Lecture 6
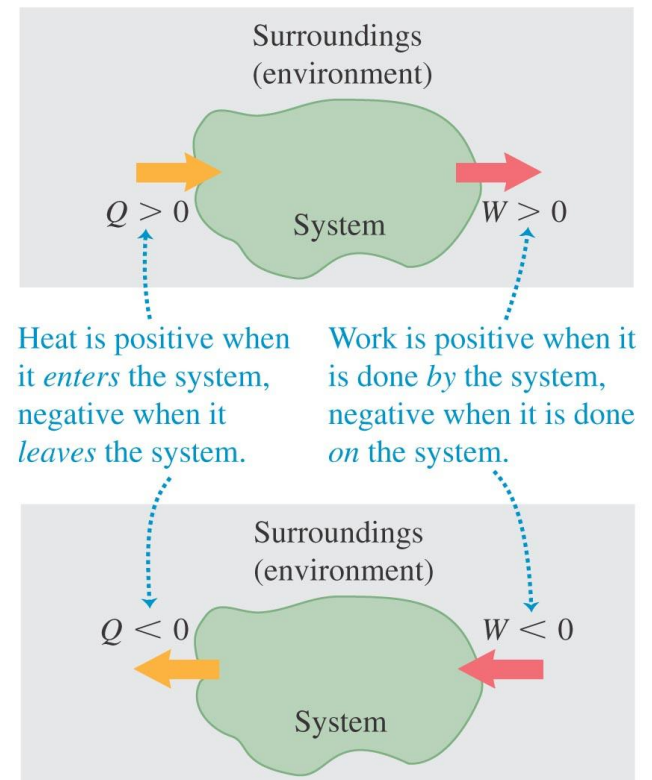# (First Law of Thermodynamics)

Physics 161-01 Spring 2012

Douglas Fields

Thermodynamic Systems and Processes

- A *thermodynamic system* is any collection of objects that may exchange energy with its surroundings.

- 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.
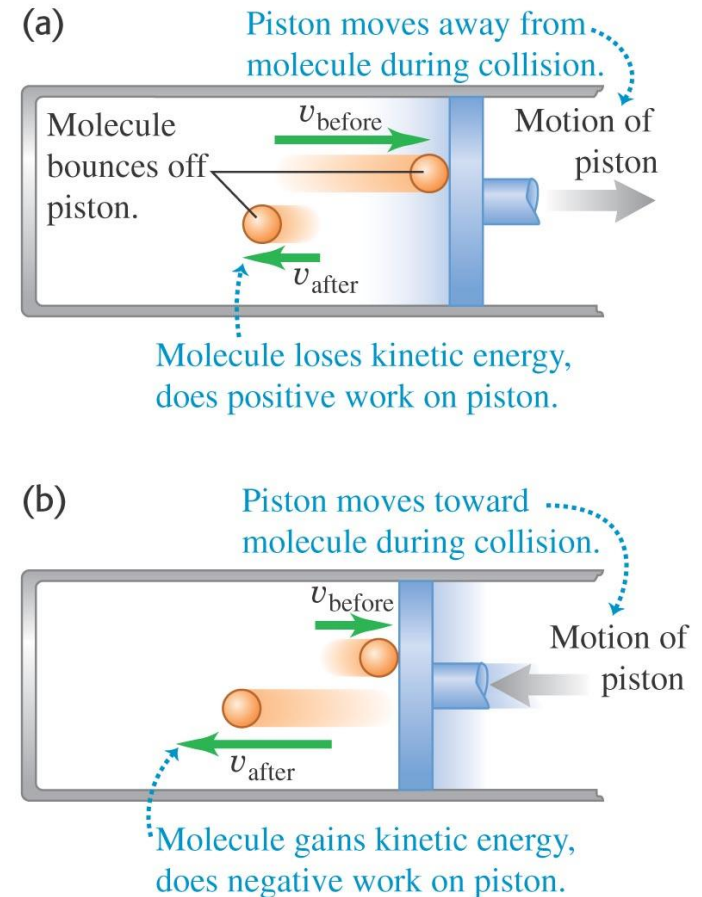

Surroundings (environment)

$Q > 0$ System $W > 0$

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.

Surroundings (environment)

$Q < 0$ $W < 0$ System

Thermodynamic State

- A *thermodynamic state* is a thermodynamic system with a particular set of thermodynamic variables – p, V and T.

- Changes in the state can occur through expansion or contraction, or by adding or taking away heat (by contact with another substance at a different temperature).

Work Done During Volume Changes

- The work done by a system can be understood in one of two ways:

  - On a microscopic level the atoms bounce off of the walls of the container (or the piston as in the case of the figure), and either

    - Lose kinetic energy by doing positive work on the piston (volume increase) or

    - Gain kinetic energy by doing negative work on the piston (volume decrease).

(a)

Piston moves away from molecule during collision.

Molecule bounces off piston.

v_{before}

Motion of piston

v_{after}

Molecule loses kinetic energy, does positive work on piston.

(b)

Piston moves toward molecule during collision.

v_{before}

Motion of piston

v_{after}

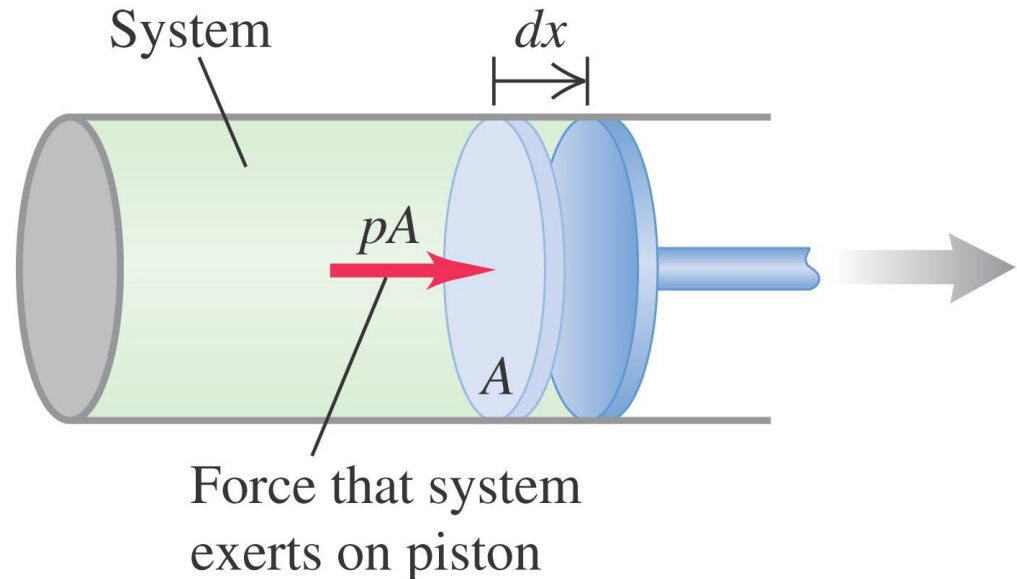Molecule gains kinetic energy, does negative work on piston.

Work Done During Volume Changes

- The work done by a system can be understood in one of two ways:
  - On a macroscopic level the pressure of the substance over the area of the walls of the container (or the piston as in the case of the figure), either
    - Does positive work on the piston (volume increase, force in same direction as displacement) or
    - Does negative work on the piston (volume decrease, force in the opposite direction as displacement).

$$dW = Fdx$$

$$= pAdx$$

$$= pdV \Rightarrow$$

$$W = \int_{V_1}^{V_2} pdV$$

System

dx

pA

A

Force that system exerts on piston
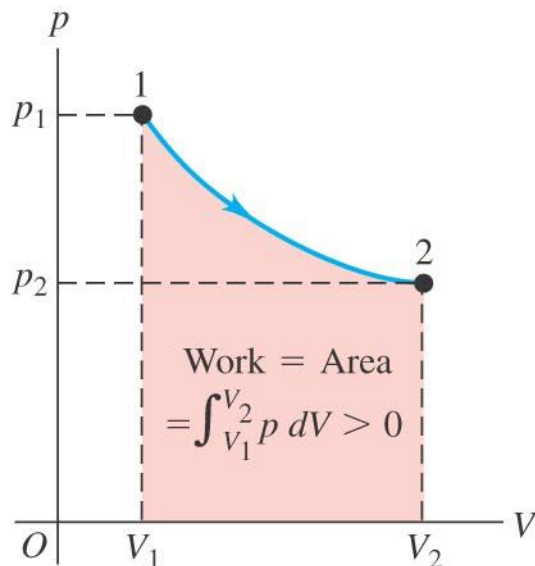
Work Done During Volume Changes

- The work done equals the area under the curve on a *pV*-diagram.
- Work is positive for expansion and negative for compression.

(a) *pV*-diagram for a system undergoing an expansion with varying pressure

$$\text{Work} = \text{Area} = \int_{V_1}^{V_2} p\, dV > 0$$

(b) *pV*-diagram for a system undergoing a compression with varying pressure

Cross-hatching indicates negative work.

$$\text{Work} = \text{Area} = \int_{V_1}^{V_2} p\, dV < 0$$
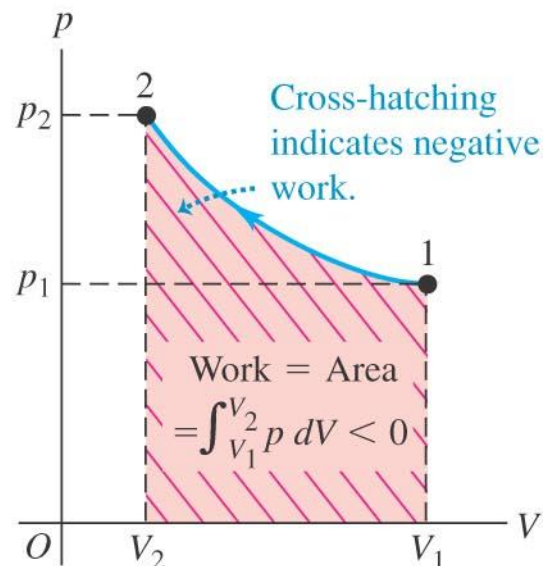
(c) *pV*-diagram for a system undergoing an expansion with constant pressure

$$\text{Work} = \text{Area} = p(V_2 - V_1) > 0$$
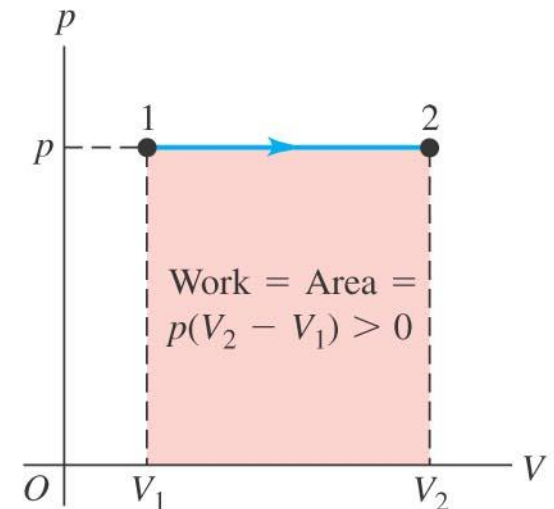
Example 19.1 **Isothermal expansion of an ideal gas**

As an ideal gas undergoes an *isothermal* (constant-temperature) expansion at temperature T, its volume changes from V_1 to V_2. How much work does the gas do?

SOLUTION

IDENTIFY and SET UP: The ideal-gas equation, Eq. (18.3), tells us that if the temperature T of n moles of an ideal gas is constant, the quantity $pV = nRT$ is also constant: p and V are inversely related. If V changes, p changes as well, so we *cannot* use Eq. (19.3) to calculate the work done. Instead we must use Eq. (19.2). To evaluate the integral in Eq. (19.2) we must know p as a function of V; for this we use Eq. (18.3).

EXECUTE: From Eq. (18.3),

$$p = \frac{nRT}{V}$$

We substitute this into the integral of Eq. (19.2), take the constant factor nRT outside, and evaluate the integral:

$$W = \int_{V_1}^{V_2} p \, dV$$

$$= nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\frac{V_2}{V_1} \quad \text{(ideal gas, isothermal process)}$$

We can rewrite this expression for W in terms of p_1 and p_2. Because $pV = nRT$ is constant,

$$p_1V_1 = p_2V_2 \quad \text{or} \quad \frac{V_2}{V_1} = \frac{p_1}{p_2}$$

so

$$W = nRT \ln\frac{p_1}{p_2} \quad \text{(ideal gas, isothermal process)}$$

EVALUATE: We check our result by noting that in an expansion $V_2 > V_1$ and the ratio V_2/V_1 is greater than 1. The logarithm of a number greater than 1 is positive, so $W > 0$, as it should be. As an additional check, look at our second expression for W: In an isothermal expansion the volume increases and the pressure drops, so $p_2 < p_1$, the ratio $p_1/p_2 > 1$, and $W = nRT \ln(p_1/p_2)$ is again positive.

These results also apply to an isothermal *compression* of a gas, for which $V_2 < V_1$ and $p_2 > p_1$.

Paths Between States

- A state of a substance is when it has particular thermodynamic properties (p, V, T).
- It has been shown experimentally that two identical substances at the same p, V and T are indistinguishable, regardless of how they got into their present state.
- There are, however, an endless choice of ways to take a substance from one state to the other.
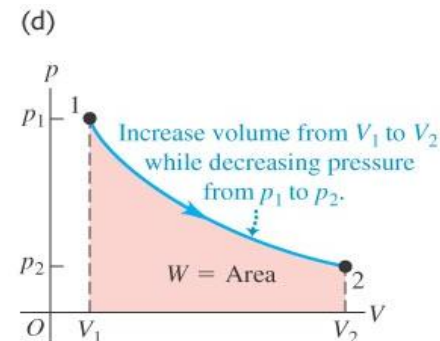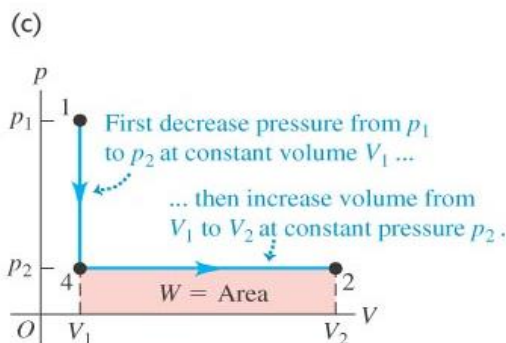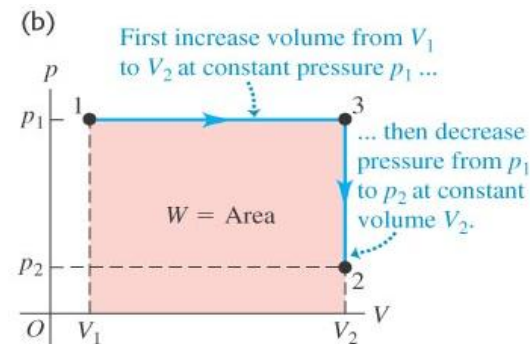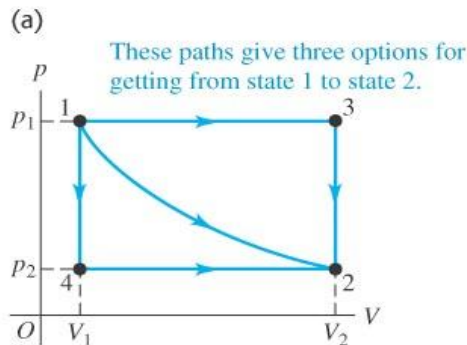
1ˢᵗ Law of Thermodynamics

- *First law of thermodynamics*: The change in the internal energy U of a system is equal to the heat added minus the work done by the system: $\Delta U = Q - W$.
- 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 $dU = dQ - dW$.

(a) More heat is added to system than system does work: Internal energy of system increases.

Surroundings (environment)

$Q = 150\,J$ $W = 100\,J$

System

$\Delta U = Q - W = +50\,J$
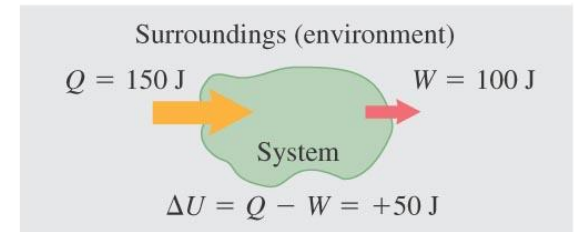
(b) More heat flows out of system than work is done: Internal energy of system decreases.

Surroundings (environment)

$Q = -150\,J$ $W = -100\,J$

System

$\Delta U = Q - W = -50\,J$
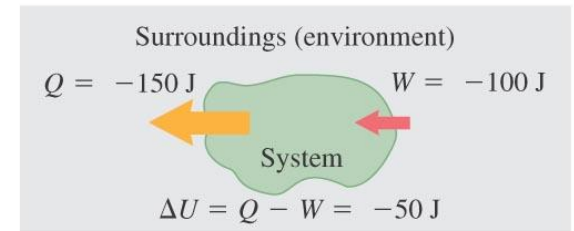
(c) Heat added to system equals work done by system: Internal energy of system unchanged.

Surroundings (environment)

$Q = 150\,J$ $W = 150\,J$

System

$\Delta U = Q - W = 0$
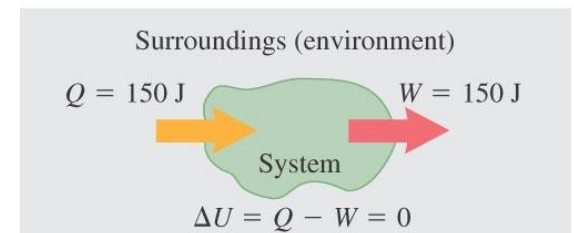
Internal Energy

- The internal energy of a system is defined as the sum of the kinetic energies of the constituent particles plus the potential energies *of the interactions among these particles.*

- If one raises a glass of water, the internal energy doesn't change because the potential energy change is related to the interaction between the water molecules and the earth.

- However, if the water freezes, at the same temperature as before, the internal potential energy changes, and hence the internal energy changes, even though it is at the same temperature.

Internal Energy of an Ideal Gas

- Because an ideal gas has no interactions between the particles, *the internal energy of an ideal gas depends only on its temperature*, not on its pressure or volume.

- So, consider a constant volume process going from one temperature to a higher temperature:

$$dU = dQ - dW$$

$$\text{but, } dW = 0$$

$$dU = dQ = nC_V dT$$

- This is the change in internal energy of an ideal gas between two temperatures, regardless of how we go between those two temperatures!

Free Expansion

- There is a subtle, but important caveat to what we have talked about so far.
- Let us consider two different cases involving expansion of an ideal gas at constant temperature.
    1. Isothermal expansion by adding heat.

(a) System does work on piston; hot plate adds heat to system ($W > 0$ and $Q > 0$).
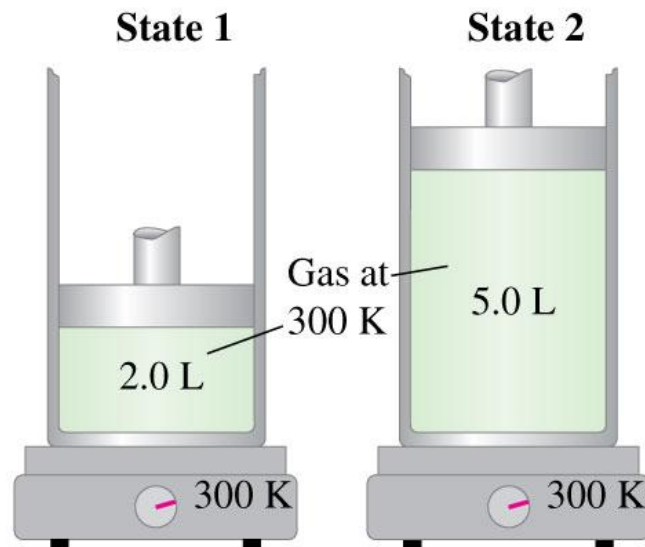
State 1   State 2

Gas at 300 K

2.0 L   5.0 L

300 K   300 K

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Free Expansion

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- Let us consider two different cases involving expansion of an ideal gas at constant temperature.
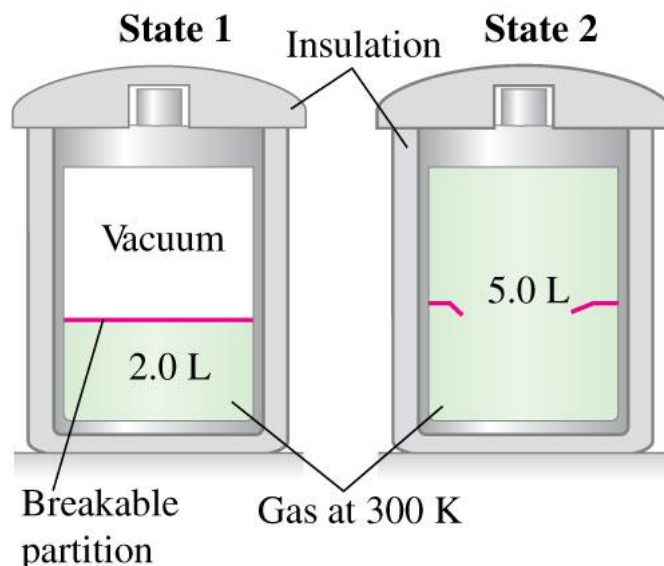   1. Isothermal expansion by adding heat.
    2. Isothermal Free expansion.

(b) System does no work; no heat enters or leaves system $(W = 0$ and $Q = 0)$.
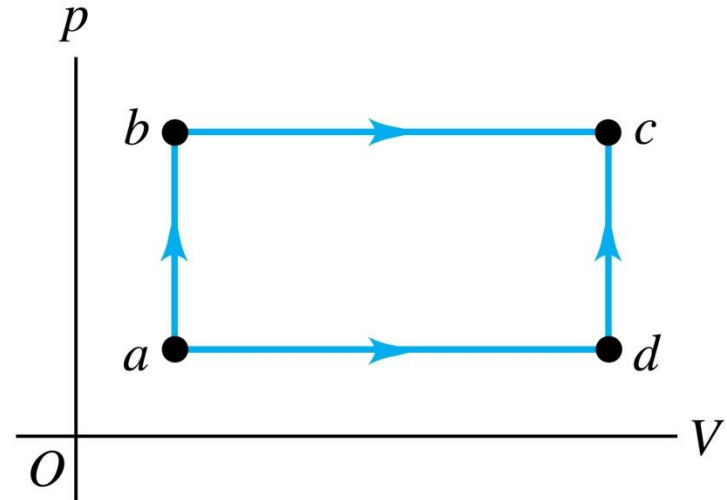
State 1   Insulation   State 2

Vacuum

5.0 L

2.0 L

Breakable partition   Gas at 300 K

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CPS 6-1

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. 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.

CPS 6-1

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
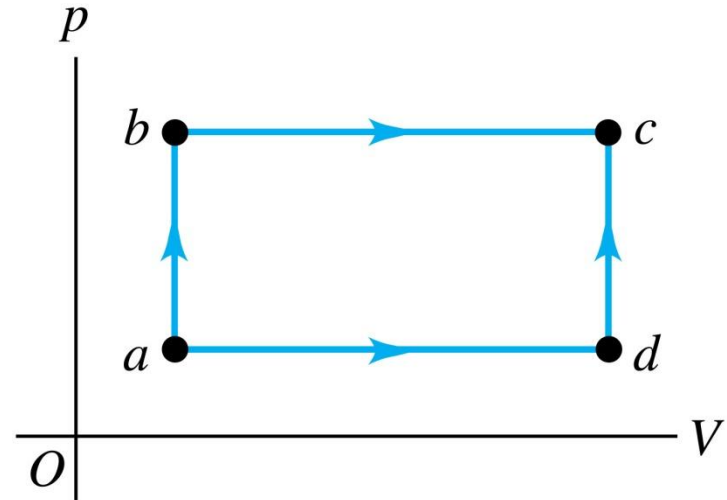• via state *d* (at lower right)

For which path is *W* > 0?
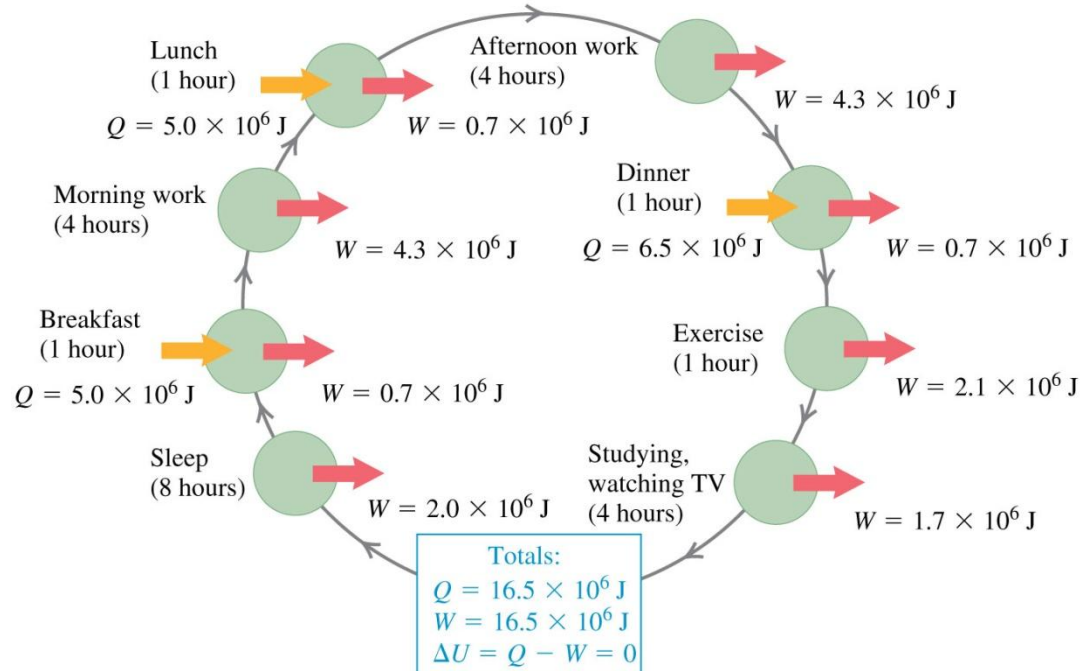

A.   path *abc* only

B.   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.

Cyclic Processes

- In a cyclic process, the system goes from a particular state, through some other states, and then returns to its original state.
- During this process, heat can be added and/or taken out, and work can be done by and/or on the system.
- But there is no net change in internal energy because it returns to the original state.

Lunch (1 hour)
$Q = 5.0 \times 10^6$ J

Afternoon work (4 hours)
$W = 0.7 \times 10^6$ J
$W = 4.3 \times 10^6$ J

Morning work (4 hours)
$W = 4.3 \times 10^6$ J

Dinner (1 hour)
$Q = 6.5 \times 10^6$ J
$W = 0.7 \times 10^6$ J

Breakfast (1 hour)
$Q = 5.0 \times 10^6$ J
$W = 0.7 \times 10^6$ J

Exercise (1 hour)
$W = 2.1 \times 10^6$ J

Sleep (8 hours)
$W = 2.0 \times 10^6$ J

Studying, watching TV (4 hours)
$W = 1.7 \times 10^6$ J

Totals:
$Q = 16.5 \times 10^6$ J
$W = 16.5 \times 10^6$ J
$\Delta U = Q - W = 0$

Problem-Solving Strategy 19.1 The First Law of Thermodynamics

IDENTIFY *the relevant concepts:* The first law of thermodynamics is the statement of the law of conservation of energy in its most general form. You can apply it to *any* thermodynamic process in which the internal energy of a system changes, heat flows into or out of the system, and/or work is done by or on the system.

SET UP *the problem* using the following steps:
1. Define the thermodynamic system to be considered.
2. If the thermodynamic process has more than one step, identify the initial and final states for each step.
3. List the known and unknown quantities and identify the target variables.
4. Confirm that you have enough equations. You can apply the first law, $\Delta U = Q - W$, just once to each step in a thermodynamic process, so you will often need additional equations. These may include Eq. (19.2), $W = \int_{V_1}^{V_2} p \, dV$, which gives the work W done in a volume change, and the equation of state of the material that makes up the thermodynamic system (for an ideal gas, $pV = nRT$).

EXECUTE *the solution* as follows:
1. Be sure to use consistent units. If p is in Pa and V in m^3, then W is in joules. If a heat capacity is given in terms of calories,

convert it to joules. When you use $n = m_{total}/M$ to relate total mass m_{total} to number of moles n, remember that if m_{total} is in kilograms, M must be in *kilograms* per mole; M is usually tabulated in *grams* per mole.
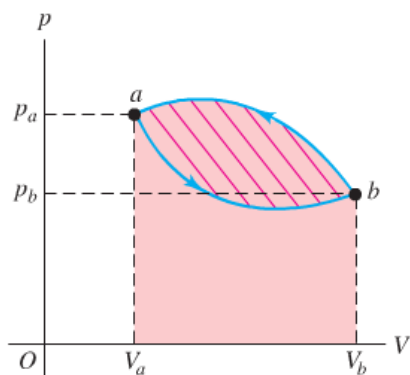2. The internal energy change ΔU in any thermodynamic process or series of processes is independent of the path, whether the substance is an ideal gas or not. If you can calculate ΔU for *any* path between given initial and final states, you know ΔU for *every possible path* between those states; you can then relate the various energy quantities for any of those other paths.
3. In a process comprising several steps, tabulate Q, W, and ΔU for each step, with one line per step and with the Q's, W's, and ΔU's forming columns (see Example 19.4). You can apply the first law to each line, and you can add each column and apply the first law to the sums. Do you see why?
4. Using steps 1–3, solve for the target variables.

EVALUATE *your answer:* Check your results for reasonableness. Ensure that each of your answers has the correct algebraic sign. A positive Q means that heat flows *into* the system; a negative Q means that heat flows *out of* the system. A positive W means that work is done *by* the system on its environment; a negative W means that work is done *on* the system by its environment.

Example 19.3 **A cyclic process**

Figure 19.12 shows a pV-diagram for a *cyclic* process in which the initial and final states of some thermodynamic system are the same. As shown, the state of the system starts at point a and proceeds counterclockwise in the pV-diagram to point b, then back to a; the total work is $W = -500$ J. (a) Why is the work negative? (b) Find the change in internal energy and the heat added during this process.

19.12 The net work done by the system in the process aba is -500 J. What would it have been if the process had proceeded clockwise in this pV-diagram?

EXECUTE: (a) The work done in any step equals the area under the curve in the pV-diagram, with the area taken as positive if $V_2 > V_1$

SOLUTION

IDENTIFY and SET UP: We must relate the change in internal energy, the heat added, and the work done in a thermodynamic process. Hence we can apply the first law of thermodynamics. The process is cyclic, and it has two steps: $a \rightarrow b$ via the lower curve in Fig. 19.12 and $b \rightarrow a$ via the upper curve. We are asked only about the *entire* cyclic process $a \rightarrow b \rightarrow a$.

and negative if $V_2 < V_1$; this rule yields the signs that result from the actual integrations in Eq. (19.2), $W = \int_{V_1}^{V_2} p \, dV$. The area under the lower curve $a \rightarrow b$ is therefore positive, but it is smaller than the absolute value of the (negative) area under the upper curve $b \rightarrow a$. Therefore the net area (the area enclosed by the path, shown with red stripes) and the net work W are negative. In other words, 500 J more work is done *on* the system than *by* the system in the complete process.

(b) In any cyclic process, $\Delta U = 0$, so $Q = W$. Here, that means $Q = -500$ J; that is, 500 J of heat flows *out of* the system.

EVALUATE:
In cyclic processes, the total work is positive if the process goes clockwise around the pV-diagram representing the cycle, and negative if the process goes counterclockwise (as here).

Example 19.4 **Comparing thermodynamic processes**

The pV-diagram of Fig. 19.13 shows a series of thermodynamic processes. In process ab, 150 J of heat is added to the system; in process bd, 600 J of heat is added. Find (a) the internal energy change in process ab; (b) the internal energy change in process abd (shown in light blue); and (c) the total heat added in process acd (shown in dark blue).

SOLUTION

IDENTIFY and SET UP: In each process we use $\Delta U = Q - W$ to determine the desired quantity. We are given $Q_{ab} = +150$ J and $Q_{bd} = +600$ J (both values are positive because heat is *added* to the system). Our target variables are (a) ΔU_{ab}, (b) ΔU_{abd}, and (c) Q_{acd}.

EXECUTE: (a) No volume change occurs during process ab, so the system does no work: $W_{ab} = 0$ and so $\Delta U_{ab} = Q_{ab} = 150$ J.

(b) Process bd is an expansion at constant pressure, so from Eq. (19.3),

$$W_{bd} = p(V_2 - V_1)$$
$$= (8.0 \times 10^4 \text{ Pa})(5.0 \times 10^{-3} \text{ m}^3 - 2.0 \times 10^{-3} \text{ m}^3)$$
$$= 240 \text{ J}$$

The total work for the two-step process abd is then

$$W_{abd} = W_{ab} + W_{bd} = 0 + 240 \text{ J} = 240 \text{ J}$$

and the total heat is

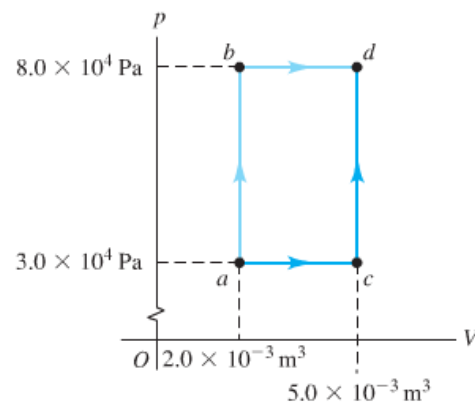$$Q_{abd} = Q_{ab} + Q_{bd} = 150 \text{ J} + 600 \text{ J} = 750 \text{ J}$$

Applying Eq. (19.4) to abd, we then have

$$\Delta U_{abd} = Q_{abd} - W_{abd} = 750 \text{ J} - 240 \text{ J} = 510 \text{ J}$$

(c) Because ΔU is *independent of the path* from a to d, the internal energy change is the same for path acd as for path abd:

$$\Delta U_{acd} = \Delta U_{abd} = 510 \text{ J}$$

19.13 A pV-diagram showing the various thermodynamic processes.

The total work for path acd is

$$W_{acd} = W_{ac} + W_{cd} = p(V_2 - V_1) + 0$$
$$= (3.0 \times 10^4 \text{ Pa})(5.0 \times 10^{-3} \text{ m}^3 - 2.0 \times 10^{-3} \text{ m}^3)$$
$$= 90 \text{ J}$$

Now we apply Eq. (19.5) to process acd:

$$Q_{acd} = \Delta U_{acd} + W_{acd} = 510 \text{ J} + 90 \text{ J} = 600 \text{ J}$$

We tabulate the quantities above:

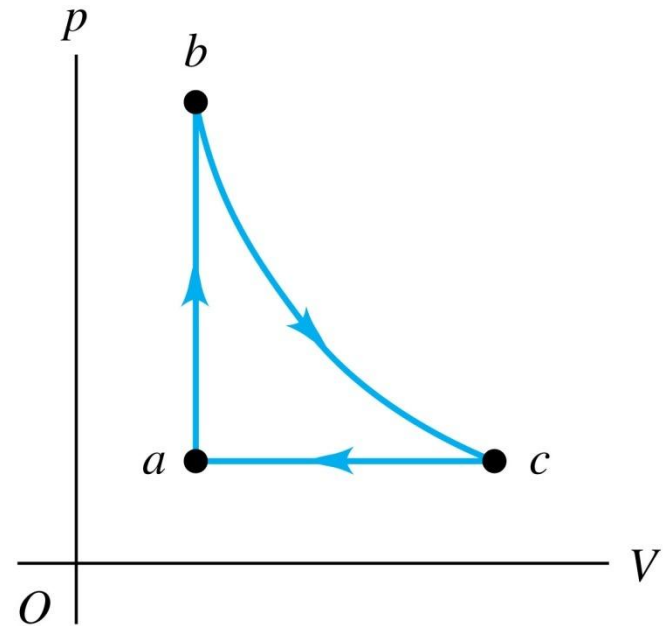| Step	Q	W	$\Delta U = Q - W$	Step	Q	W	$\Delta U = Q - W$
ab	150 J	0 J	150 J	ac	?	90 J	?
bd	600 J	240 J	360 J	cd	?	0 J	?
abd	750 J	240 J	510 J	acd	600 J	90 J	510 J

EVALUATE: Be sure that you understand how each entry in the table above was determined. Although ΔU is the same (510 J) for abd and acd, W (240 J versus 90 J) and Q (750 J versus 600 J) are quite different. Although we couldn't find Q or ΔU for processes ac and cd, we could analyze the composite process acd by comparing it with process abd, which has the same initial and final states and for which we have more information.

CPS 6-2

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

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

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

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

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

CPS 6-2

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,

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

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

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