

Learning Goals for Chapter 19

Looking forward at ...

- how to calculate work done by a system when its volume changes.
- how to interpret and use the first law of thermodynamics.
- four important kinds of thermodynamic processes.
- why the internal energy of an ideal gas depends on temperature only.
- the difference between molar heat capacities at constant volume and at constant pressure.
- how to analyze adiabatic processes in an ideal gas.

Introduction

 A steam locomotive operates using the laws of thermodynamics, but so do air conditioners and car engines.



• We shall revisit the conservation of energy in the form of the first law of thermodynamics.

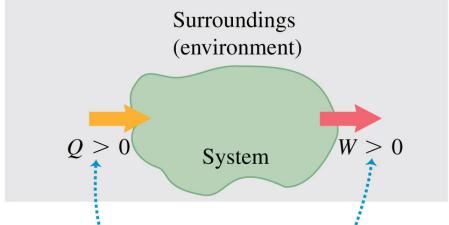
Thermodynamics systems

- A thermodynamic system is any collection of objects that may exchange energy with its surroundings.
- The popcorn in the pot is a thermodynamic system.
- In the thermodynamic process shown here, heat is added to
 - the system, and the system does work on its surroundings to lift the lid of the pot.



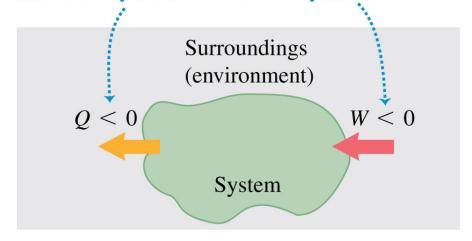
Thermodynamics systems

- In a *thermodynamic process*, changes occur in the state of the system.
- Careful of signs!
- Q is positive when heat flows into a system.
- W is the work done by the system, so it is positive for expansion.



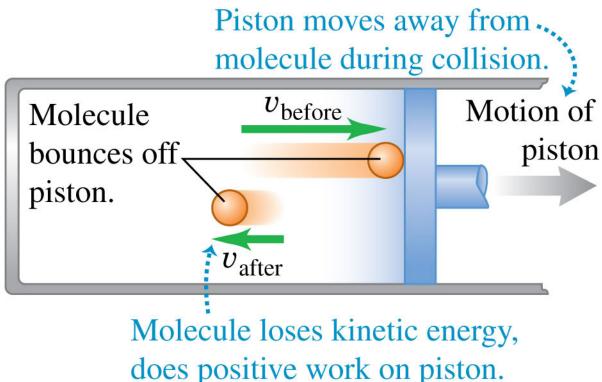
Heat is positive when it *enters* the system, negative when it *leaves* the system.

Work is positive when it is done by the system, negative when it is done on the system.



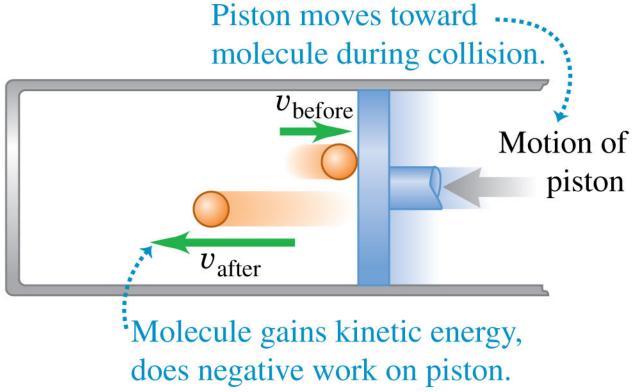
Work done during volume changes

- We can understand the work done by a gas in a volume change by considering a molecule in the gas.
- When one such molecule collides with a surface moving to the right, so the volume of the gas increases, the molecule does *positive* work on the piston.



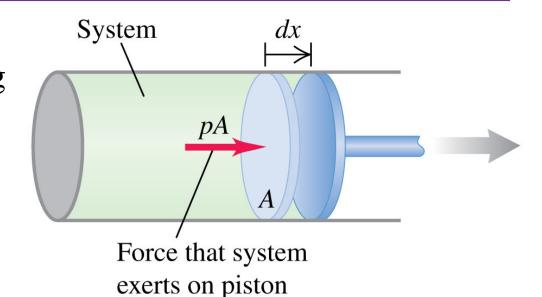
Work done during volume changes

- If the piston moves toward the left as in the figure shown here, so the volume of the gas decreases; positive work is done on the molecule during the collision.
- Hence the gas molecules do *negative* work on the piston.



Work done during volume changes

• The infinitesimal work done by the system during the small expansion dx is dW = pA dx.

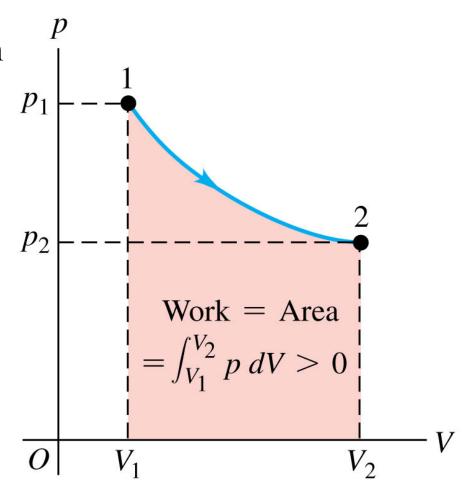


• In a finite change of volume from V_1 to V_2 :

Work done in a West with respect to volume
$$W_1$$
 West with respect to volume W_2 West with respect to volume W_1 Lower limit = initial volume

Work on a pV-diagram

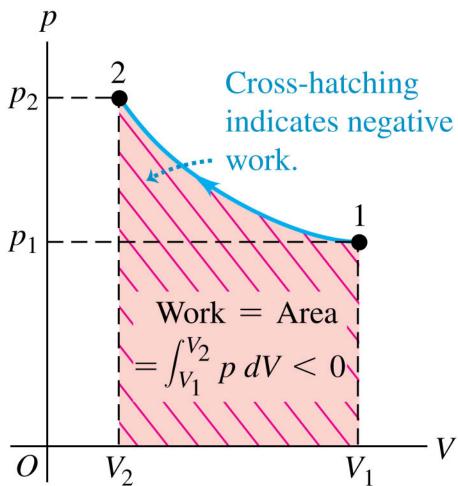
- The work done equals the area under the curve on a pV-diagram.
- Shown in the graph is a system undergoing an **expansion** with varying pressure.



Work on a pV-diagram

• Shown in the graph is a system undergoing a **compression** with varying pressure.

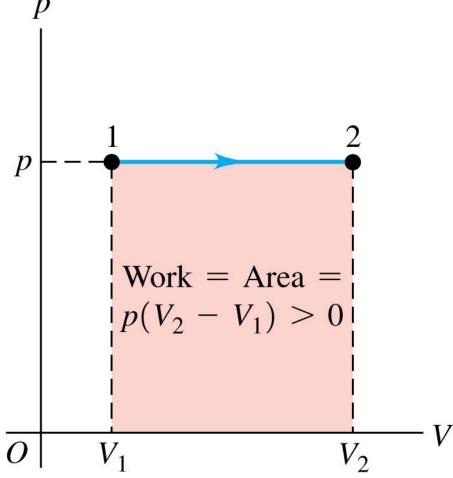
• In this case the work is negative.



Work on a pV-diagram

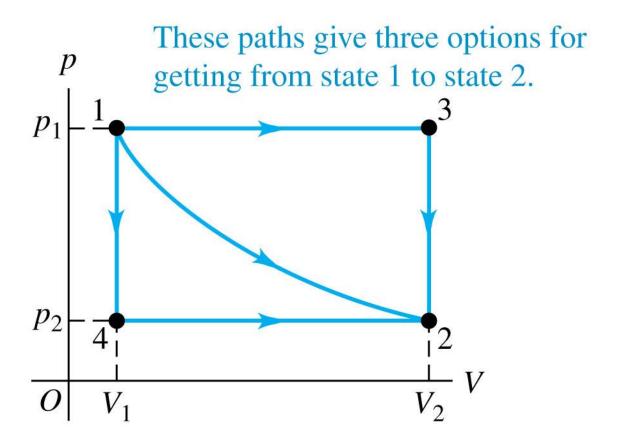
• Shown in the graph is a system undergoing an expansion with **constant** pressure.

• In this case, $W = p(V_2 - V_1)$



Work depends on the path chosen: Slide 1 of 4

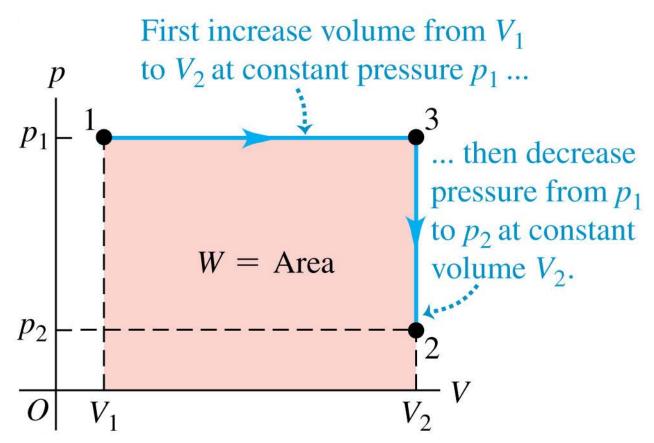
• Consider three different paths on a *pV*-diagram for getting from state 1 to state 2.



Work depends on the path chosen: Slide 2 of 4

• The system does a large amount of work under the path

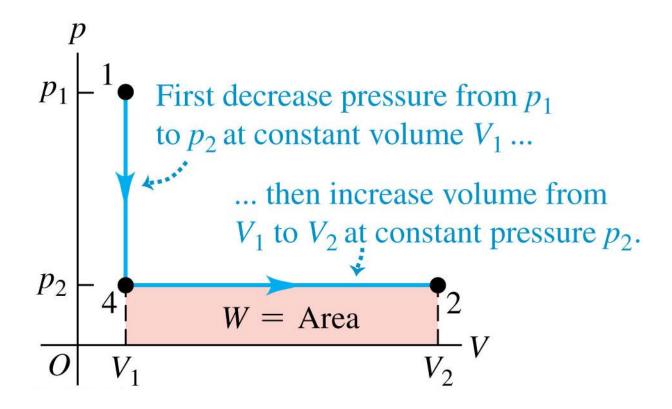
$$1 \rightarrow 3 \rightarrow 2$$
.



Work depends on the path chosen: Slide 3 of 4

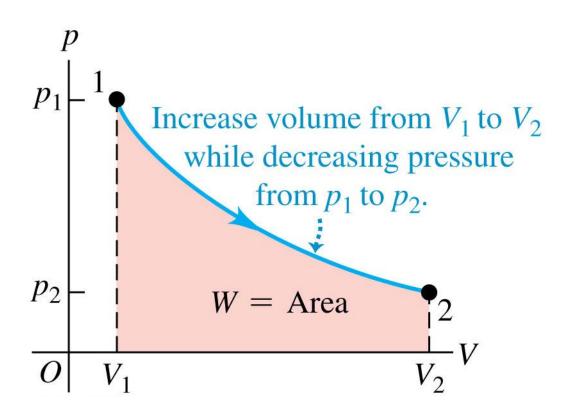
The system does a small amount of work under the path

$$1 \rightarrow 4 \rightarrow 2$$
.



Work depends on the path chosen: Slide 4 of 4

• Along the smooth curve from 1 to 2, the work done is different from that for either of the other paths.

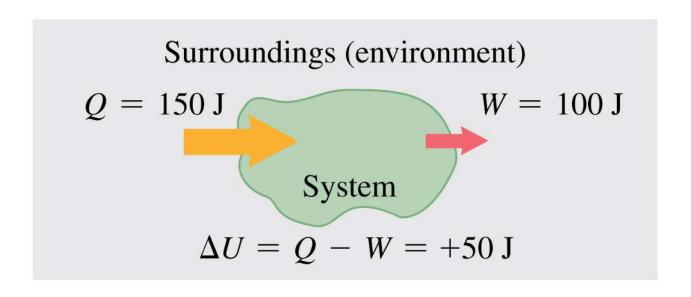


• The change in the internal energy U of a system is equal to the heat added minus the work done by the system:

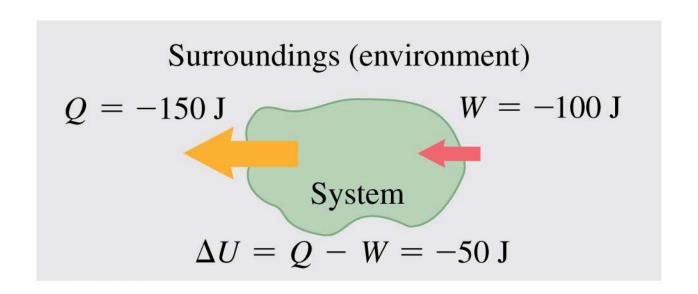
First law of thermodynamics: Internal energy change of thermodynamic system $\Delta U = Q - W$ Heat added to system ... Work done by system

- The first law of thermodynamics is just a generalization of the conservation of energy.
- Both Q and W depend on the path chosen between states, but ΔU is independent of the path.
- If the changes are infinitesimal, we write the first law as dU = dQ dW.

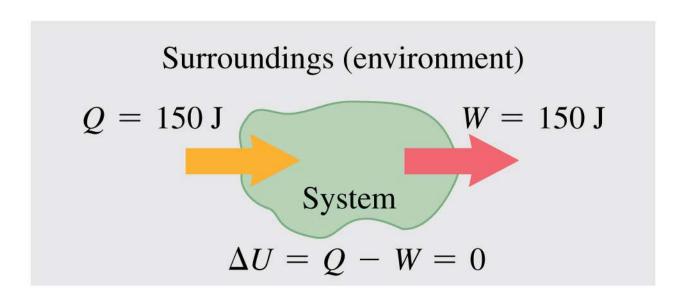
- In a thermodynamic process, the internal energy U of a system may *increase*.
- In the system shown below, more heat is added to the system than the system does work.
- So the internal energy of the system increases.



- In a thermodynamic process, the internal energy U of a system may decrease.
- In the system shown below, more heat flows out of the system than work is done.
- So the internal energy of the system decreases.



- In a thermodynamic process, the internal energy U of a system may remain the same.
- In the system shown below, the heat added to the system equals the work done by the system.
- So the internal energy of the system is unchanged.



First law of exercise thermodynamics

- Your body is a thermodynamic system.
- When you do a push-up, your body does work, so W > 0.
- Your body also warms up during exercise; by perspiration and other means the body rids itself of this heat, so Q < 0.



- Since Q is negative and W is positive, U = Q W < 0 and the body's internal energy decreases.
- That's why exercise helps you lose weight: It uses up some of the internal energy stored in your body in the form of fat.

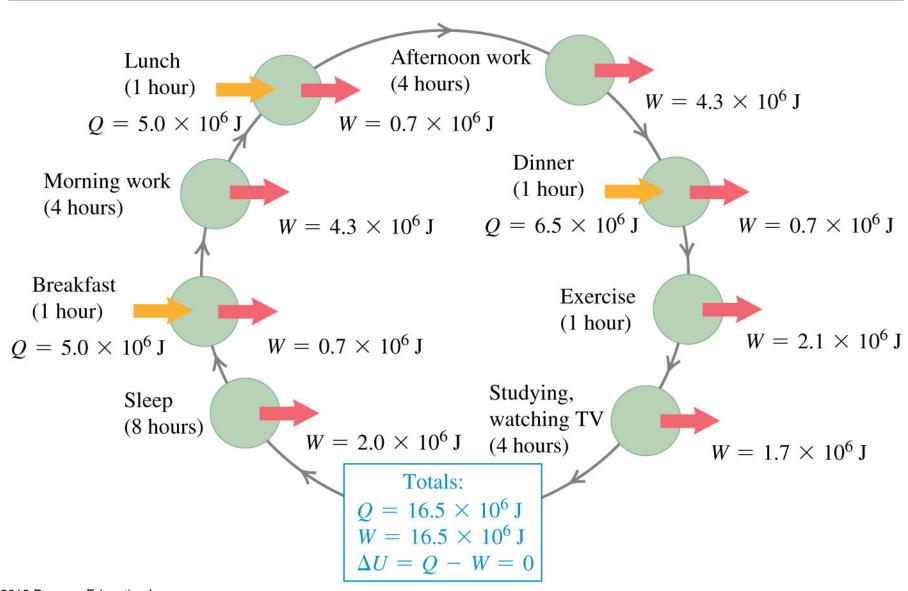
Internal energy

• The internal energy of a cup of coffee depends on just its thermodynamic state—how much water and ground coffee it contains, and what its temperature is.



• It does not depend on the history of how the coffee was prepared—that is, the thermodynamic path that led to its current state.

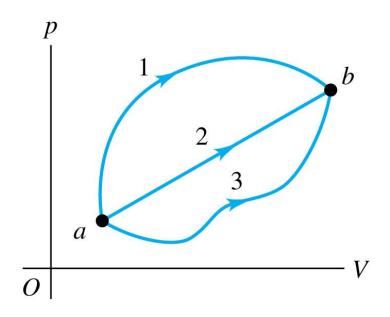
Cyclic thermodynamic process for a human day





Q19.1

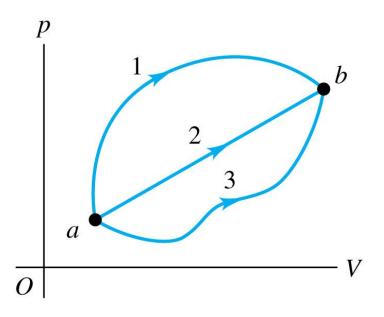
A system can be taken from state a to state b along any of the three paths shown in the p-V diagram. If state b has greater internal energy than state a, along which path is the absolute value |Q| of the heat transfer the greatest?



- A. path 1
- B. path 2
- C. path 3
- D. |Q| is the same for all three paths.
- E. Not enough information is given to decide.



A system can be taken from state *a* to state *b* along any of the three paths shown in the *p-V* diagram. If state *b* has greater internal energy than state *a*, along which path is there a net flow of heat *out* of the system?



A. path 1

B. path 2

C. path 3

D. all of paths 1, 2, and 3

E. none of paths 1, 2, or 3

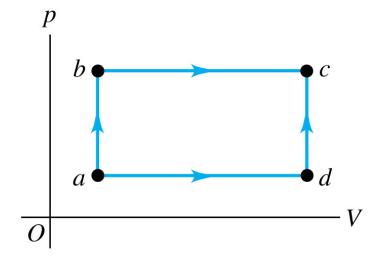


Q19.3

This p-V diagram shows two ways to take a system from state a (at lower left) to state c (at upper right):

- via state b (at upper left), or
- via state d (at lower right)

For which path is W > 0?



- A. path *abc* only
- B. path adc only
- C. both path *abc* and path *adc*
- D. neither path abc nor path adc
- E. The answer depends on what the system is made of.

In an isothermal expansion of an ideal gas, the amount of heat that flows into the gas

- A. is greater than the amount of work done by the gas.
- B. equals the amount of work done by the gas.
- C. is less than the amount of work done by the gas, but greater than zero.
- D. is zero.
- E. is negative (heat flows *out of* the gas).

You put a flame under a piece of metal, raising the temperature of the metal and making the metal expand. The metal is surrounded by air. What are the signs of ΔU , Q, and W for the metal in this process?

A.
$$\Delta U > 0$$
, $Q > 0$, $W > 0$

B.
$$\Delta U < 0$$
, $Q > 0$, $W > 0$

C.
$$\Delta U > 0$$
, $Q > 0$, $W < 0$

D.
$$\Delta U < 0$$
, $Q > 0$, $W < 0$

E. None of these

When you are exercising on a stationary bicycle or rowing machine, what are the signs of ΔU , Q, and W for your body?

A.
$$\Delta U > 0$$
, $Q = 0$, $W > 0$

B.
$$\Delta U < 0$$
, $Q = 0$, $W > 0$

C.
$$\Delta U < 0$$
, $Q > 0$, $W > 0$

D.
$$\Delta U < 0$$
, $Q < 0$, $W > 0$

E. None of these

An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. For this complete cycle,

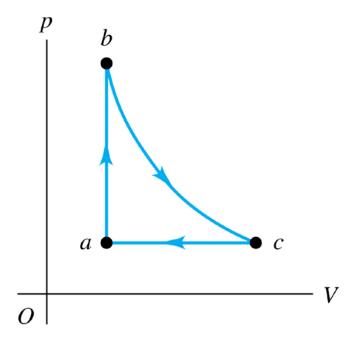
A.
$$Q > 0$$
, $W > 0$, $\Delta U = 0$

B.
$$Q < 0, W > 0, \Delta U = 0$$

C.
$$Q = 0, W > 0, \Delta U < 0$$

D.
$$Q = 0, W < 0, \Delta U > 0$$

E.
$$Q > 0$$
, $W > 0$, $\Delta U > 0$



An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. For process $a \rightarrow b$,

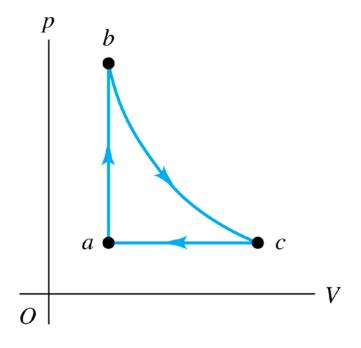
A.
$$Q > 0, \Delta U > 0$$

B.
$$Q > 0$$
, $\Delta U = 0$

C.
$$Q = 0, \Delta U > 0$$

D.
$$Q = 0, \Delta U < 0$$

E.
$$Q < 0, \Delta U < 0$$



An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. For process $b \rightarrow c$,

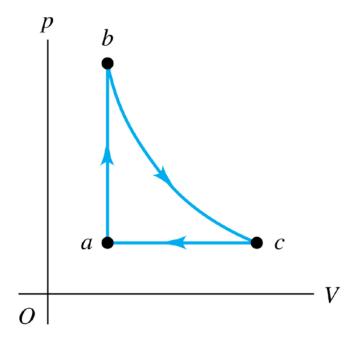
A.
$$Q > 0, \Delta U > 0$$

B.
$$Q > 0$$
, $\Delta U = 0$

C.
$$Q = 0, \Delta U > 0$$

D.
$$Q = 0, \Delta U < 0$$

E.
$$Q < 0, \Delta U < 0$$



An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. For process $c \rightarrow a$,

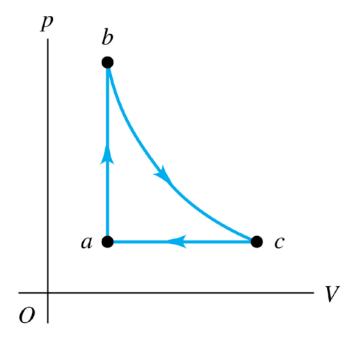
A.
$$Q > 0, \Delta U > 0$$

B.
$$Q > 0$$
, $\Delta U = 0$

C.
$$Q = 0, \Delta U > 0$$

D.
$$Q = 0, \Delta U < 0$$

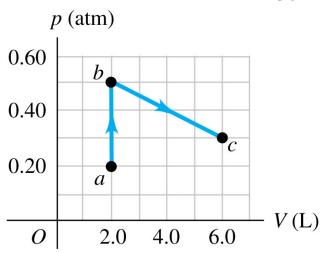
E.
$$Q < 0, \Delta U < 0$$



Exercises

• Two moles of an ideal gas are compressed in a cylinder at a constant temperature of 65.0° C until the original pressure has tripled. (a) sketch a pV-diagram for this process. (b) calculate the amount of work done.

• The process *abc* shown in the *pV*-diagram involves 0.0175 mole of an ideal gas. (a) What was the lowest temperature the gas reached in this process? Where did it occur? (b) How much work was done by or on the gas from *a* to *b*? From *b* to *c*? (c) If 215 J of heat was put into the gas during *abc*, how many of those joules went into internal energy?



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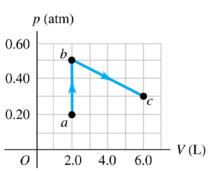
Exercises (hints & answers)

• Two moles of an ideal gas are compressed in a cylinder at a constant temperature of 65.0° C until the original pressure has tripled. (a) sketch a pV-diagram for this process. (b) calculate the amount of work done.

$$W = \int_{1}^{2} p dV = \int_{1}^{2} \frac{nRT}{V} dV = -nRT \ln 3$$
(-6177J)

• The process *abc* shown in the *pV*-diagram involves 0.0175 mole of an ideal gas. (a) What was the lowest temperature the gas reached in this process? Where did it occur? (b) How much work was done by or on the gas from *a* to *b*? From *b* to *c*? (c) If 215 J of heat was put into the gas during *abc*, how many of those joules went into internal energy?

$$pV = nRT; W = \int_{1}^{2} pdV; \Delta U = Q - W$$
(278K, a; $W_{ab} = 0, W_{bc} = 162J; 53J$)



Four kinds of thermodynamic processes

- There are four specific kinds of thermodynamic processes that occur often in practical situations:
 - Adiabatic: No heat is transferred into or out of the system, so Q = 0. Also, $U_2 U_1 = -W$.
 - **Isochoric**: The volume remains constant, so W = 0.
 - **Isobaric**: The pressure remains constant, so $W = p(V_2 V_1)$.
 - **Isothermal**: The temperature remains constant.

Adiabatic process

- When the cork is popped on a bottle of champagne, the pressurized gases inside the bottle expand rapidly and do positive work on the outside air.
- There is little time for the gases to exchange heat with their surroundings, so the expansion is nearly adiabatic.
- Hence the internal energy of the expanding gases decreases

 $(\Delta U = -W)$ and their temperature drops.

• This makes water vapor condense and form a miniature cloud.



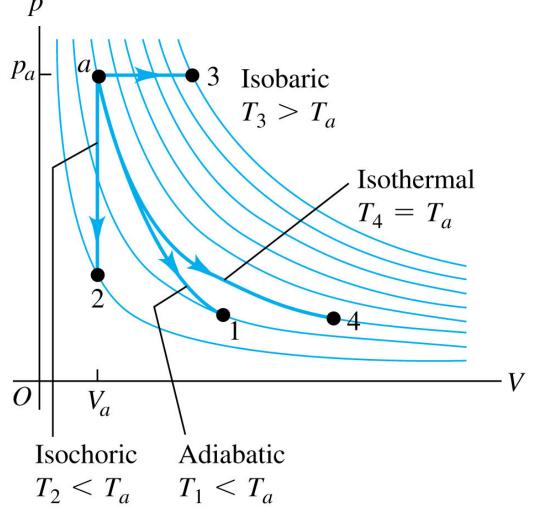
Isobaric process

- Most cooking involves isobaric processes.
- That's because the air pressure above a saucepan or frying pan, or inside a microwave oven, remains essentially constant while the food is being heated.



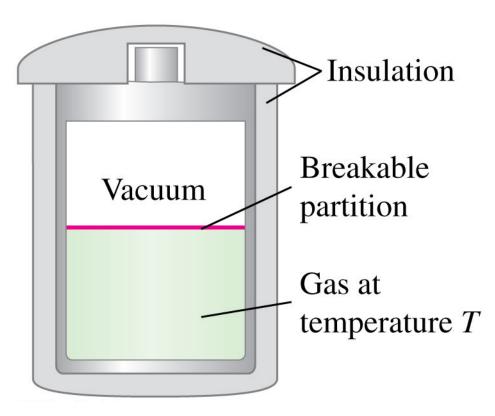
The four processes on a pV-diagram

• Shown are the paths on a pV-diagram for all four different processes for a constant amount of an ideal gas, all starting at state a.



Internal energy of an ideal gas

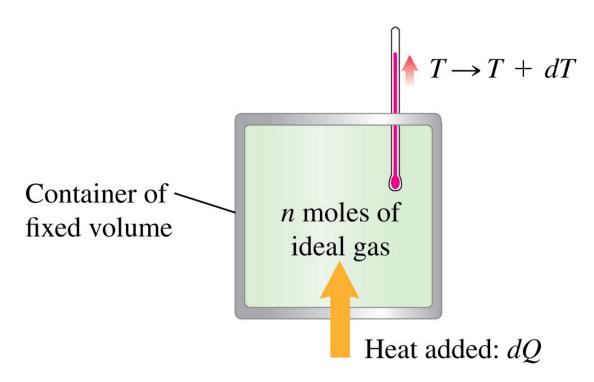
- The internal energy of an ideal gas depends *only* on its *temperature*, not on its pressure or volume.
- The temperature of an ideal gas does *not* change during a free expansion.



Heat capacities of an ideal gas

- C_V is the molar heat capacity at constant volume.
- To measure C_V , we raise the temperature of an ideal gas in a rigid container with constant volume, ignoring its thermal expansion.

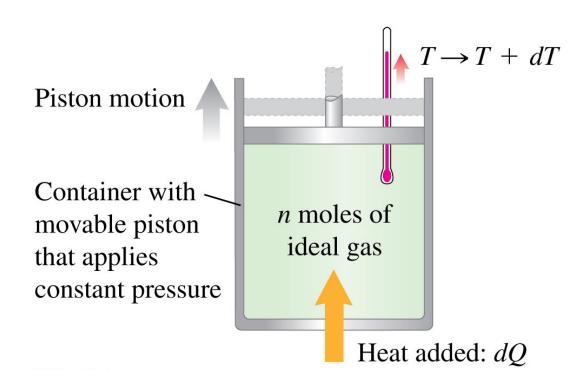
Constant volume: $dQ = nC_V dT$



Heat capacities of an ideal gas

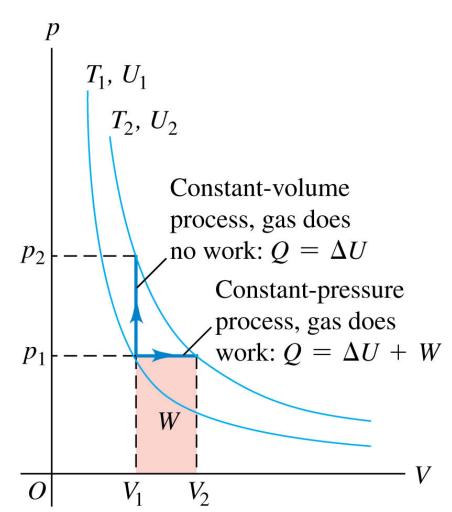
- C_p is the molar heat capacity at constant pressure.
- To measure C_p , we let the gas expand just enough to keep the pressure constant as the temperature rises.

Constant pressure: $dQ = nC_p dT$



Relating C_p and C_V for an ideal gas

- To produce the same temperature change, more heat is required at constant pressure than at constant volume since ΔU is the same in both cases.
- This means that $C_p > C_V$.
- $C_p = C_V + R$.
- R is the gas constant $R = 8.314 \text{ J/mol} \cdot \text{K}$.



The ratio of heat capacities

• The ratio of heat capacities is:

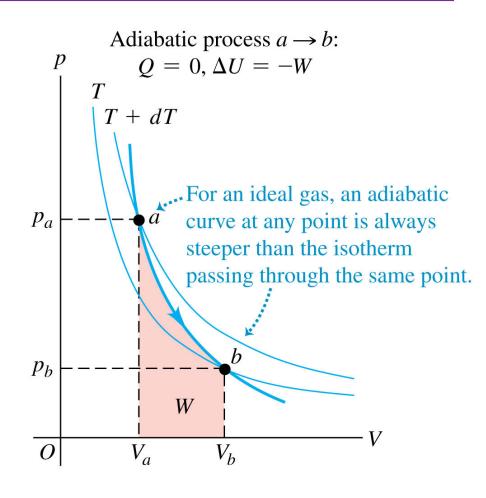
- For monatomic ideal gases, $\gamma = 1.67$.
- For diatomic ideal gases, $\gamma = 1.40$.

TABLE 19.1 Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	C_V (J/mol·K)	C_p (J/mol·K)	$C_p - C_V$ (J/mol·K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H_2	20.42	28.74	8.32	1.41
	N_2	20.76	29.07	8.31	1.40
	O_2	20.85	29.17	8.32	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO_2	28.46	36.94	8.48	1.30
	SO_2	31.39	40.37	8.98	1.29
	H_2S	25.95	34.60	8.65	1.33

Adiabatic processes for an ideal gas

- In an adiabatic process, no heat is transferred in or out of the gas, so Q = 0.
- Shown is a *pV*-diagram for an adiabatic expansion.
- As the gas expands, it does positive work *W* on its environment, so its internal energy decreases, and its temperature drops.



• Note that an adiabatic curve at any point is always steeper than an isotherm at that point.

Adiabatic ideal gas: relating V, T and p

- In an adiabatic process, Q = 0, then dU = -dW = -pdV for an infinitesimal adiabatic process. Therefore, $n C_V dT = -pdV$.
- Ideal gas, $p = \frac{nRT}{V}, \Rightarrow nC_V dT = -\frac{nRT}{V} dV, \Rightarrow \frac{dT}{T} = -\frac{R}{C_V} \frac{dV}{V}$
- Since $\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}, \frac{R}{C_V} = \gamma 1, \Rightarrow \frac{dT}{T} = -(\gamma 1)\frac{dV}{V}$
 - $\Rightarrow \ln T + (\gamma 1) \ln V = \text{constant}, \Rightarrow \ln (TV^{\gamma 1}) = \text{constant},$

$$\Rightarrow TV^{\gamma-1} = \text{constant} \Rightarrow T_a V_a^{\gamma-1} = T_b V_b^{\gamma-1}$$

• Since $T = pV/nR, \Rightarrow$

$$pV^{\gamma} = \text{constant}, \Rightarrow p_1V_1^{\gamma} = p_2V_2^{\gamma}$$

Work done by an ideal gas in an adiabatic process

- Q=0, $W=-\Delta U$,
- For an ideal gas, $\Delta U = nC_V(T_2 T_1)$.

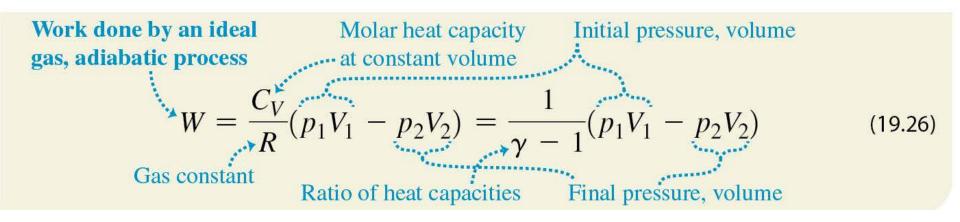
Work done by Mumber of moles

an ideal gas,
adiabatic process

$$W = nC_V(T_1 - T_2)$$
Final temperature

Molar heat capacity at constant volume

(19.25)



Exhaling adiabatically

- Put your hand a few centimeters in front of your mouth, open your mouth wide, and exhale.
- Your breath will feel warm on your hand, because the exhaled gases emerge at roughly the temperature of your body's interior.
- Now purse your lips as though you were going to whistle, and again blow on your hand.
- The exhaled gases will feel much cooler.
- In this case the gases undergo a rapid, essentially adiabatic expansion as they emerge from between your lips, so the temperature of the exhaled gases decreases.





An ideal gas is taken around the cycle shown in this p-V diagram, from a to c to b and back to a. Process $c \to b$ is adiabatic. For process $c \to b$,

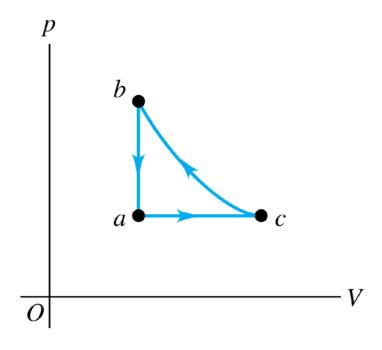
A.
$$Q > 0$$
, $W > 0$, $\Delta U = 0$

B.
$$Q > 0$$
, $W > 0$, $\Delta U > 0$

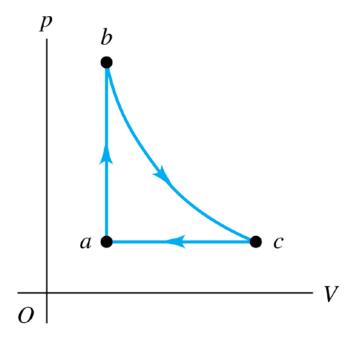
C.
$$Q = 0, W > 0, \Delta U < 0$$

D.
$$Q = 0, W < 0, \Delta U > 0$$

E.
$$Q < 0$$
, $W < 0$, $\Delta U = 0$



An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. Rank the following processes in order of the value of the internal energy ΔU of the ideal gas in the process, from most positive to most negative.

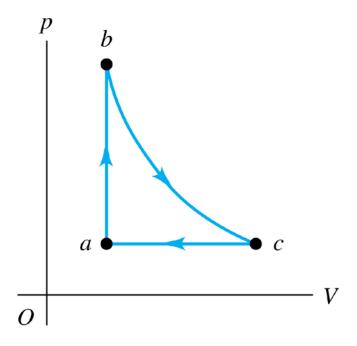


A.
$$a \rightarrow b$$

B.
$$b \rightarrow c$$

$$C. c \rightarrow a$$

An ideal gas is taken around the cycle shown in this p-V diagram, from a to b to c and back to a. Process $b \rightarrow c$ is isothermal. Rank the following processes in order of the value of the work W done by the ideal gas in the process, from most positive to most negative.



A.
$$a \rightarrow b$$

B.
$$b \rightarrow c$$

$$C. c \rightarrow a$$



Exercises

• When a quantity of monatomic ideal gas expands at a constant pressure of 4.00×10^4 Pa, the volume of the gas increases from 2.00×10^{-3} m³ to 8.00×10^{-3} m³. What is the change in the internal energy of the gas?

• A cylinder contains 0.100 mole of an ideal monatomic gas. Initially the gas is at 1.00 ×10⁵ Pa and occupies of volume of 2.50 × 10⁻³ m³.(a) Find the initial temperature of the gas in kelvins. (b) If the gas is allowed to expand to twice the initial volume, find the final temperature in kelvins and pressure of the gas if the expansion is (i) isothermal; (ii) isobaric; (iii) adiabatic.



Exercises (hints & answers)

• When a quantity of monatomic ideal gas expands at a constant pressure of 4.00×10^4 Pa, the volume of the gas increases from 2.00×10^{-3} m³ to 8.00×10^{-3} m³. What is the change in the internal energy of the gas?

$$\Delta U = nC_V \Delta T$$
; or $\Delta U = Q - W = nC_p \Delta T - p\Delta V$
(360J)

• A cylinder contains 0.100 mole of an ideal monatomic gas. Initially the gas is at 1.00 ×10⁵ Pa and occupies of volume of 2.50 × 10⁻³ m³.(a) Find the initial temperature of the gas in kelvins. (b) If the gas is allowed to expand to twice the initial volume, find the final temperature in kelvins and pressure of the gas if the expansion is (i) isothermal; (ii) isobaric; (iii) adiabatic.

$$pV = nRT; T_1V_1^{\gamma - 1} = T_2V_2^{\gamma - 1}; P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

 $(301K;301K,5.00 \times 10^4 \text{ Pa}; 602K, 1.00 \times 10^5 \text{ Pa}, 189K, 3.14 \times 10^4 \text{ Pa}.)$



Exercises

• The compression ratio of a diesel engine is 15 to 1: that is, air in a cylinder is compressed to 1/15 of its initial volume. (a) If the initial pressure is 1.01×10^5 Pa and the initial temperature is $27 \, \text{C}$, find the final pressure and the temperature after adiabatic compression. (b) How much work does the gas do during the compression if the initial volume of the cylinder is 1.00L? Use the value $C_V = 20.8 \, \text{J/mole} \cdot \text{K}$ and $\gamma = 1.4$ for air.

• A typical dorm room or bedroom contains about 2500 moles of air. Find the change in the internal energy of this much air when it is cooled from 35.0 °C to 26.0 °C at a constant pressure of 1.00 atm. Treat the air as an ideal gas with $\gamma = 1.4$.



Exercises (hints & answers)

• The compression ratio of a diesel engine is 15 to 1: that is, air in a cylinder is compressed to 1/15 of its initial volume. (a) If the initial pressure is 1.01×10^5 Pa and the initial temperature is $27 \, \text{°C}$, find the final pressure and the temperature after adiabatic compression. (b) How much work does the gas do during the compression if the initial volume of the cylinder is $1.00 \, \text{L}$? Use the value $C_V = 20.8 \, \text{J/mole·K}$ and $\gamma = 1.4$ for air.

$$TV^{\gamma-1} = \text{constant}; pV^{\gamma} = \text{constant}; W = \frac{1}{\gamma - 1} (p_1 V_1 - p_2 V_2)$$
(44 atm, 613°C; -494J)

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$$\Delta U = nC_V (T_2 - T_1); \gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}$$
(-4.68 × 10⁵ J)