Conservation of Energy

Energy can neither by created nor destroyed, but only transferred from one system to another and transformed from one form to another.

Conservation of Energy

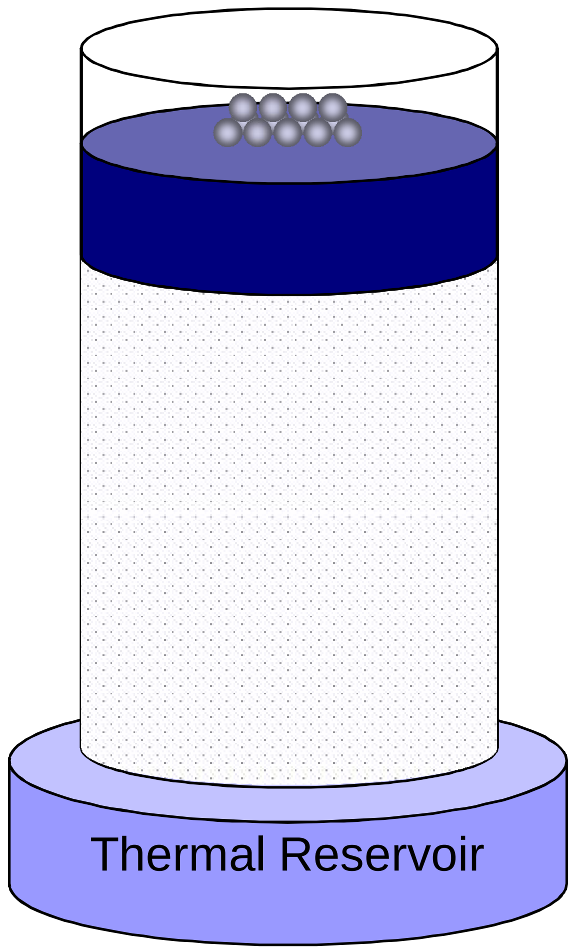
Consider at a gas in a cylinder with a moveable piston and insulating walls

ΔU = Internal Energy

Q = Heat transfer

W = Work done

$$\Delta U = Q + W$$



$Q(+)$ = System Gains Heat

$Q(-)$ = System Loses Heat

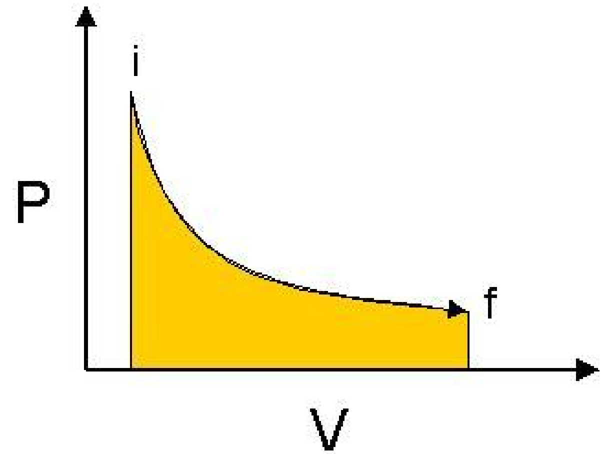
$W(+)$ = Work Done On System

$W(-)$ = Work Done By System

Energy IN is positive, whether it is heat or work.

If you see D*U* = *Q* – *W*, work done on the system is considered (–).

Work and the First Law



Q: Is the work done *by* the system, positive or negative?

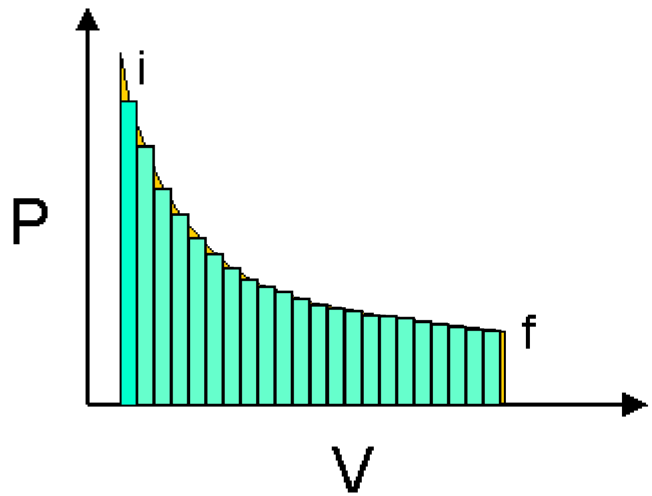
A: The volume has expanded (V_f - V_i > 0) so the the gas does work on its environment and gives energy away, so the work done by the system is considered negative.

Q: Is the heat, *Q*, positive, negative, or 0 for this change?

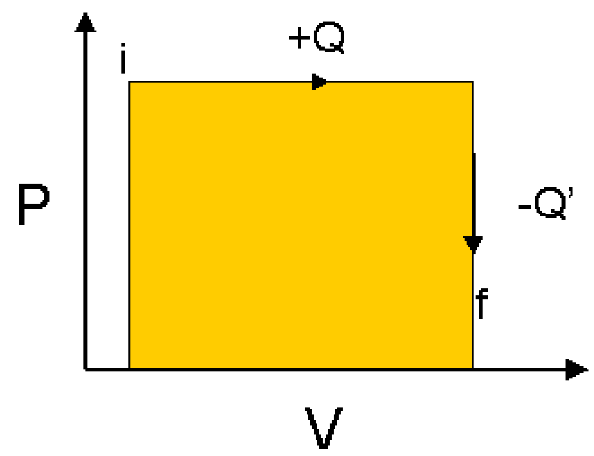
A: The *P* a 1/*V* dependence shows that *nRT* has not changed during the transition so *Q* = 0.

Work and the First Law

The magnitude of work done is equal to the area under the curve. Think of a small rectangle formed by *P*D*V*. The equation $W = \int P dV$ ~ S *P*D*V* tells us to sum the *P*D*V*'s under the curve (from V_i to V_f).



Work and the First Law

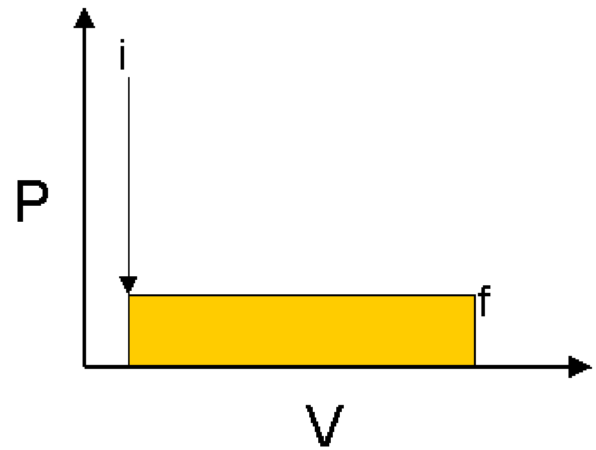


Q: Is the amount of heat added to increase the volume equal to the amount of heat lost to drop the pressure?

A: No. In the first example, lead shot was removed from the container on top of the piston to produce work. Here, there must be some "agent" to cause work to be done. In this case heat transforms into internal energy which performs work.

Work and the First Law

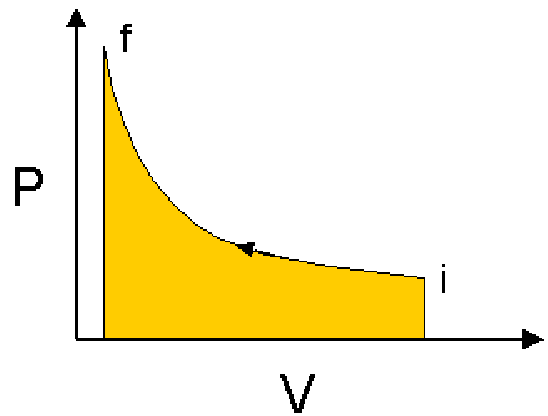
Can you think of what must be done to take the system along the path outlined below?



A: In the first step, the pressure decreased but the volume was fixed. Looking at the equation $PV = nRT$, either the number of moles of gas in the system was changed, or the temperature was dropped. Since there is no inlet/outlet to introduce or remove gas molecules from the system, it must be a heat loss ($-Q$). Once the P_f was reached, the volume of the gas was expanded. This could be achieved by removing lead shot from the container on top of the piston while adding heat ($+Q$).

Work and the First Law

Can you think of what might cause the system to follow the P-V path shown below?



The volume decreases, and pressure increases, following a *P* a 1/*V* curve. This can be achieved by adding lead shot to the container on the piston.

Q: Is the work done *by* the system *positive* or *negative* in this case?

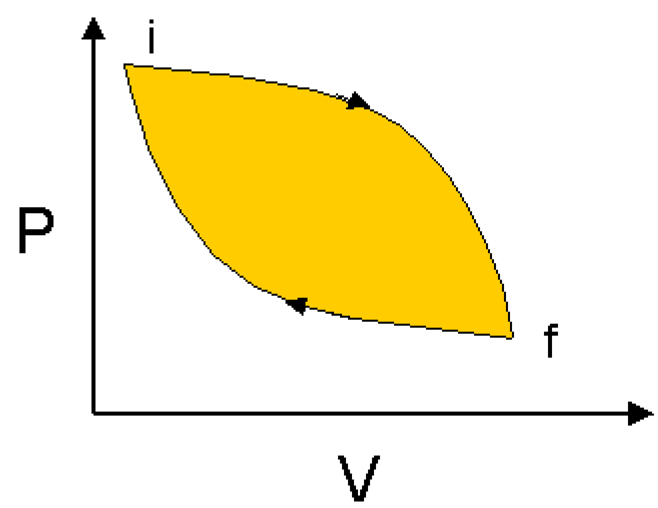
A: Here, the volume of the gas decreased ($V_f < V_i$) so the work done *by the system* is negative.

Q: Is the work done *on* the system *positive* or *negative*?

A: The work done on the system is positive. The work done on the system by some external force = - Work done by the system.

Work and the First Law

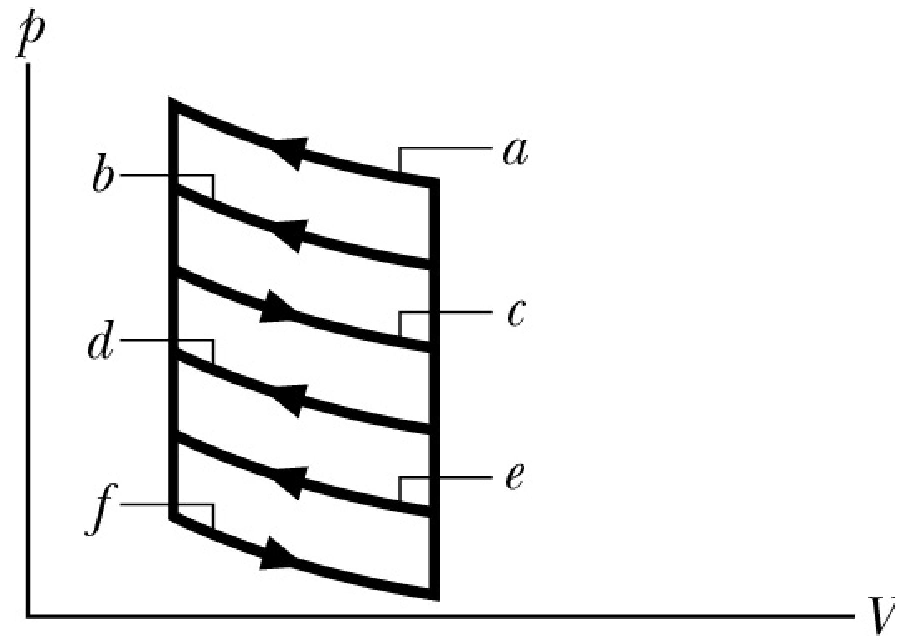
When a system moves from an initial to a final state then back to its initial state, it is called a thermodynamic cycle. The work done during a thermodynamic cycle is just the sum of the work along each path. Since the work done by the system is *negative* along the upper curve, and *positive* along the lower curve, then the net work done is the area between the curves.



Concept Check – Work and the First Law

The P-V diagram shows six curved paths (connected by vertical paths) that can be followed by a gas. Which two of them should be part of a closed cycle if the net work done by the gas is to be at its maximum negative value?

1. a and f
2. a and b
3. a and c
4. c and d
5. c and e



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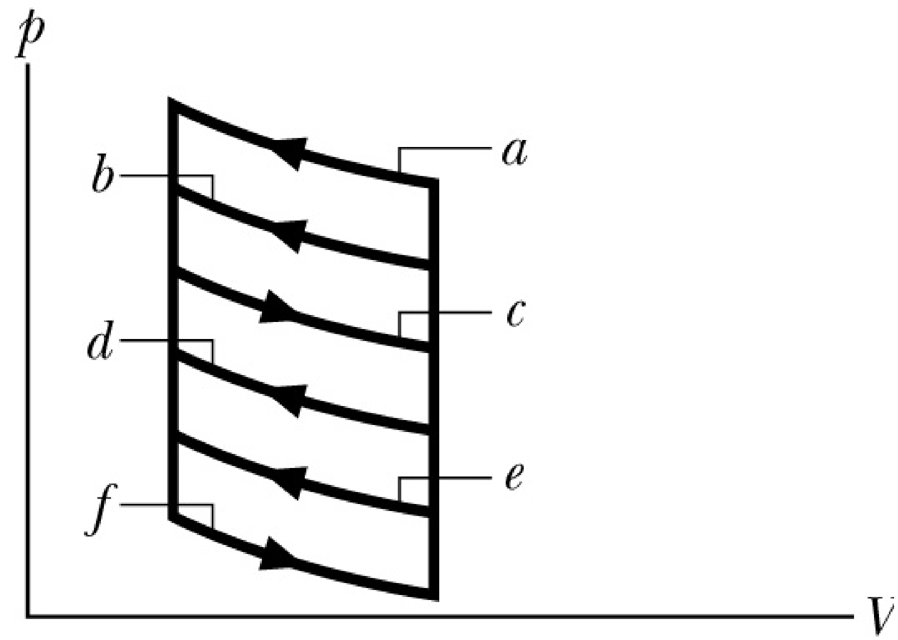
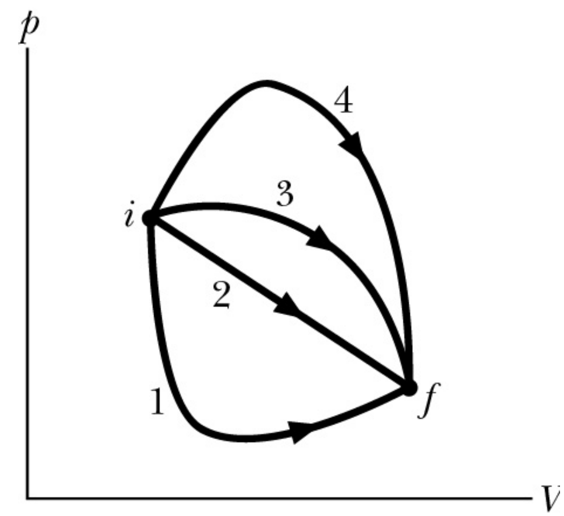


The maximum work is given by a system that follows path a then f, but this work would be *positive* (why?). Maximum *negative* work done by the system would be given by following path c-e.

Concept Check – Work and the First Law (2)

The figure shows four paths on a P-V diagram along which a gas can be taken from an initial to final state. Rank the paths according to the change in internal energy, ΔU_{int}.



1. 1>2>3>4
2. 4>3>2>1
3. 1=2=3=4
4. Impossible to tell

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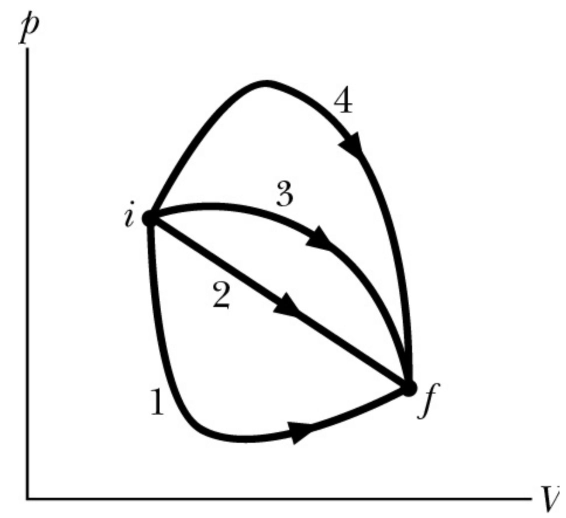

1. 1>2>3>4
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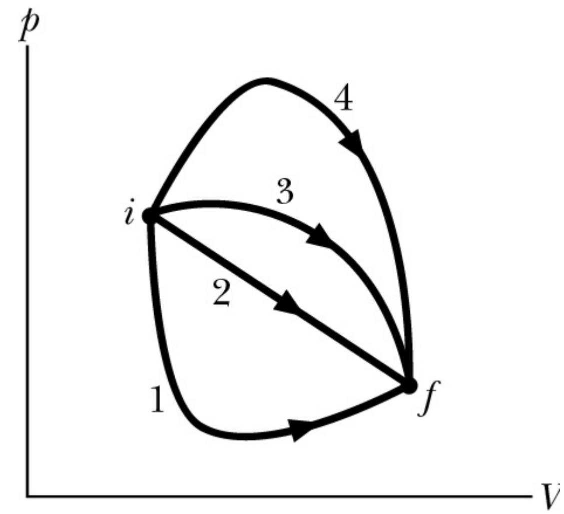
ΔU is a state function. It does not depend on the path from the initial state to the final state.

Concept Check – Work and the First Law (3)

The figure shows four paths on a P-V diagram along which a gas can be taken from an initial to final state. Rank the paths according to the magnitude of work done by the gas.



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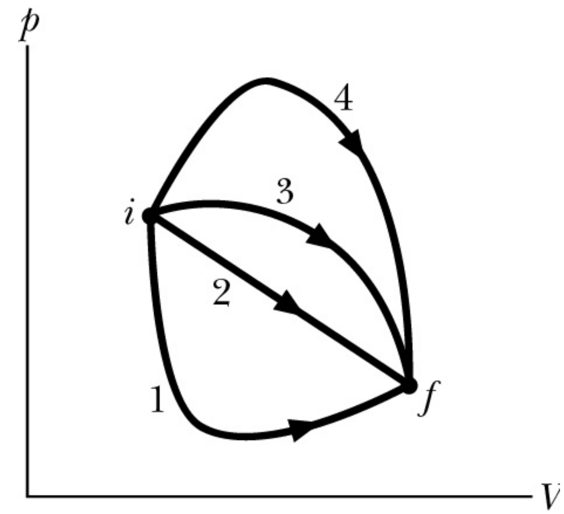

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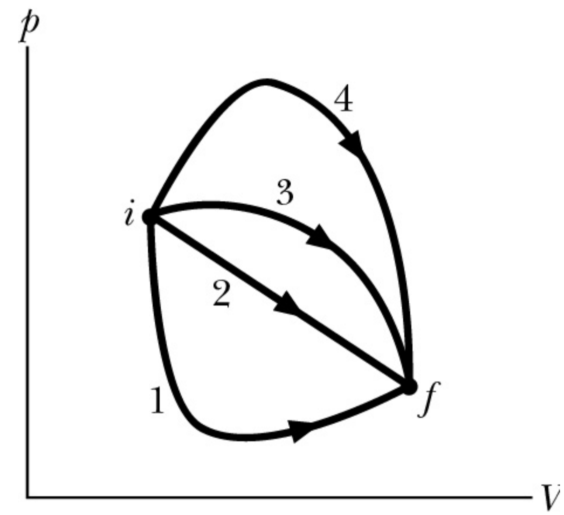
The area under the curve is the work done by the system on the environment. The greatest area represents the greatest magnitude, so 4>3>2>1

Concept Check – Work and the First Law (4)

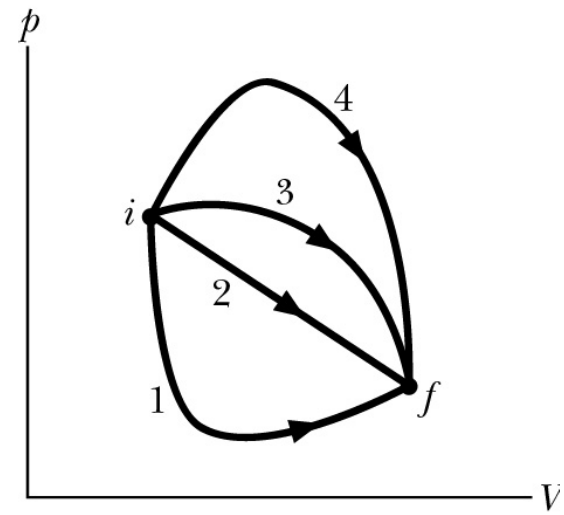
The figure shows four paths on a P-V diagram along which a gas can be taken from an initial to final state. Rank the paths according to the magnitude of the *energy transferred as heat*.



1. 1>2>3>4
2. 4>3>2>1
3. 1=2=3=4
4. Impossible to tell

Concept Check – Work and the First Law (4)

The figure shows four paths on a P-V diagram along which a gas can be taken from an initial to final state. Rank the paths according to the magnitude of the *energy transferred as heat*.



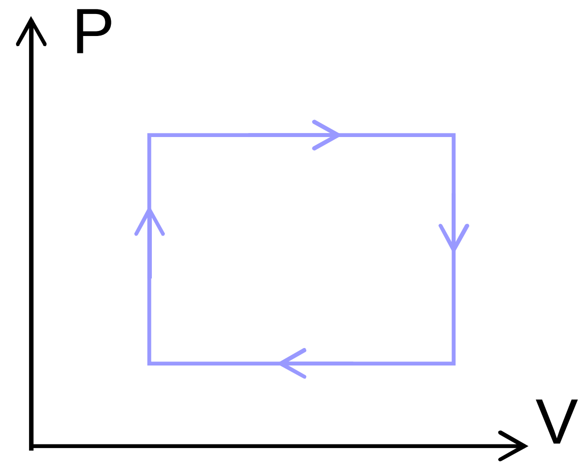
1. 1>2>3>4
2. 4>3>2>1
3. 1=2=3=4
4. Impossible to tell

The magnitude of the energy transferred as heat is given by $DU = Q + W$, so $Q = DU - W$. The work done by the gas is negative for all cases because the gas expands in each case. The change in internal energy is the same for each case because the initial and final states are the same, so the ranking is 4>3>2>1

Concept Check – Work

In the closed thermodynamic cycle shown in the P-V diagram, the work done by the gas is:

1. positive
2. zero
3. negative



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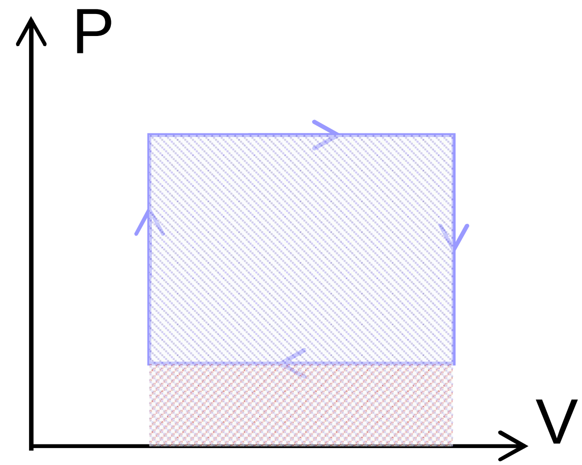


The gas expands at a higher pressure and compresses at a lower pressure. In general, clockwise = negative work; counterclockwise = positive work. The area beneath the entire curve represents the work done by the gas and is negative. The area beneath just the lower portion of the curve is the work done to the gas and is positive. The area enclosed by the rectangle represents the total work done by the gas.

Thermal Processes

Previously we saw that heat added to a system could be used to perform work. The relationship between heat and work is the called First Law of Thermodynamics

$$\Delta U = Q + W$$

$$\Delta U = \text{change in internal energy}$$

$$Q = \text{heat added } (+)/\text{taken away}(-)$$

$$W = \text{work done by } (-)/\text{on } (+) \text{ a system}$$

$Q(+) = \text{System Gains Heat}$

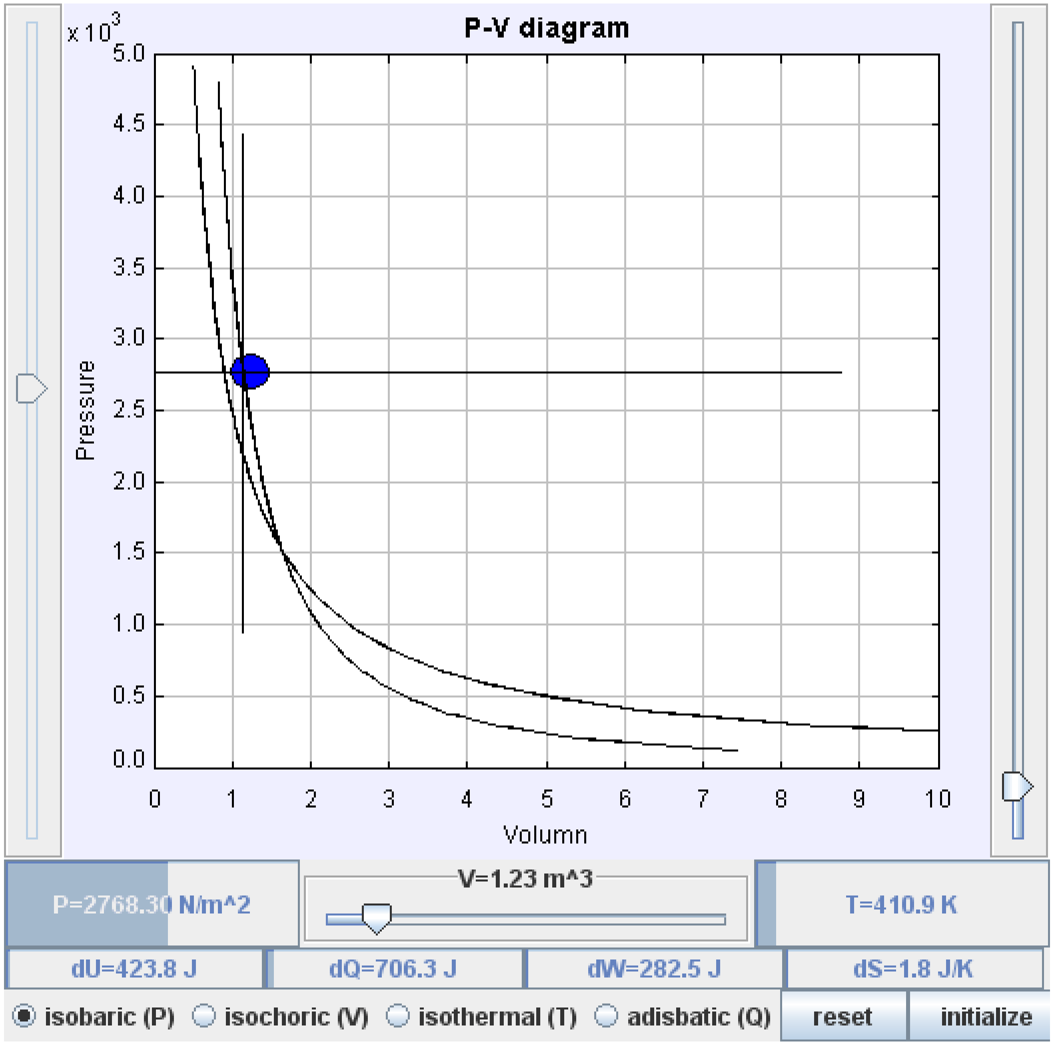
$Q(-) = \text{System Loses Heat}$

$W(+) = \text{Work Done On System}$

$W(-) = \text{Work Done By System}$

Energy IN is positive, whether it is heat or work.

Thermal Processes

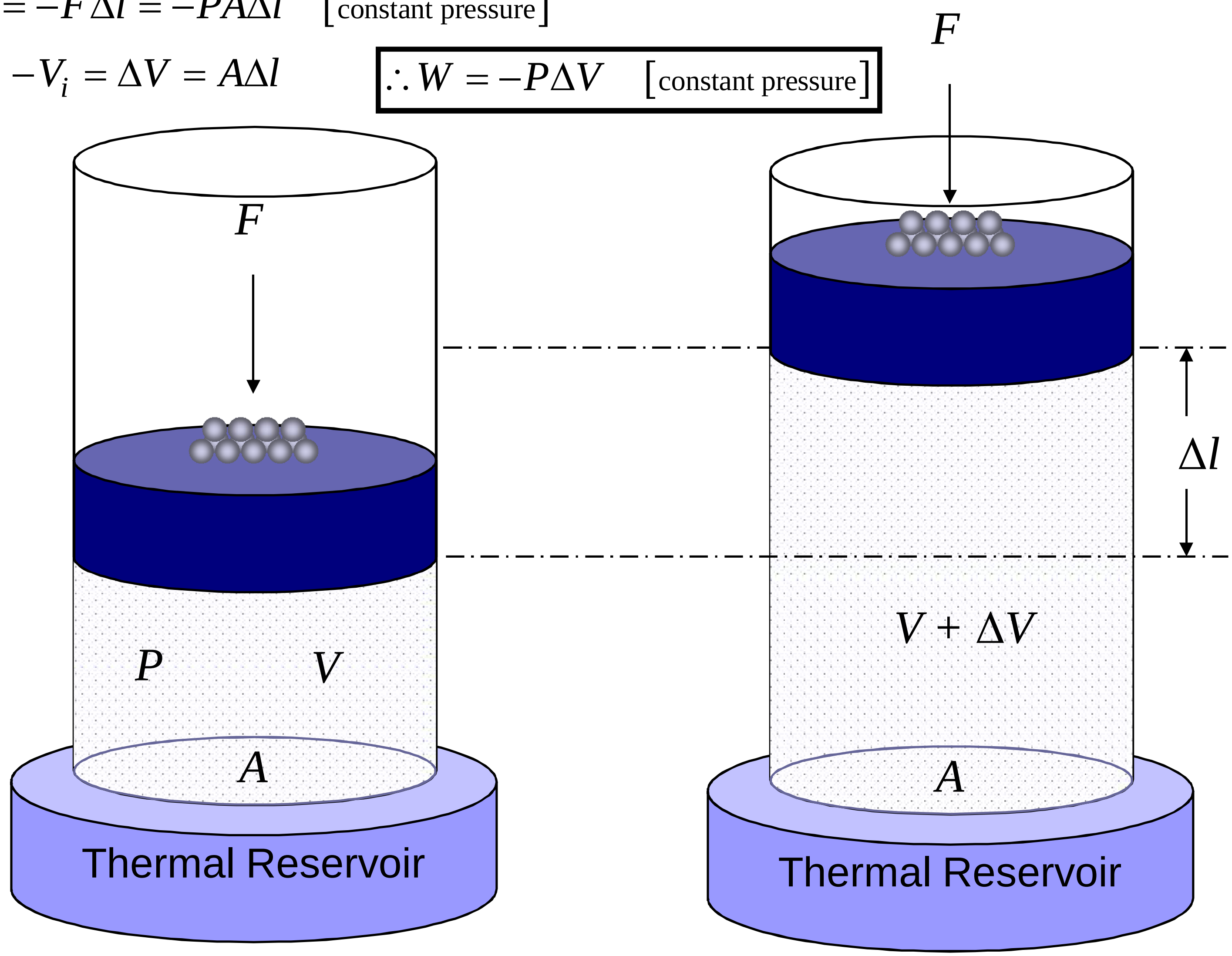


Isobaric Processes

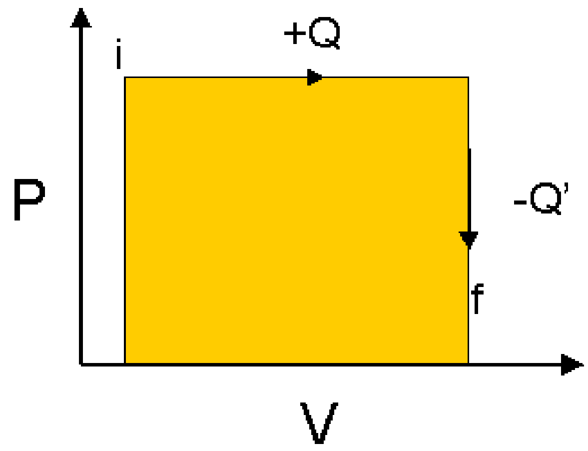
$$W = -F\Delta l = -PA\Delta l \quad [\text{constant pressure}]$$

$$V_f - V_i = \Delta V = A\Delta l$$

$$\therefore W = -P\Delta V \quad [\text{constant pressure}]$$



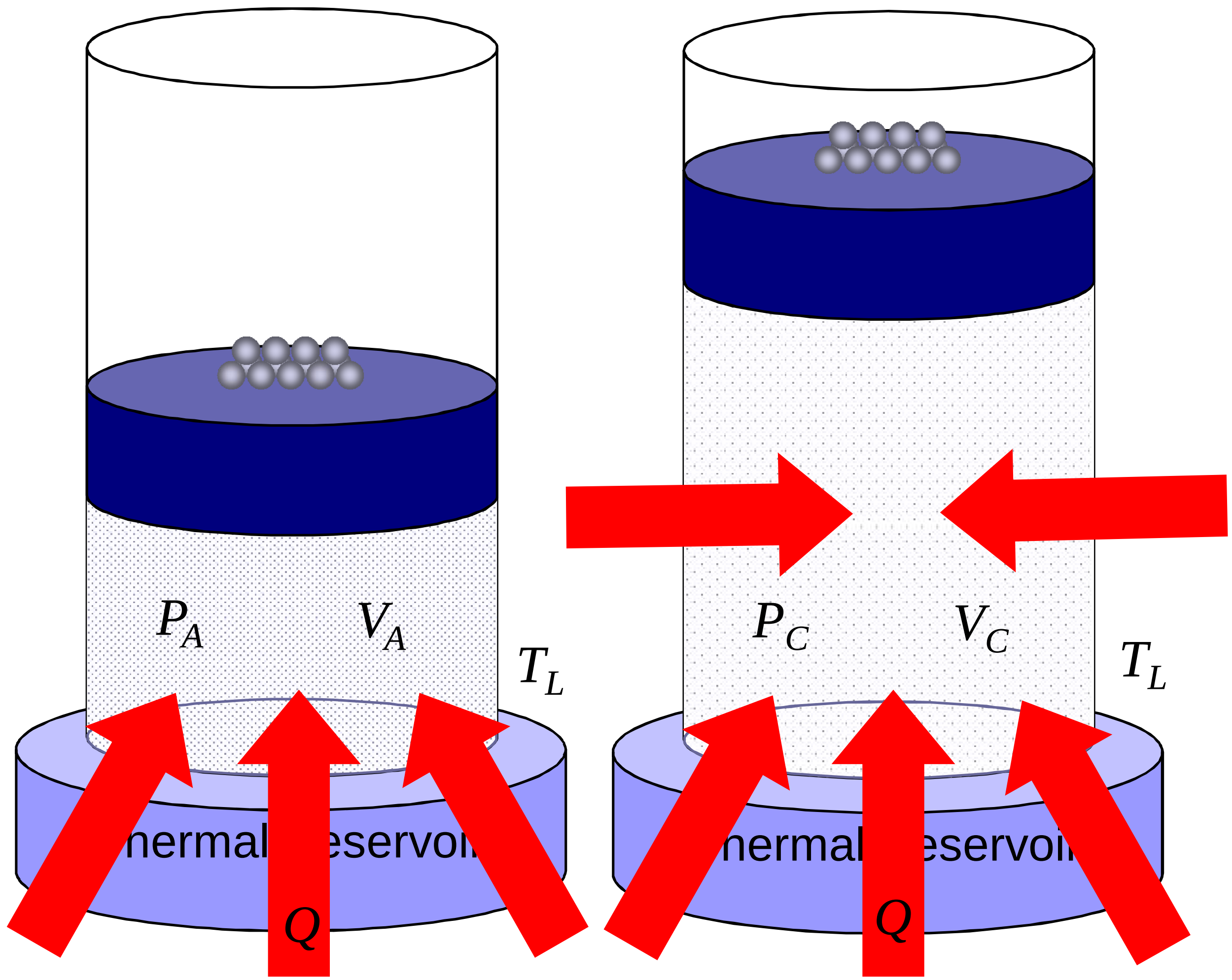
Isobaric Processes



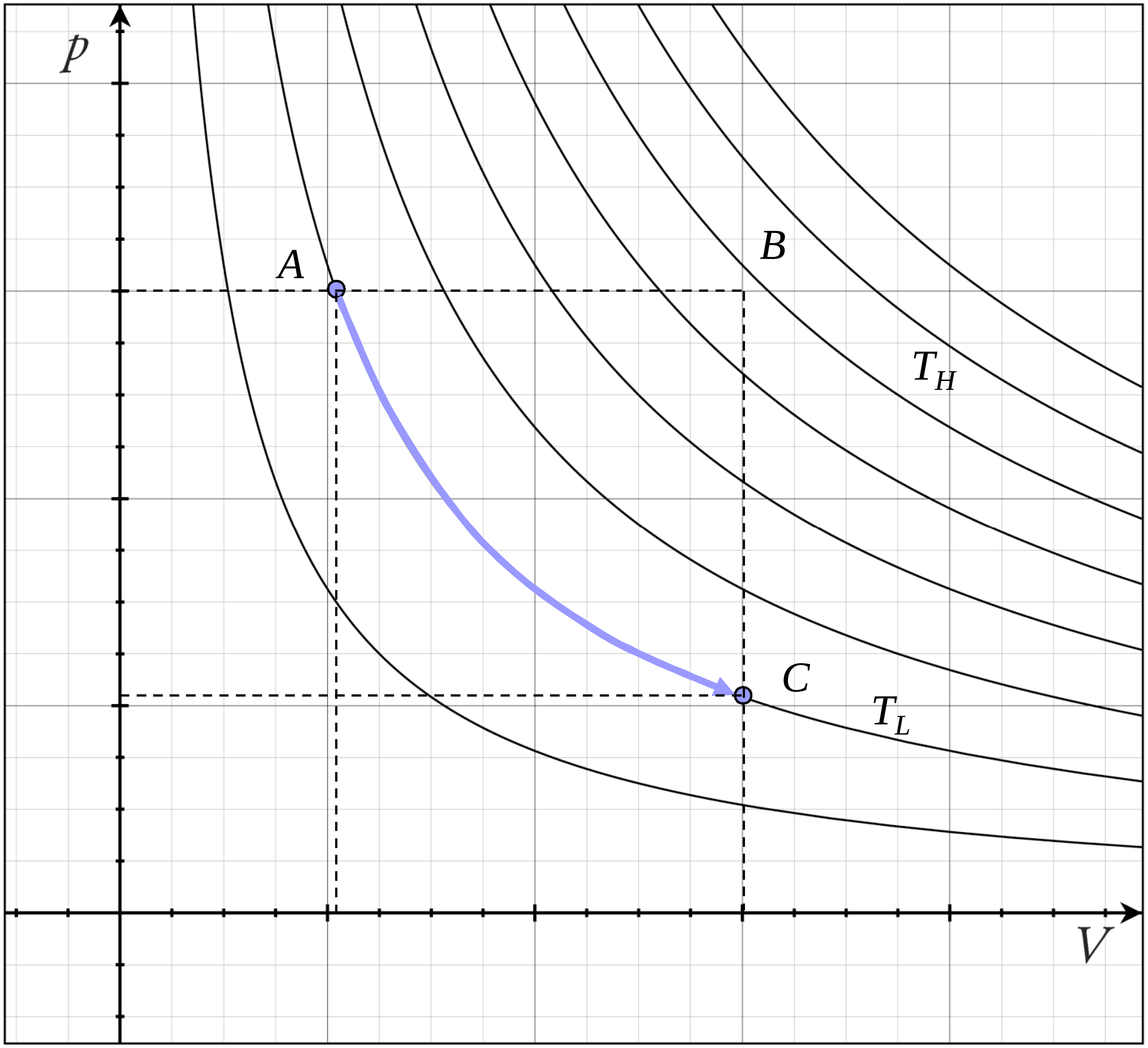
Isothermal Change

$$\Delta U = 0$$

$$Q = -W$$



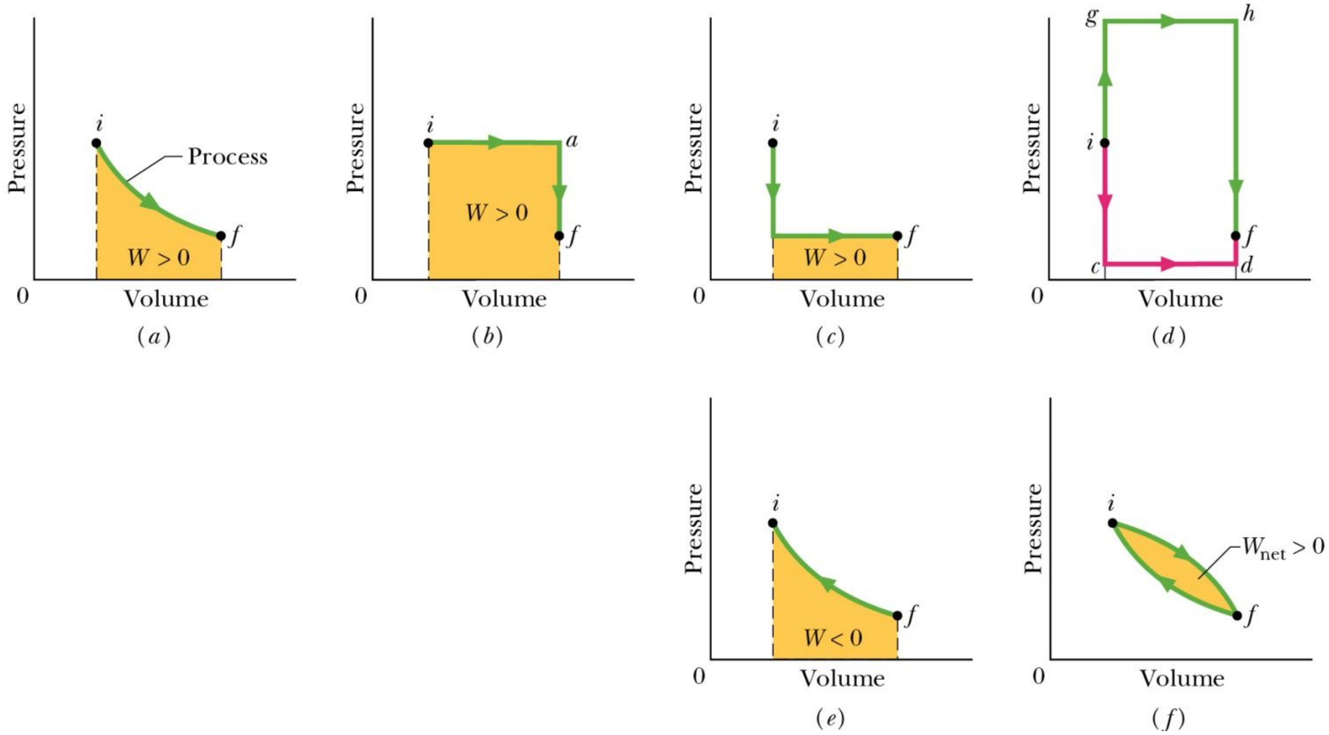
Isothermal Change



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

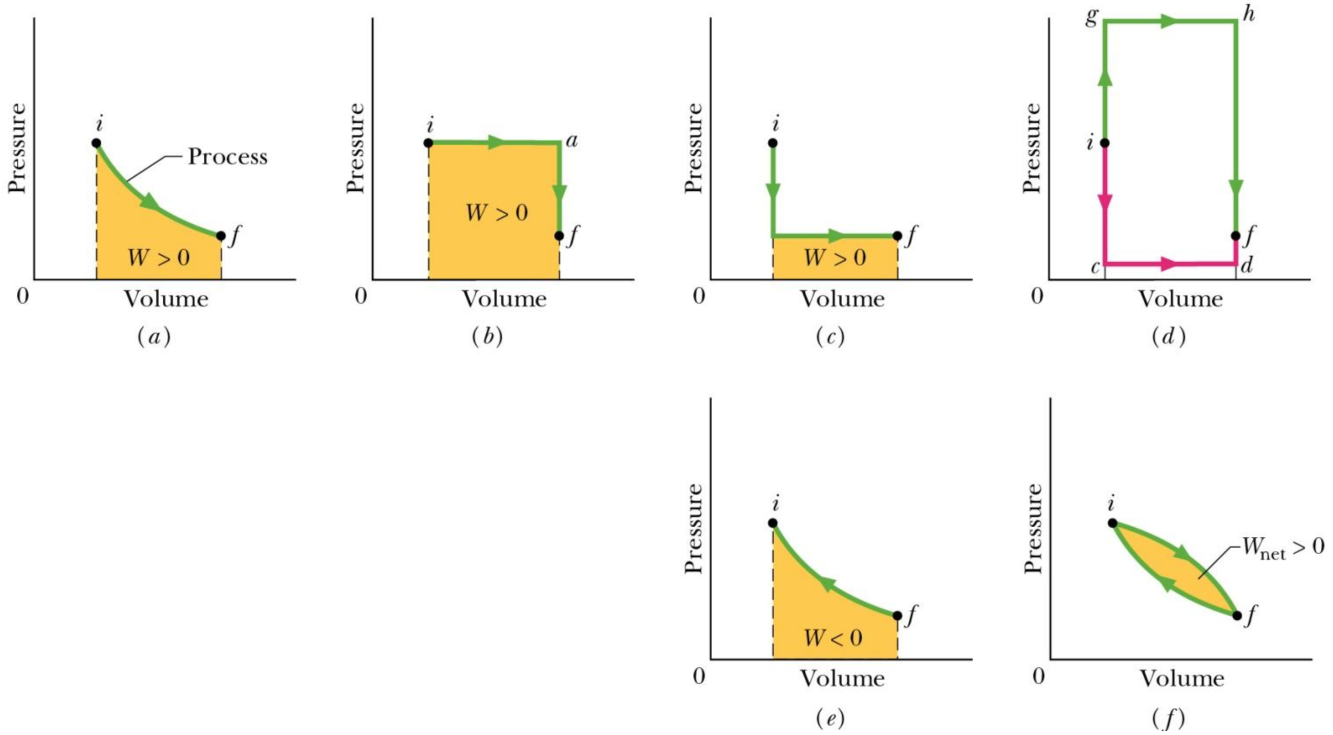
Concept Check – Adiabatic Processes

Which diagram below shows an adiabatic process?



Concept Check – Thermal Processes

Which diagram below shows an adiabatic process?

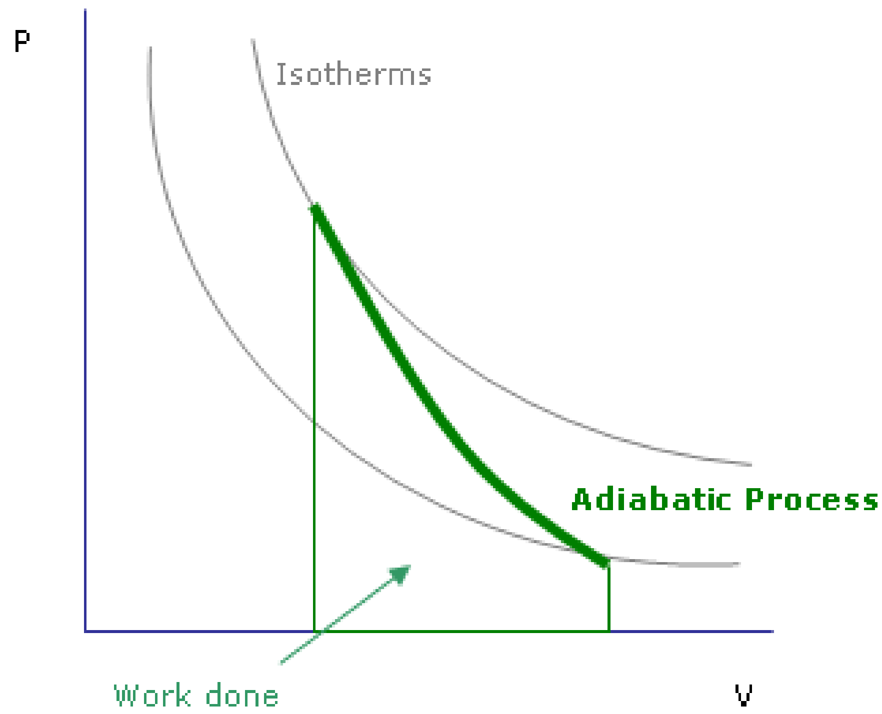


a) and e) could describe adiabatic processes. Note that adiabatic processes are not the same as isothermal (constant T) processes although they have similar curves on a PV diagram. Adiabatic processes follow a steeper path than isotherms on a PV diagram and cross isotherms. In an adiabatic process the temperature of the gas changes without any Q input or output. It happens too quick for any heat transfer to occur.

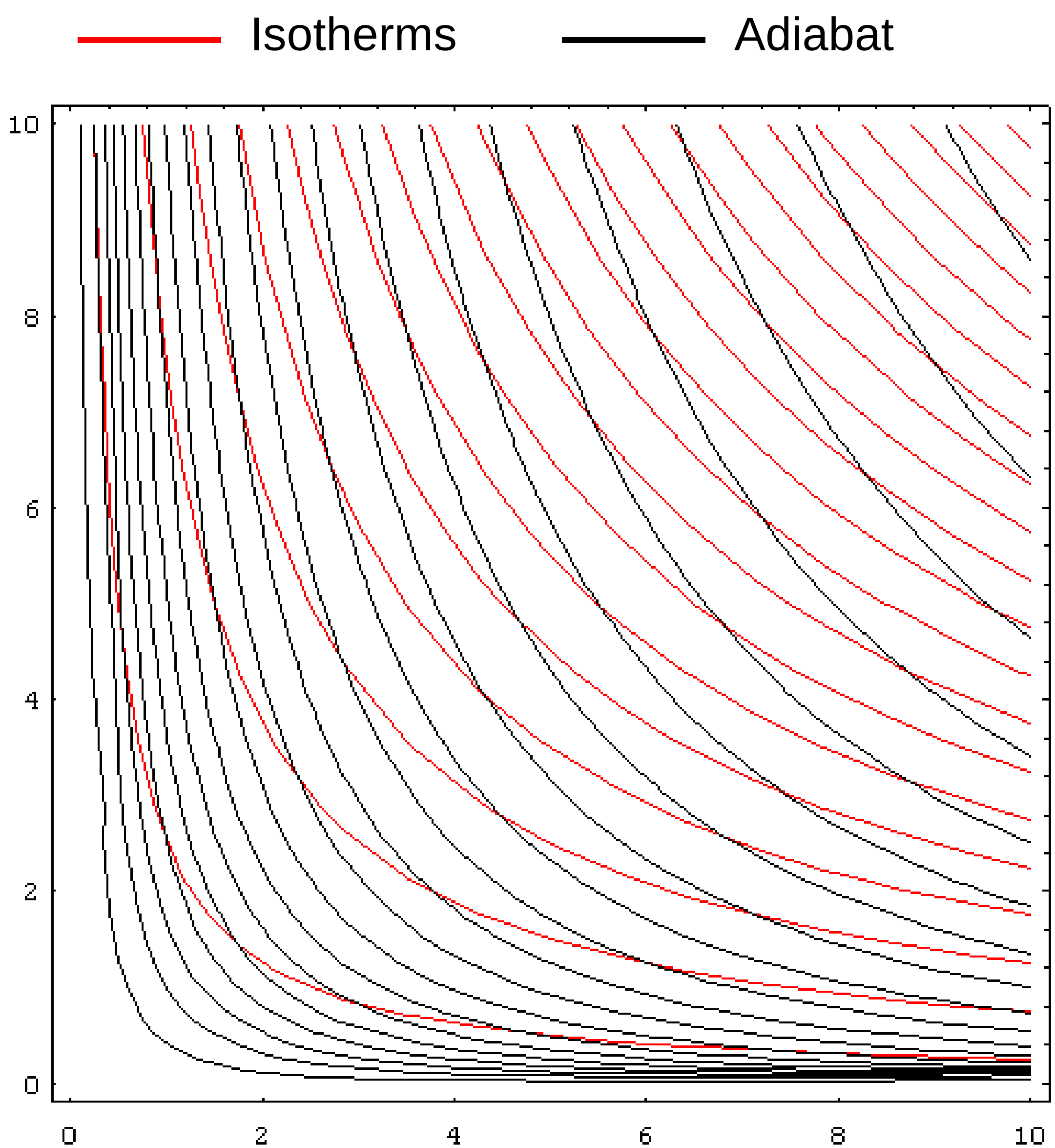
Adiabatic Processes

In an adiabatic process, $Q = 0$

$$\Delta U = W$$



Adiabatic Processes



$$PV^{\gamma} = \text{constant}$$

$$\gamma = 1.67 \ [\text{monatomic}]$$

$$\gamma \approx 1.4 \ [\text{diatomic}]$$

$$\gamma = 1.3 \ [\text{polyatomic}]$$

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

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$