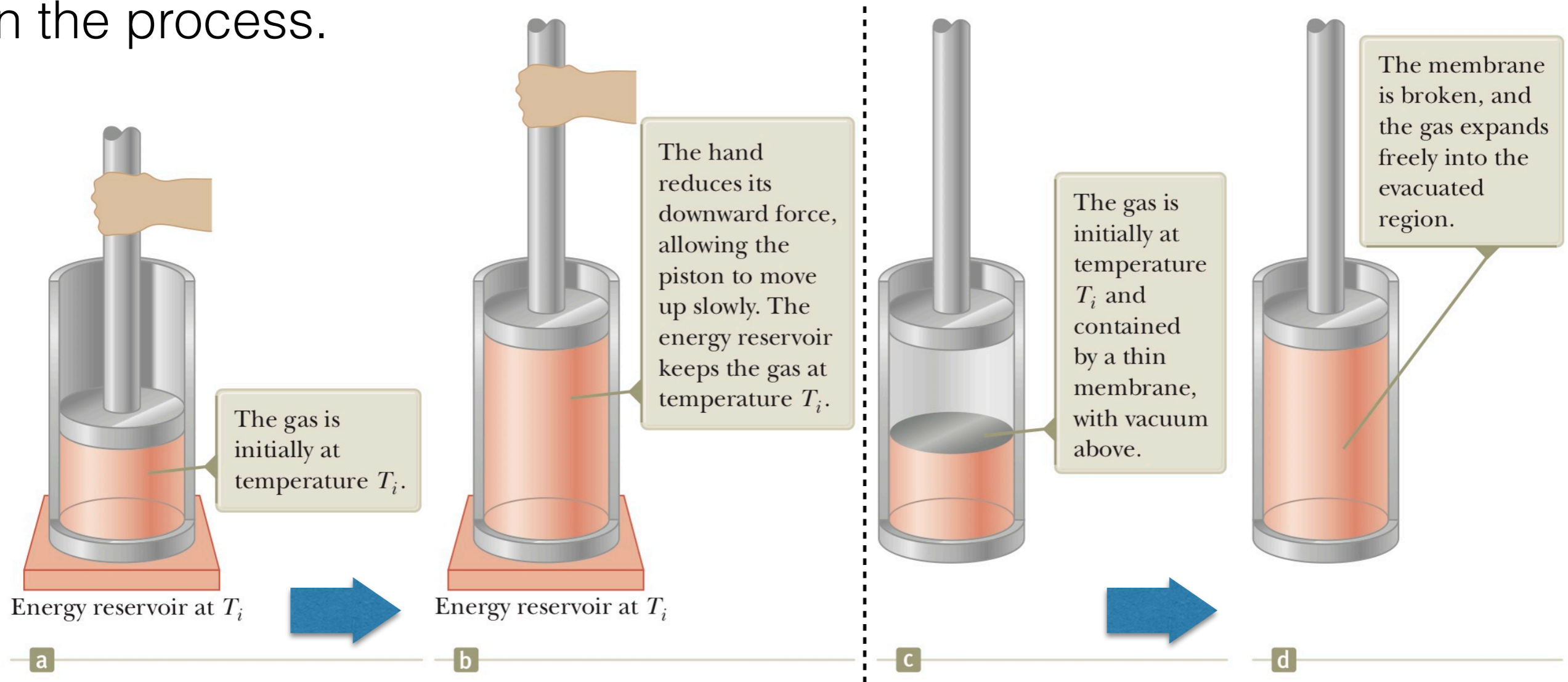


c

For the process of compressing a gas in a cylinder, **the work done depends on the particular path** taken between the initial and final states.

# Work and Heat in Thermodynamic Processes

The energy transfer  $Q$  into or out of a system by heat also depends on the process.



# The First Law of Thermodynamics

The first law of thermodynamics is a special case of the law of conservation of energy that describes processes in which only the internal energy changes and the only energy transfers are by heat and work

$$\Delta E_{\text{int}} = Q + W$$

$Q$  is the energy transfer to a system (to a gas)

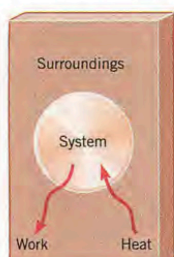
- Consider + when
- Consider - when

$W$  is the work done to a system (to a gas)

- Consider + when
- Consider - when

$\Delta E_{\text{int}}$  is the change of the internal energy of the system. It depends only on the temperature of the system.

# The First Law of Thermodynamics



(a)



(b)

**Figure 15.3** (a) The system gains energy in the form of heat but loses energy because work is done by the system. (b) The system gains energy in the form of heat and also gains energy because work is done on the system.

**Problem-solving insight**

When using the first law of thermodynamics, as expressed by Equation 15.1, be careful to follow the proper sign conventions for the heat  $Q$  and the work  $W$ .

*done on the system.* A system can gain or lose energy simultaneously in the form of heat  $Q$  and work  $W$ . The change in internal energy due to both factors is given by Equation 15.1. Thus, the **first law of thermodynamics** is just the conservation-of-energy principle applied to heat, work, and the change in the internal 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  $W$ :

$$\Delta U = U_f - U_i = Q - W \quad (15.1)$$

$Q$  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 illustrates the use of Equation 15.1 and the sign conventions for  $Q$  and  $W$ .

**Example 1** Positive and Negative Work

Figure 15.3 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.

**Reasoning** In Figure 15.3a the system loses more energy in doing work than it gains in the form of heat, so the internal energy of the system decreases. Thus, we expect the change in the internal energy,  $\Delta U = U_f - U_i$ , to be negative. In part *b* of the drawing, the system gains energy in the form of both heat and work. The internal energy of the system increases, and we expect  $\Delta U$  to be positive.

**Solution** (a) The heat is positive,  $Q = +1500$  J, since it is gained by the system. The work is positive,  $W = +2200$  J, since it is done *by* the system. According to the first law of thermodynamics

$$\Delta U = Q - W = (+1500 \text{ J}) - (+2200 \text{ J}) = \boxed{-700 \text{ J}} \quad (15.1)$$

The minus sign for  $\Delta U$  indicates that the internal energy has decreased, as expected.

(b) The heat is positive,  $Q = +1500$  J, since it is gained by the system. But the work is negative,  $W = -2200$  J, since it is done *on* the system. Thus,

$$\Delta U = Q - W = (+1500 \text{ J}) - (-2200 \text{ J}) = \boxed{+3700 \text{ J}} \quad (15.1)$$

The plus sign for  $\Delta U$  indicates that the internal energy has increased, as expected.

In the first law of thermodynamics, the internal energy  $U$ , heat  $Q$ , and work  $W$  are energy quantities, and each is expressed in energy units such as joules. However, there is a fundamental difference between  $U$ , on the one hand, and  $Q$  and  $W$  on the other. The next example sets the stage for explaining this difference.

**Example 2** An Ideal Gas

**1**

**Dual Sign Conventions** Some physics and engineering books present the first law as  $\Delta E_{\text{int}} = Q - W$ , with a minus sign between the heat and work. The reason is that work is defined in these treatments as the work done *by* the gas rather than *on* the gas, as in our treatment. The equivalent equation to Equation 20.9 in these treatments defines work as  $W = \int_{V_i}^{V_f} P dV$ . Therefore, if positive work is done by the gas, energy is leaving the system, leading to the negative sign in the first law.

In your studies in other chemistry or engineering courses, or in your reading of other physics books, be sure to note which sign convention is being used for the first law.

**2**

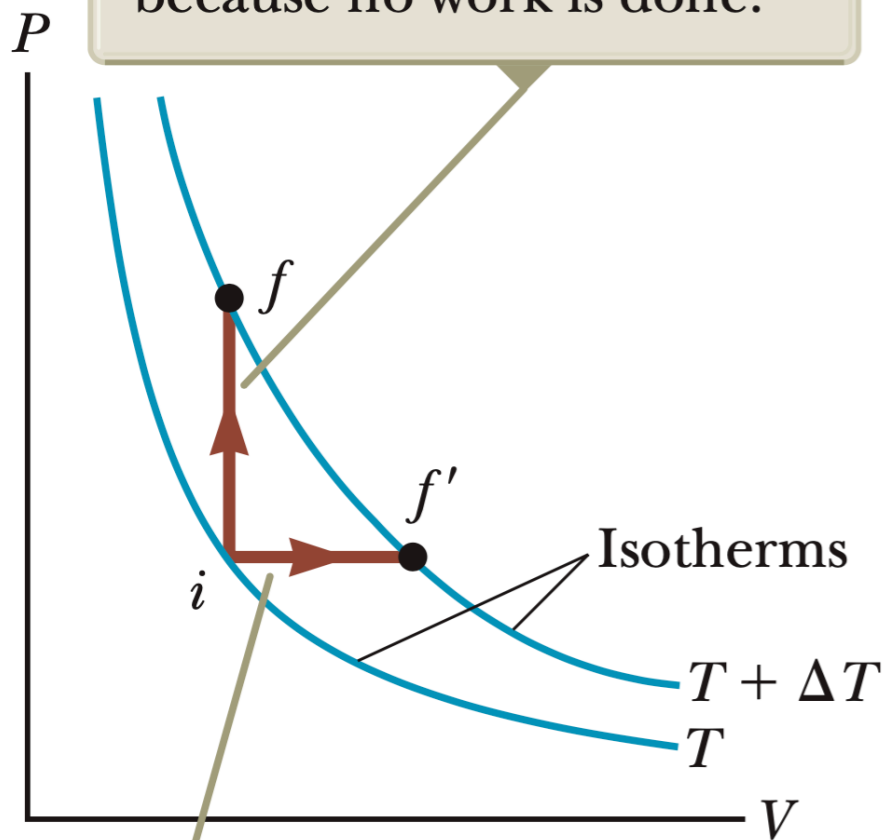
<sup>5</sup>It is an unfortunate accident of history that the traditional symbol for internal energy is  $U$ , which is also the traditional symbol for potential energy as introduced in Chapter 7. To avoid confusion between potential energy and internal energy, we use the symbol  $E_{\text{int}}$  for internal energy in this book. If you take an advanced course in thermodynamics, however, be prepared to see  $U$  used as the symbol for internal energy in the first law.



# Molar specific heat at constant volume / pressure

**Case: constant volume**

For the constant-volume path, all the energy input goes into increasing the internal energy of the gas because no work is done.



**Case: constant pressure**

Along the constant-pressure path, part of the energy transferred in by heat is transferred out by work.

Table 21.2

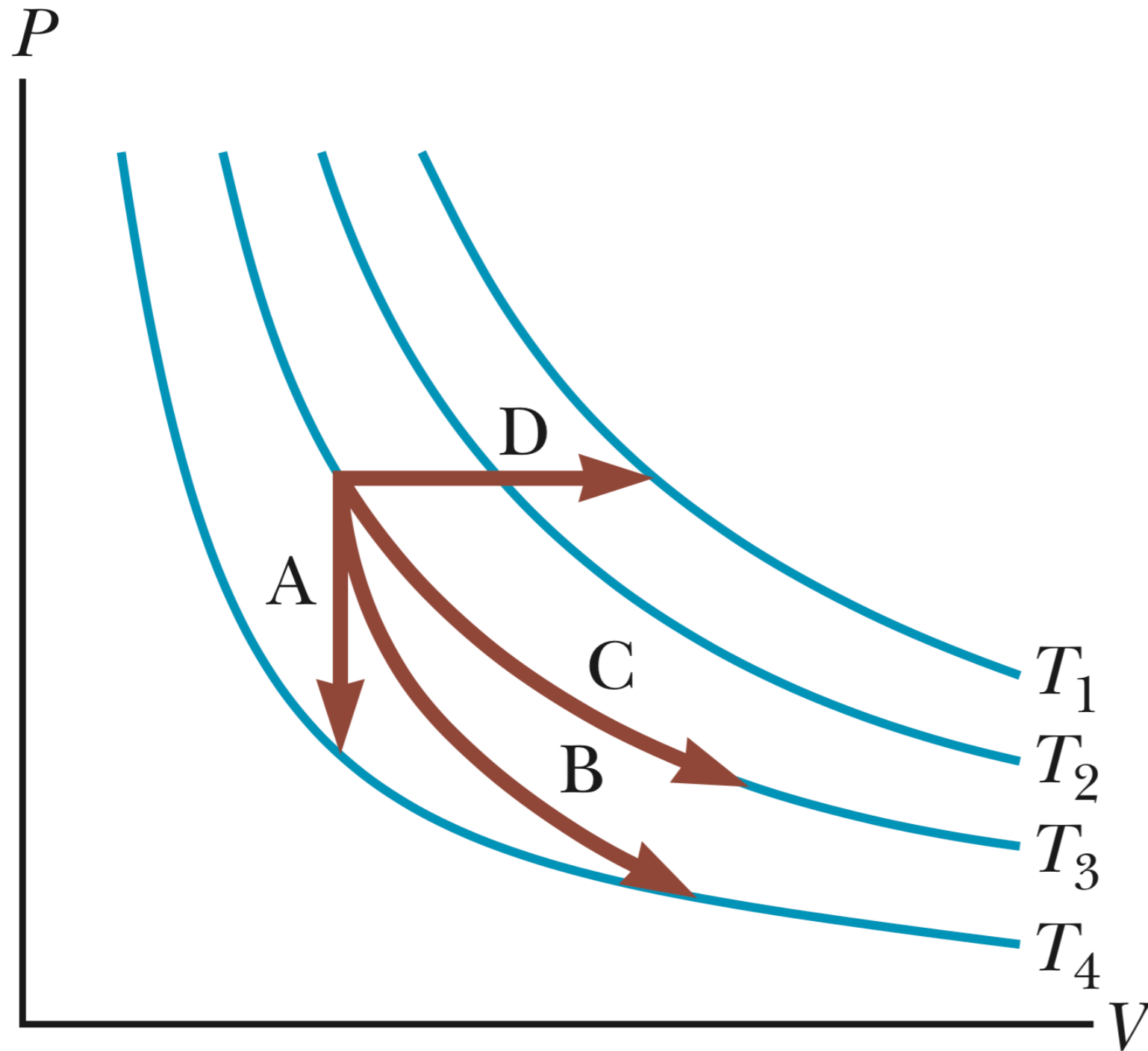
## Molar Specific Heats of Various Gases

Molar Specific Heat (J/mol · K)<sup>a</sup>

Gas	$C_P$	$C_V$	$C_P - C_V$	$\gamma = C_P/C_V$
<i>Monatomic gases</i>				
He	20.8	12.5	8.33	1.67
Ar	20.8	12.5	8.33	1.67
Ne	20.8	12.7	8.12	1.64
Kr	20.8	12.3	8.49	1.69
<i>Diatomic gases</i>				
H <sub>2</sub>	28.8	20.4	8.33	1.41
N <sub>2</sub>	29.1	20.8	8.33	1.40
O <sub>2</sub>	29.4	21.1	8.33	1.40
CO	29.3	21.0	8.33	1.40
Cl <sub>2</sub>	34.7	25.7	8.96	1.35
<i>Polyatomic gases</i>				
CO <sub>2</sub>	37.0	28.5	8.50	1.30
SO <sub>2</sub>	40.4	31.4	9.00	1.29
H <sub>2</sub> O	35.4	27.0	8.37	1.30
CH <sub>4</sub>	35.5	27.1	8.41	1.31

<sup>a</sup> All values except that for water were obtained at 300 K.

# Processes in Thermodynamics



Isochoric/Isovolumetric
Isobaric
Isothermal
Adiabatic
Free expansion
Cyclic

# Isochoric/Isovolumetric (constant volume)

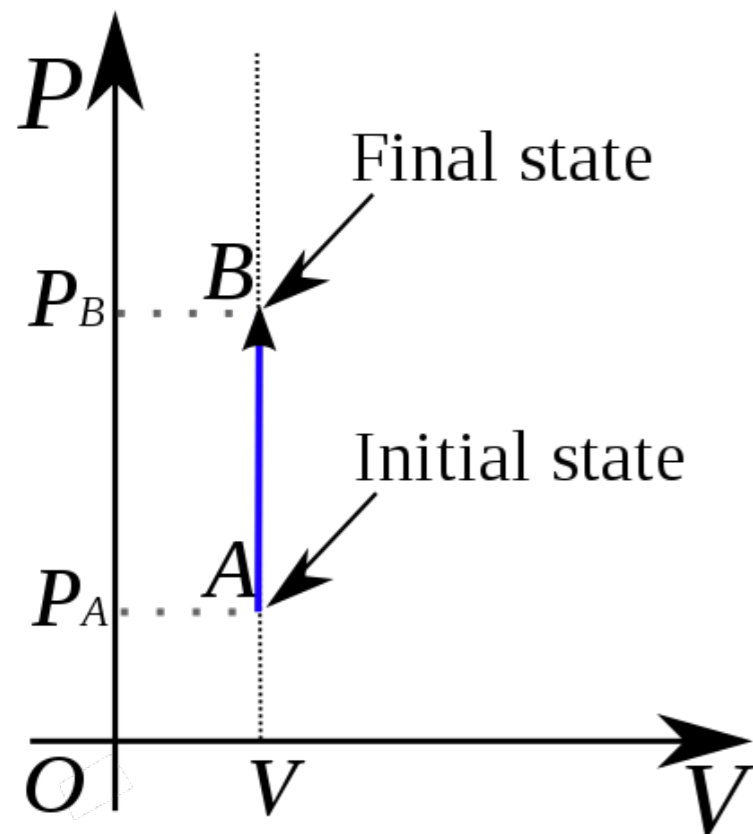


An isochoric process is a term used to describe a situation where the volume of a system remains constant.

$$dW_{\text{on gas}} =$$

From the first law we see that

$$\Delta E_{\text{int}} =$$



If energy is added by heat to a system kept at constant volume, all the transferred energy remains in the system as an increase in its internal energy.

# Isobaric (constant pressure)



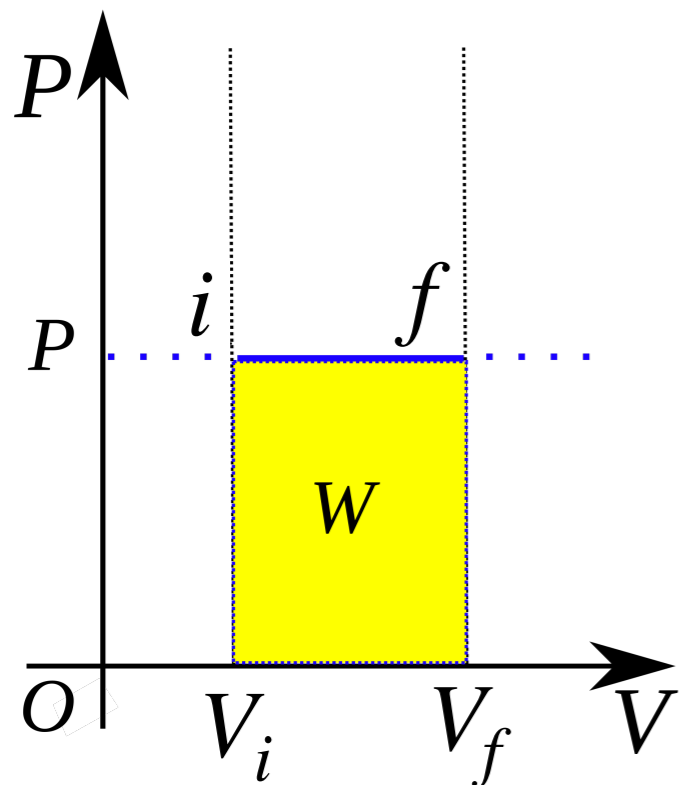
An isobaric process could be established by allowing the piston to move freely so that it is always in equilibrium between the net force from the gas pushing upward and the weight of the piston plus the force due to atmospheric pressure pushing downward.

$$W_{\text{on gas}} =$$

Case:

$$V_f > V_i \rightarrow$$

$$V_f < V_i \rightarrow$$

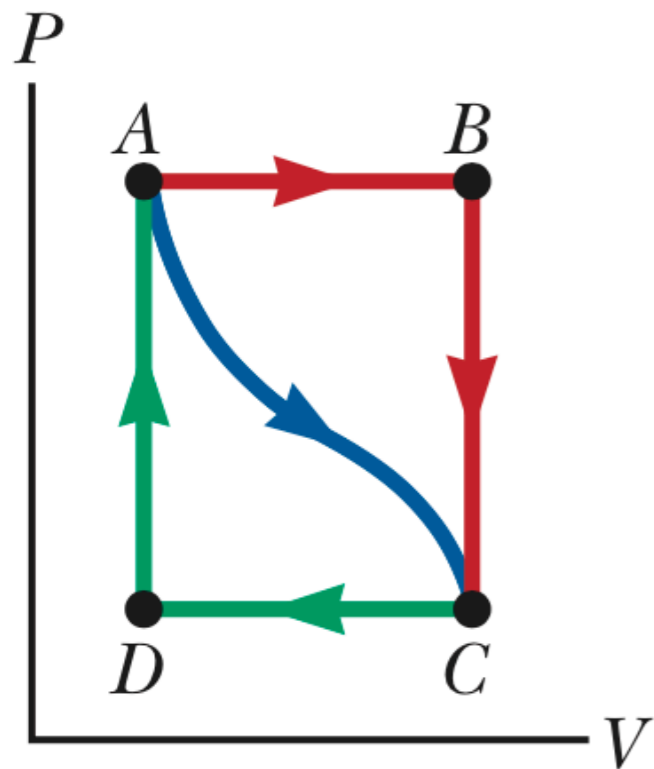


# Example

An ideal gas initially at 300 K undergoes an isobaric expansion at 2.50 kPa. If the volume increases from 1.00 m<sup>3</sup> to 3.00 m<sup>3</sup> and 12.5 kJ is transferred to the gas by heat. Find

- (a) the change in its internal energy,
- (b) its final temperature.

# Example



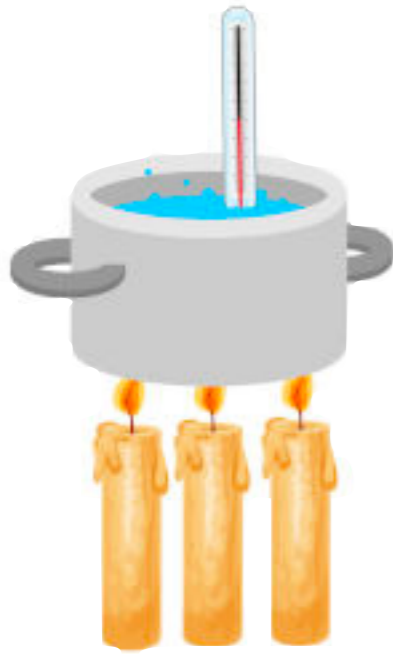
In Figure, the change in internal energy of a gas that is taken from A to C along the blue path is 1800 J. The work done on the gas along the red path ABC is 2500 J. (a) How much energy must be added to the system by heat as it goes from A through B to C?

(b) If the pressure at point A is five times that of point C, what is the work done on the system in going from C to D?

(c) What is the energy exchanged with the surroundings by heat as the gas goes from C to A along the green path?

(d) If the change in internal energy in going from point D to point A is 1500 J, how much energy must be added to the system by heat as it goes from point C to point D?

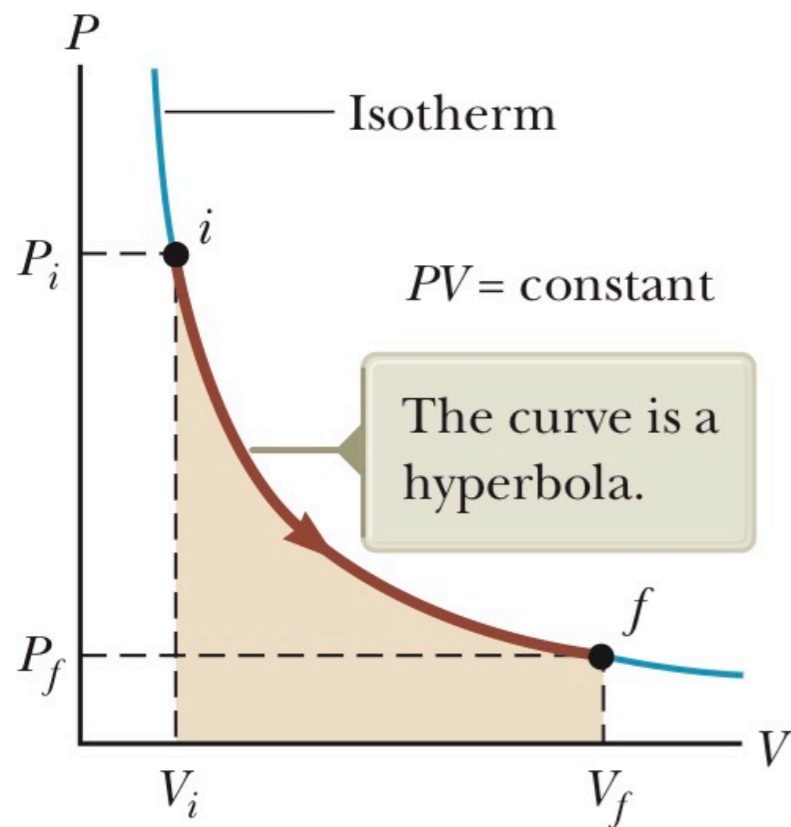
# Isothermal



A process that occurs at constant temperature. This process can be established by immersing the cylinder in an ice–water bath or by putting the cylinder in contact with some other constant-temperature reservoir.

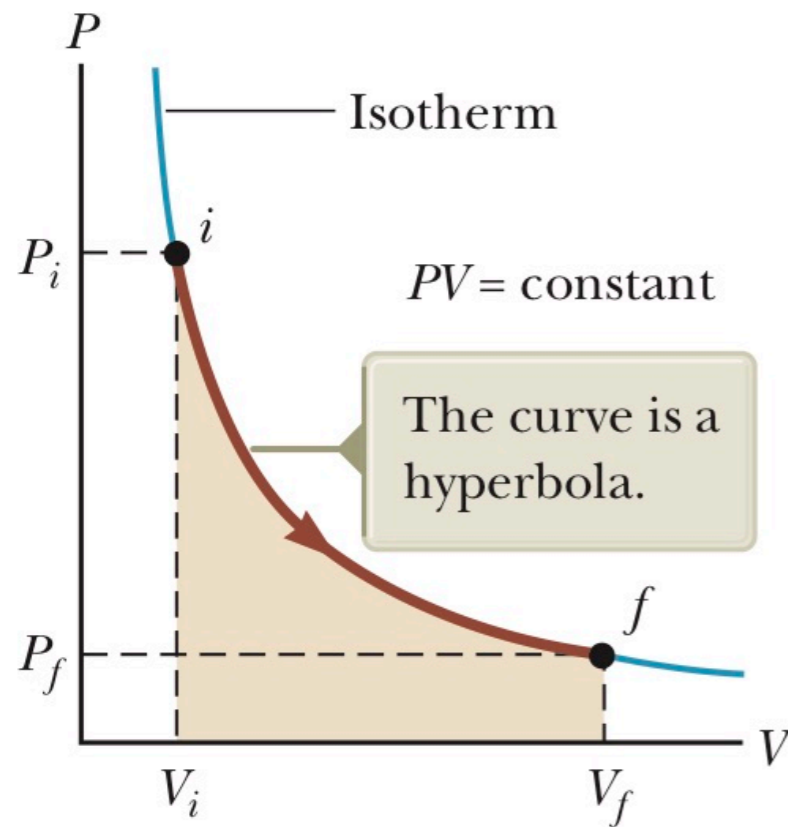
$$\Delta E_{int} =$$

From the first law we see that





# Isothermal Expansion of an Ideal gas



Start from ideal gas law

$$P = \frac{Nk_B T}{V}$$

Therefore,

$$W_{\text{on gas}} = - \int_{V_i}^{V_f} P dV$$

And since the temperature is constant, we will get

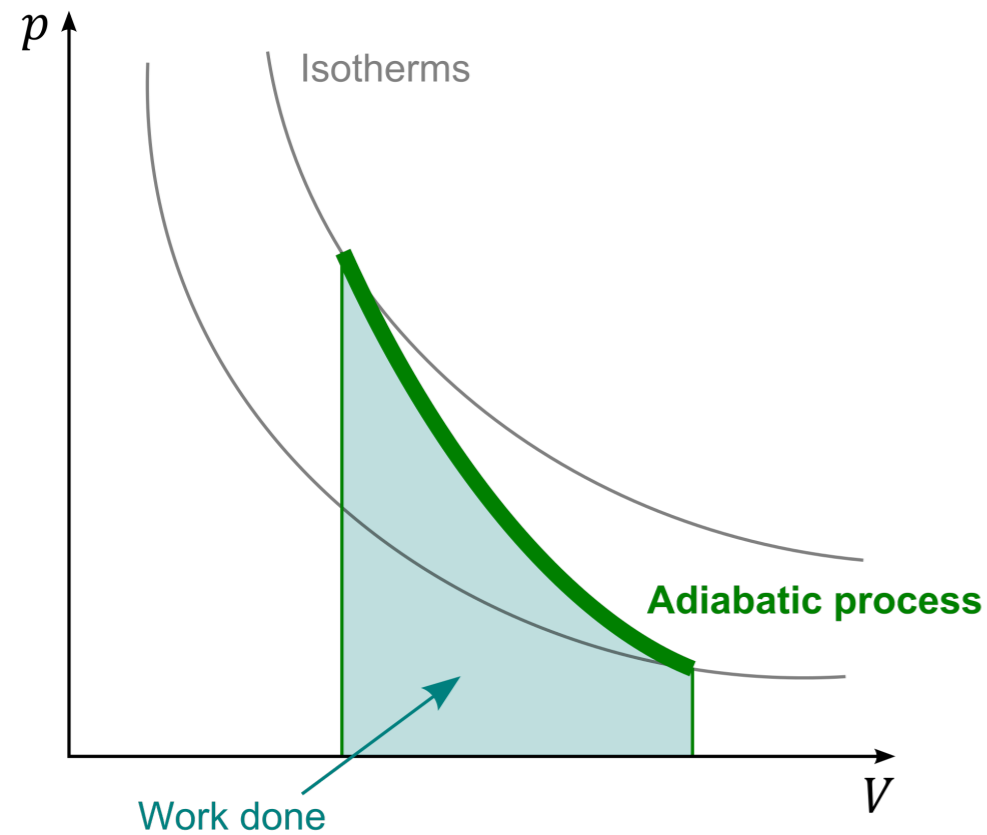
# Example

One mole of an ideal gas does 3000 J of work on its surroundings as it expands isothermally to a final pressure of 1.00 atm and volume of 25.0 L. Determine

- (a) the initial volume and
- (b) the temperature of the gas.

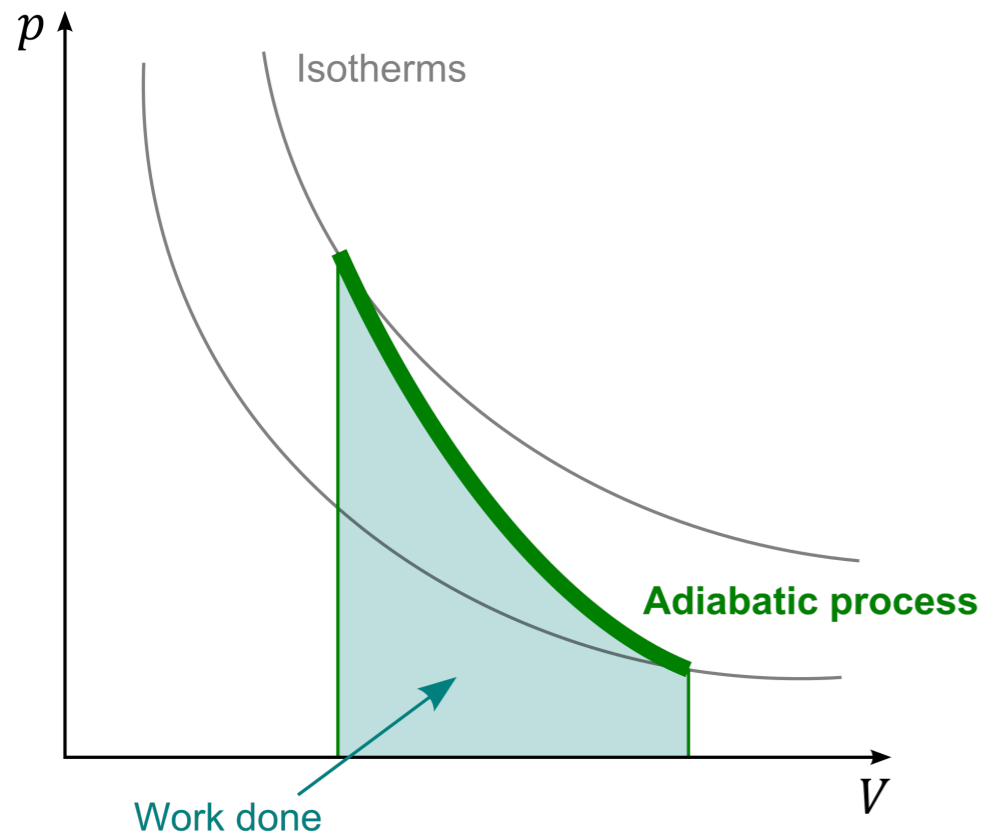
# Adiabatic

An adiabatic process is a type of thermodynamic process which occurs without transferring heat between the system and its surroundings. *Unlike an isothermal process, an adiabatic process transfers energy to the surroundings only as work.*



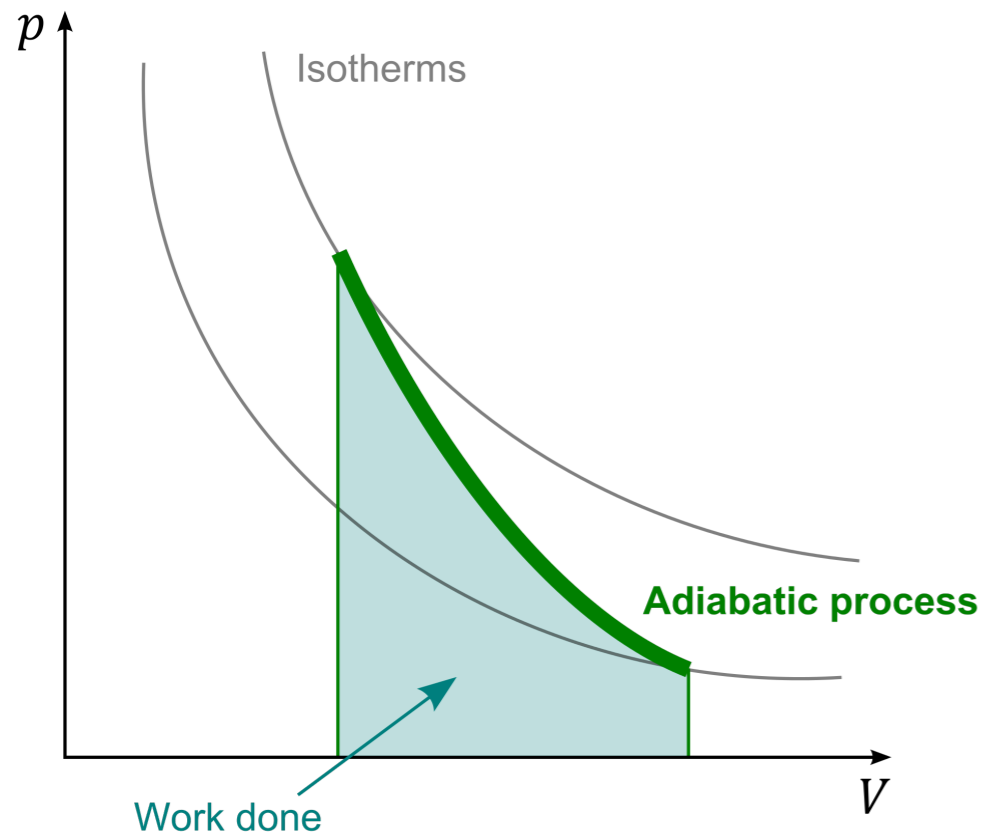
# Adiabatic

From the first law of Thermodynamics,  $\Delta E_{\text{int}} = Q + W$ , we will get

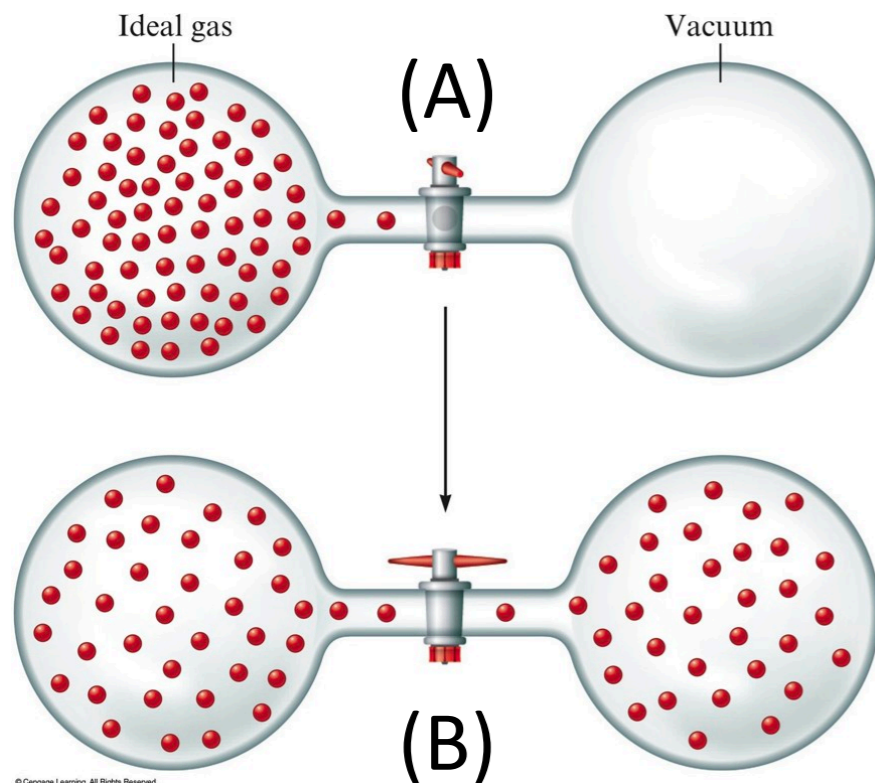


# Adiabatic

From the first law of Thermodynamics,  $\Delta E_{\text{int}} = Q + W$ , we will get



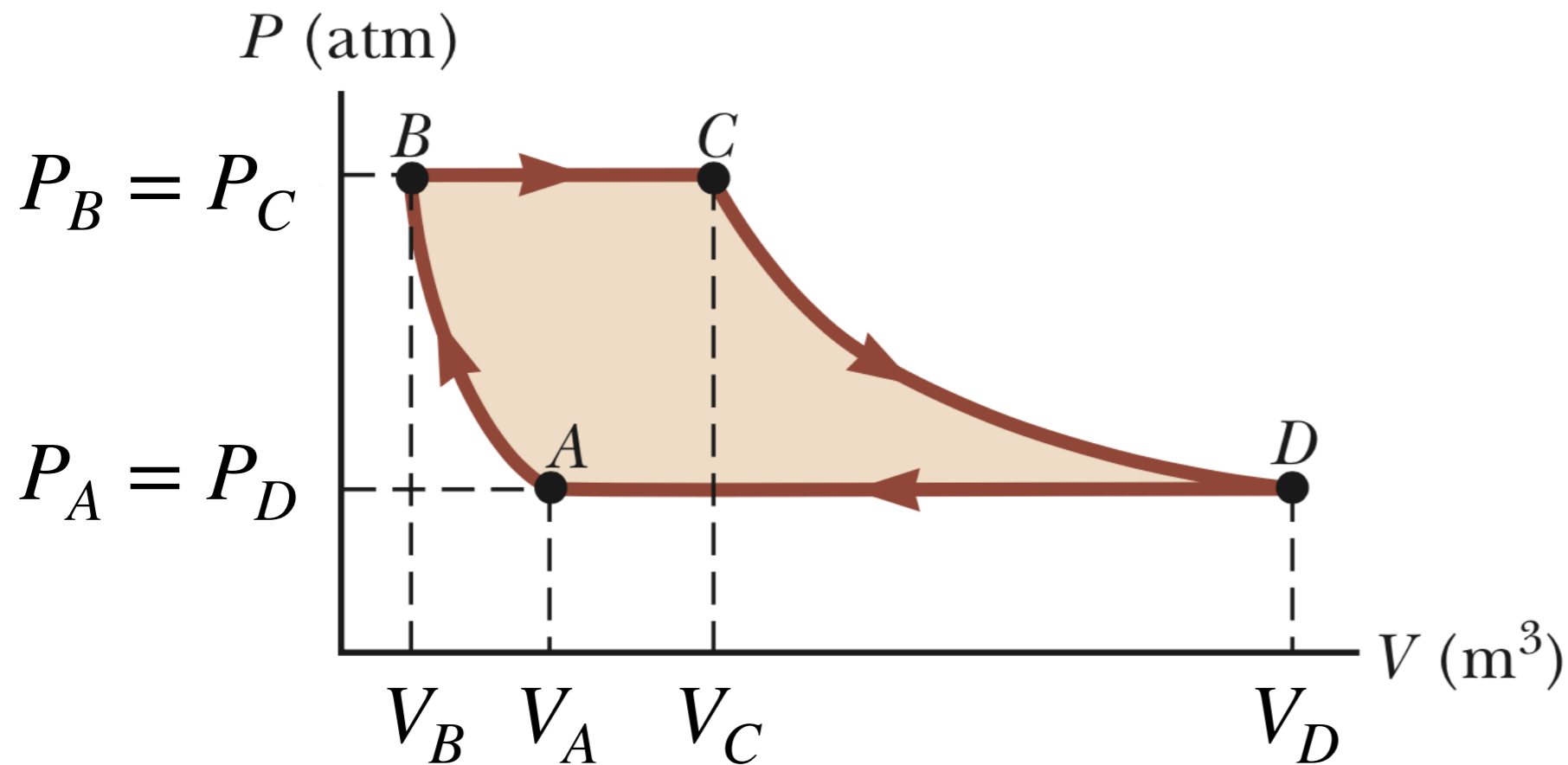
# Free expansion



For an **adiabatic free expansion** of an ideal gas, the gas is contained in an insulated container and then allowed to expand in a vacuum. Because there is no external pressure for the gas to expand against, the work done by or on the system is zero. Since this process does not involve any heat transfer or work, the first law of thermodynamics then implies that the net internal energy change of the system is zero. For an ideal gas, the temperature remains constant because the internal energy only depends on temperature in that case.

# Cyclic process

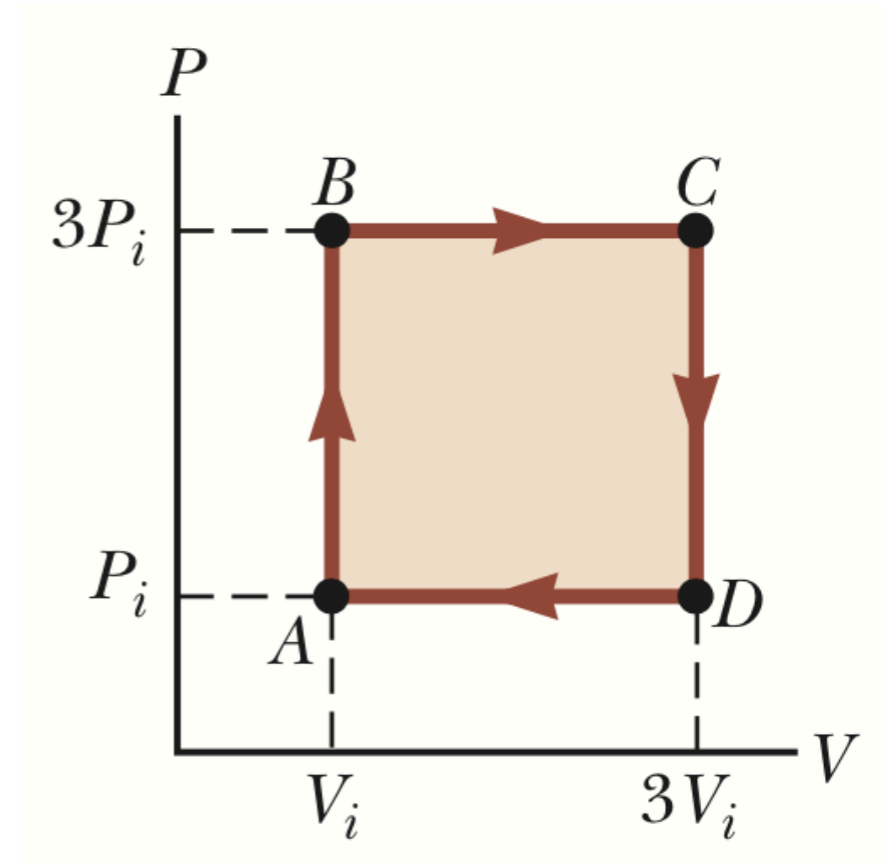
During a closed cycle, the system returns to its original thermodynamic state of temperature and pressure. Process quantities (or path quantities), such as heat and work are process dependent. For a cycle for which the system returns to its initial state the first law of thermodynamics applies:



# Example

An ideal gas initially at  $P_i$ ,  $V_i$ , and  $T_i$  is taken through a cycle as shown in the figure.

- (a) Find the net work done on the gas per cycle for 1.00 mol of gas initially at  $0^\circ\text{C}$ .
- (b) What is the net energy added by heat to the gas per cycle?



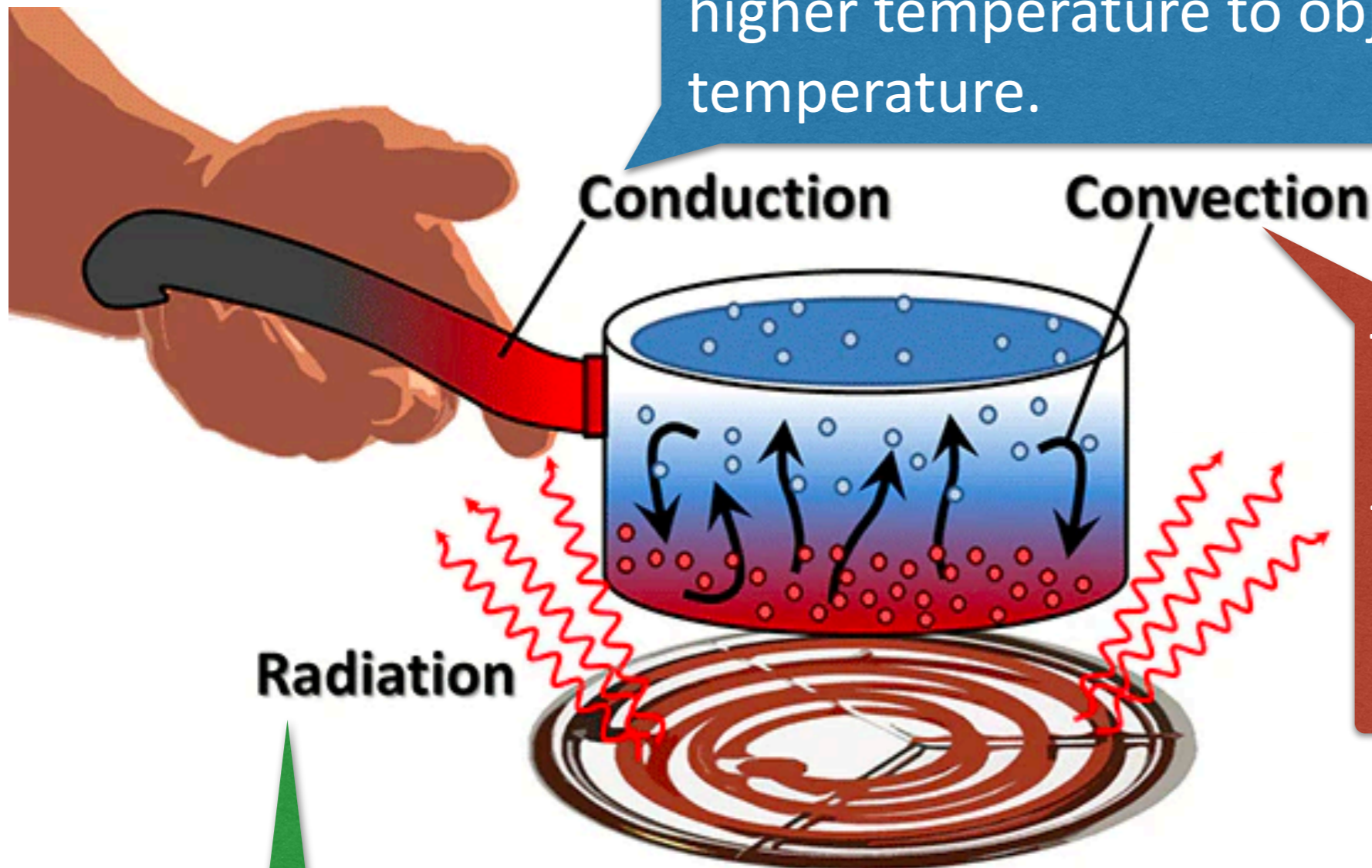


# Summary: Processes in Thermodynamics

$\Delta E_{int} = Q + W$		
Process	Conditions	Results
Isochoric/Isovolumetric		
Isobaric		
Isothermal		
Adiabatic		
Free expansion		
Cyclic		

# How is heat transferred?

The process in which heat flows from objects with higher temperature to objects with lower temperature.

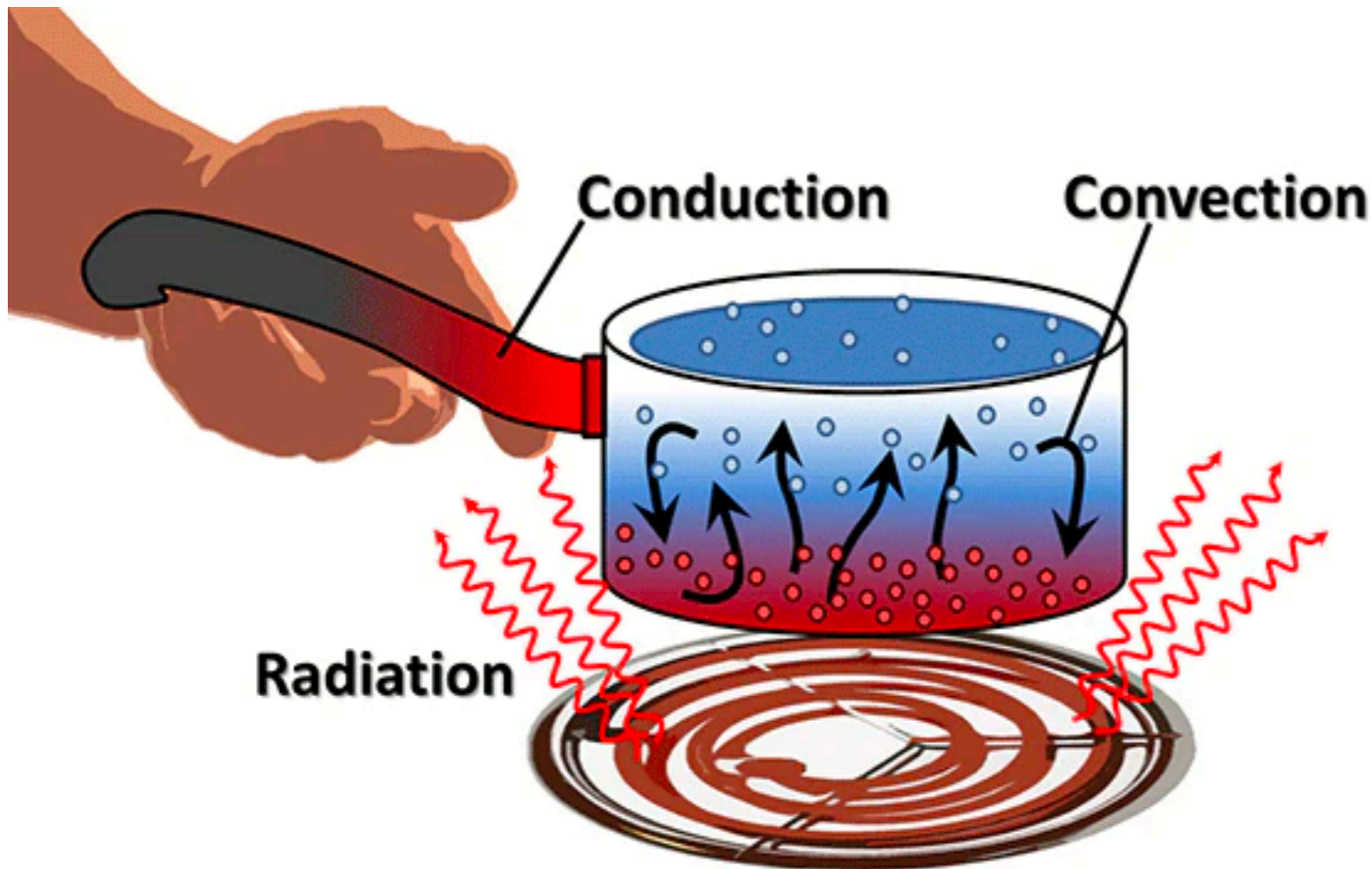


The movement of fluid molecules from higher temperature regions to lower temperature regions.

Thermal radiation is generated by the emission of electromagnetic waves. These waves carry away the energy from the emitting body.

Figure: <https://www.machinedesign.com/learning-resources/whats-the-difference-between/document/21834474/whats-the-difference-between-conduction-convection-and-radiation>

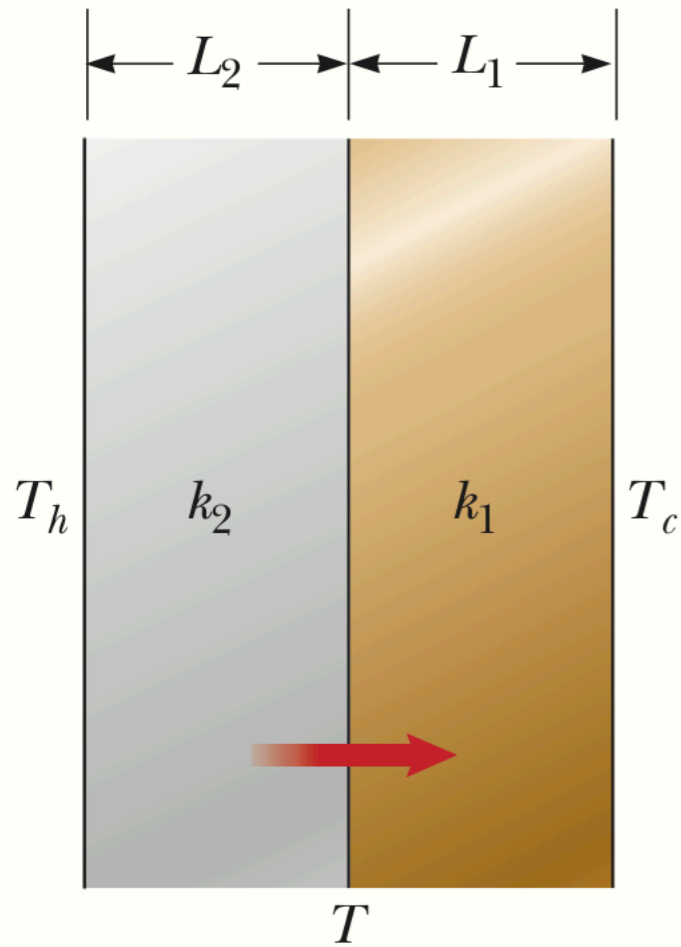
# Conduction



## Thermal Conductivities

Substance	Thermal Conductivity (W/m · °C)
<i>Metals (at 25°C)</i>	
Aluminum	238
Copper	397
Gold	314
Iron	79.5
Lead	34.7
Silver	427
<i>Nonmetals (approximate values)</i>	
Asbestos	0.08
Concrete	0.8
Diamond	2 300
Glass	0.8
Ice	2
Rubber	0.2
Water	0.6
Wood	0.08
<i>Gases (at 20°C)</i>	
Air	0.023 4
Helium	0.138
Hydrogen	0.172
Nitrogen	0.023 4
Oxygen	0.023 8

# Conduction



Two slabs of thickness  $L_1$  and  $L_2$  and thermal conductivities  $k_1$  and  $k_2$  are in thermal contact with each other as shown in Figure. The temperatures of their outer surfaces are  $T_c$  and  $T_h$ , respectively, and  $T_h > T_c$ . Determine the temperature at the interface and the rate of energy transfer by conduction through an area  $A$  of the slabs in the steady-state condition.