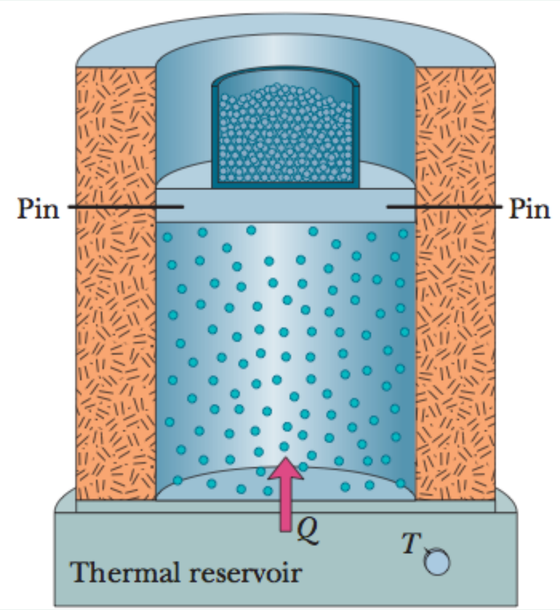
Rutgers University
Department of Physics & Astronomy

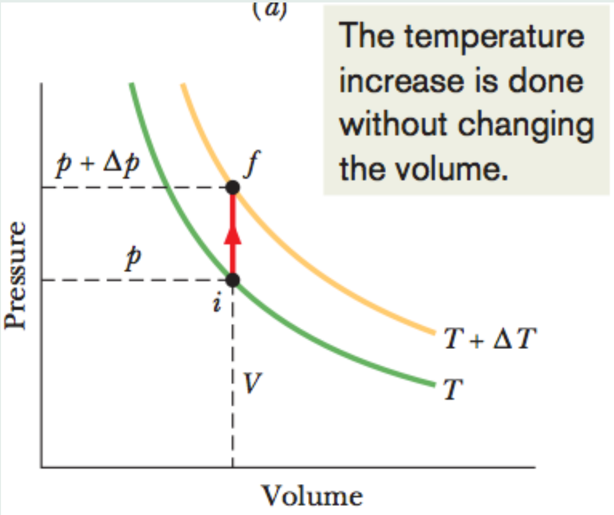
01:750:271 Honors Physics I
Fall 2015

Lecture 25

Internal energy and molar specific heat

- Constant volume



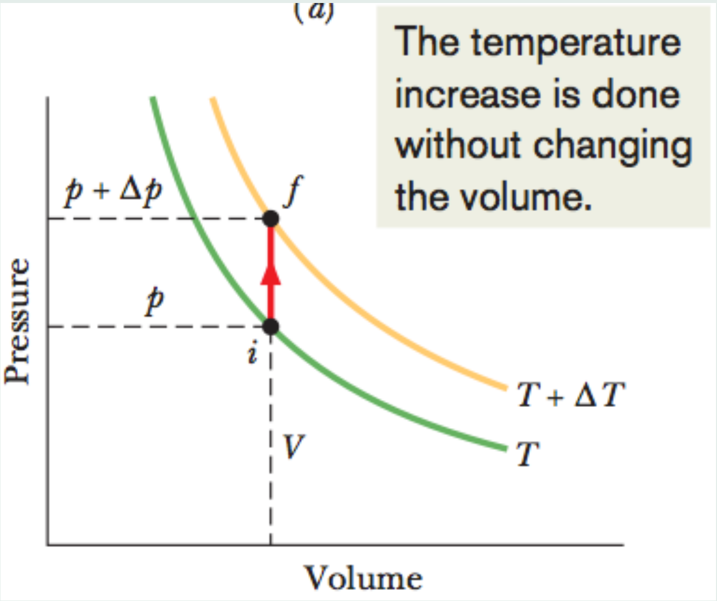


The temperature increase is done without changing the volume.

$$T \nearrow, \; V = \text{constant}$$

$$Q = nC_V \Delta T$$

C_V = molar specific heat at constant volume



The temperature increase is done without changing the volume.

$$Q = nC_V\Delta T$$

$$V = \text{constant} \quad \Rightarrow \quad W = 0$$

$$\boxed{\Delta E_{\text{int}} = nC_V\Delta T}$$

$$T \nearrow, \; V = \text{constant}$$

A change in the internal energy E_{int} of a confined ideal gas depends only on the change in the temperature, not on what type of process produces the change.

- **Internal energy for n moles of ideal gas**

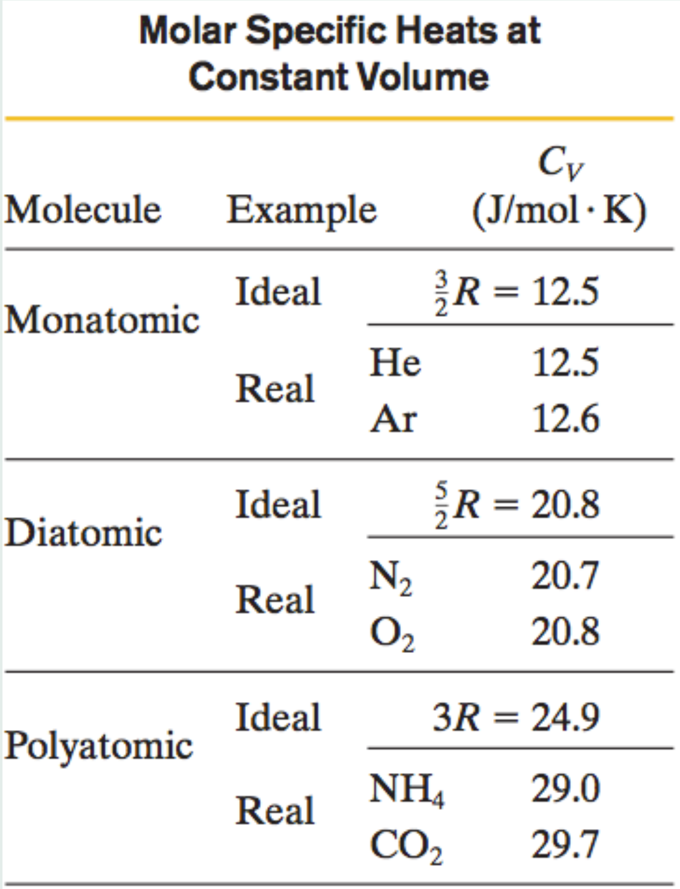
$$\boxed{E_{int} = nC_V T = n\left(\frac{f}{2}\right)RT}$$

The internal energy E_{int} an ideal gas depends only on the temperature and its molecular structure.

$f =$ number of translation and rotation degrees of freedom

Note: For $T < 1000$ K we neglect degrees of freedom of vibration; the molecule is assumed **rigid.**

Molar specific heats at constant V



Molar Specific Heats at Constant Volume

Molecule	Example		C_V (J/mol·K)
Monatomic	Ideal		$\frac{3}{2}R = 12.5$
	Real	He	12.5
		Ar	12.6
Diatomic	Ideal		$\frac{5}{2}R = 20.8$
	Real	N_2	20.7
		O_2	20.8
Polyatomic	Ideal		$3R = 24.9$
	Real	NH_4	29.0
		CO_2	29.7

- **Monatomic** ideal gas

$$C_V = \frac{3}{2}R$$

- **Diatomic** ideal gases:

$$C_V = \frac{5}{2}R$$

- **Polyatomic** ideal gases:

$$C_V = 3R$$

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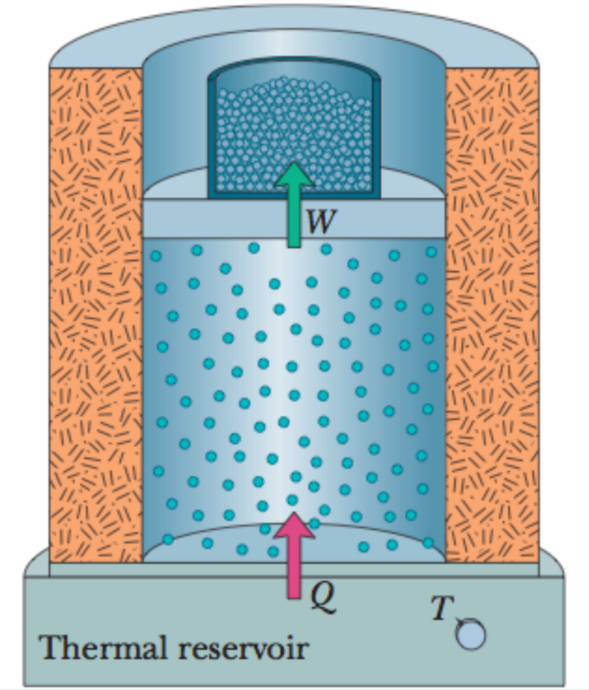
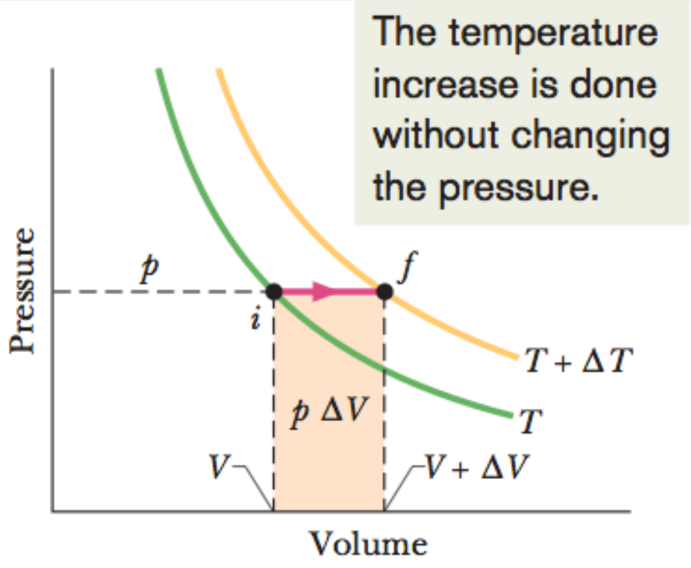
- **Molar specific heat at constant pressure**




The temperature increase is done without changing the pressure.

$$T \nearrow, \; p = \text{constant}$$

$$Q = nC_p\Delta T$$

$C_p =$ **molar specific heat at constant volume**

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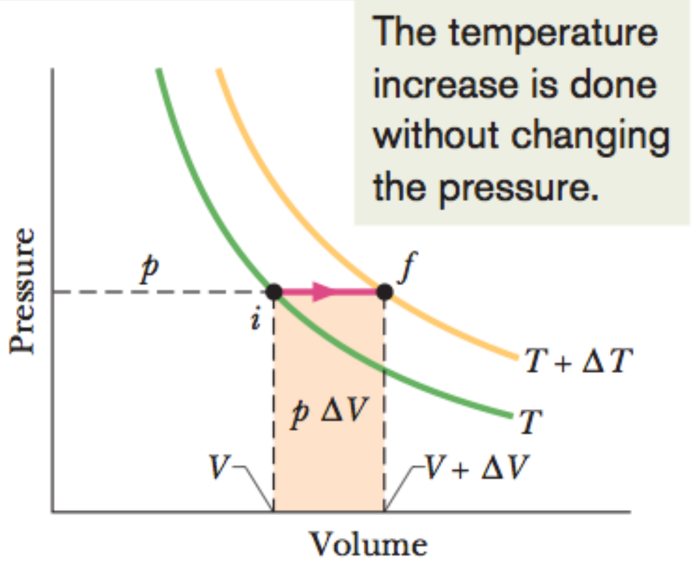

The temperature increase is done without changing the pressure.

$$T \nearrow,\ p = \text{constant}$$

$$Q = nC_p\Delta T$$

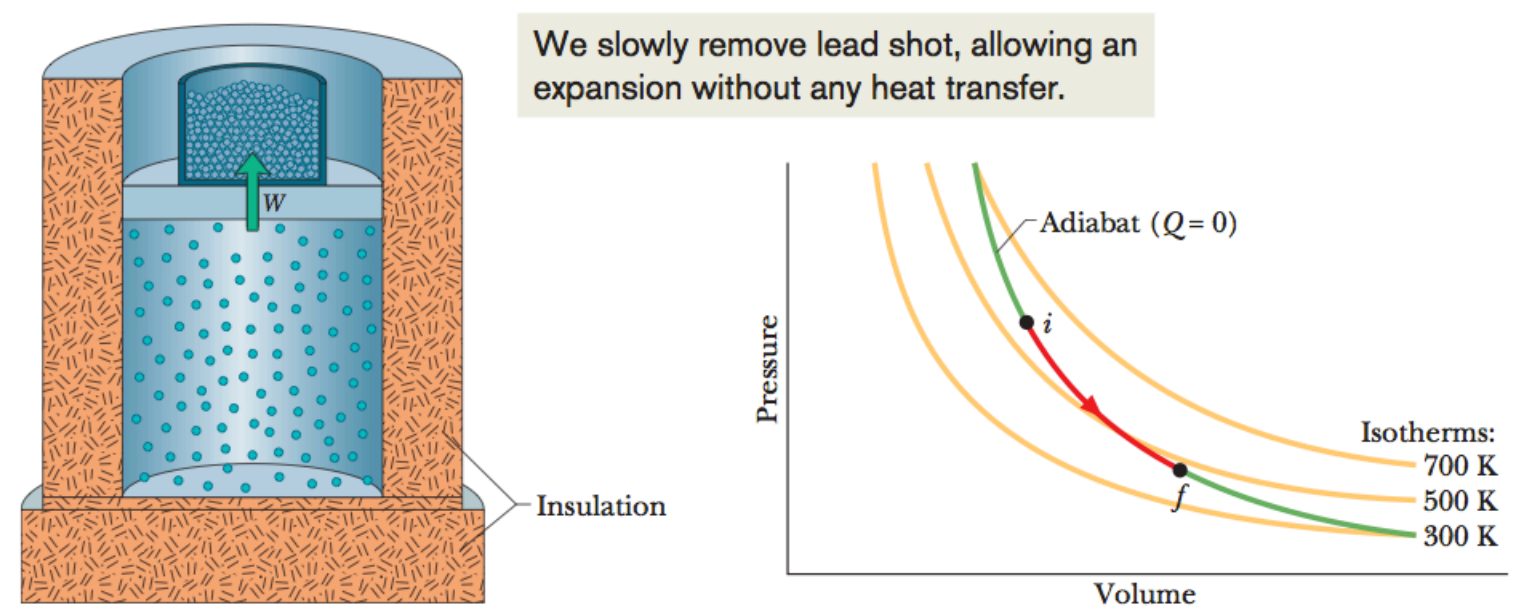
$$W = p\Delta V = nR\Delta T$$

(constant pressure)

$$\begin{aligned}\Delta E_{\text{int}} &= Q - W \\ &= nC_p\Delta T - nR\Delta T\end{aligned}$$

$$\boxed{C_p = C_V + R}$$

The adiabatic expansion of an ideal gas



We slowly remove lead shot, allowing an expansion without any heat transfer.

Adiabatic process: $Q = 0$ (no heat exchange with the environement)

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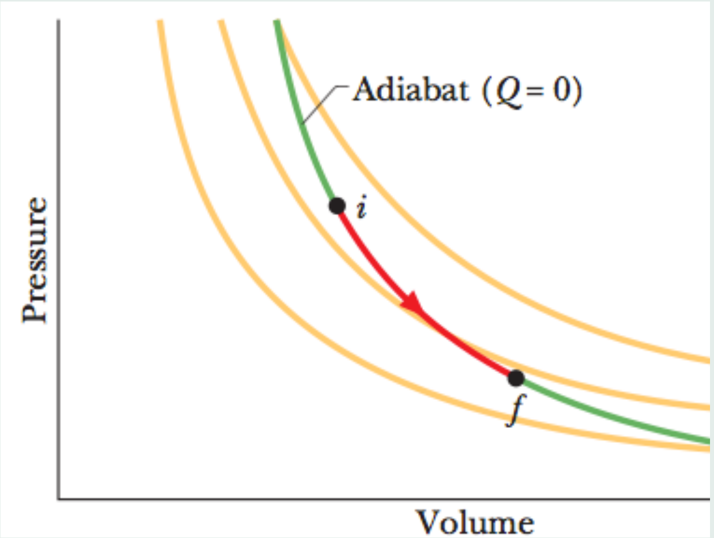
Adiabatic process



$$dE_{\text{int}} = Q - pdV$$

$$\Downarrow$$

$$ndT = -\left(\frac{p}{C_V}\right) dV \quad (a)$$

$$pV = nRT$$

$$\Downarrow$$

$$pdV + (dp)V = nRdT \quad (b)$$

(a) and (b):

$$\frac{dp}{p} + \left(\frac{C_p}{C_V}\right)\frac{dV}{V} = 0$$

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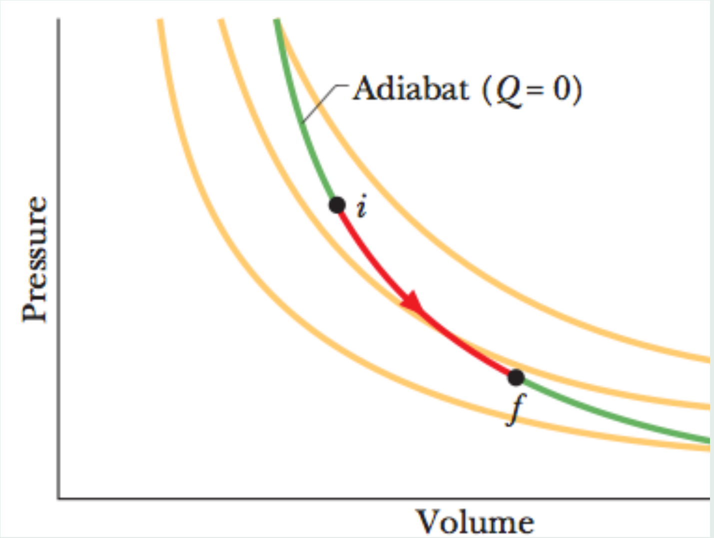
$$\frac{dp}{p} + \left(\frac{C_p}{C_V}\right)\frac{dV}{V} = 0$$

$$\Downarrow$$



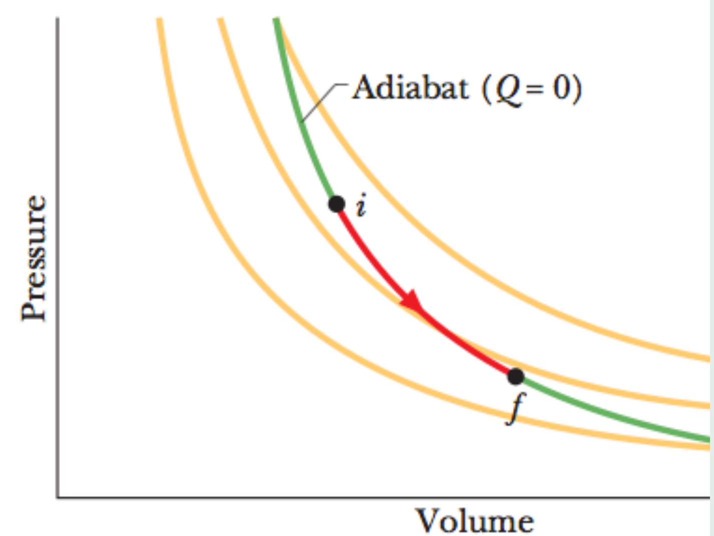
$$\ln(p) + \gamma \ln(V) = \text{constant}$$

$$\gamma = C_p/C_V$$

$$\Downarrow$$

Adiabatic process

$$\boxed{pV^\gamma = \text{constant}}$$



Adiabatic process

$$p_i V_i^{\gamma} = p_f V_f^{\gamma}$$

$$\Downarrow$$

$$\frac{nRT_i}{V_i} V_i^{\gamma} = \frac{nRT_f}{V_f} V_f^{\gamma} =$$

$$\Downarrow$$

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\boxed{TV^{\gamma-1} = \text{constant}}$$

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A monoatomic, a diatomic and a polyatomic gas expand adiabatically such that $p_f = p_i/2$ starting from the same initial volume. In which case will the final volume be higher?

$a)$ $V_{\text{mon}} < V_{\text{dia}} < V_{\text{poly}}$

$b)$ $V_{\text{mon}} > V_{\text{dia}} > V_{\text{poly}}$

$c)$ $V_{\text{dia}} < V_{\text{mon}} < V_{\text{poly}}$

$d)$ $V_{\text{poly}} < V_{\text{mon}} < V_{\text{dia}}$

$e)$ $V_{\text{dia}} < V_{\text{poly}} < V_{\text{mon}}$

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A monoatomic, a diatomic and a polyatomic gas expand adiabatically such that $p_f = p_i/2$ starting from the same initial volume. In which case will the final volume be higher?

- $a)$ $V_{\text{mon}} < V_{\text{dia}} < V_{\text{poly}}$
- $b)$ $V_{\text{mon}} > V_{\text{dia}} > V_{\text{poly}}$
- $c)$ $V_{\text{dia}} < V_{\text{mon}} < V_{\text{poly}}$
- $d)$ $V_{\text{poly}} < V_{\text{mon}} < V_{\text{dia}}$
- $e)$ $V_{\text{dia}} < V_{\text{poly}} < V_{\text{mon}}$

$$p_1 V_1^\gamma = p_2 V_2^\gamma$$

$$\frac{V_2}{V_1} = \left(\frac{p_1}{p_2}\right)^{1/\gamma} = 2^{1/\gamma}$$

$$\gamma_{\text{mon}} = \frac{5}{3} \qquad \gamma_{\text{dia}} = \frac{7}{5} \qquad \gamma_{\text{poly}} = \frac{4}{3}$$

$$\frac{1}{\gamma_{\text{mon}}} < \frac{1}{\gamma_{\text{dia}}} < \frac{1}{\gamma_{\text{poly}}}$$

- **Free expansion of an ideal gas**

An adiabatic process with **no** work **or** change in internal energy.

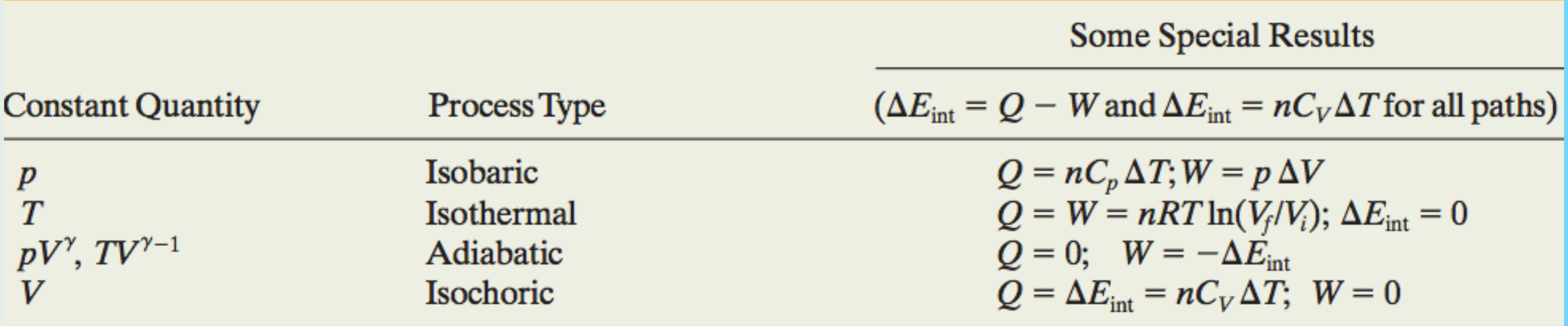
$$W = 0 \qquad \Delta E_{\text{int}} = 0 \qquad Q = 0$$

$$T_i = T_f \qquad p_i V_i = p_f V_f$$

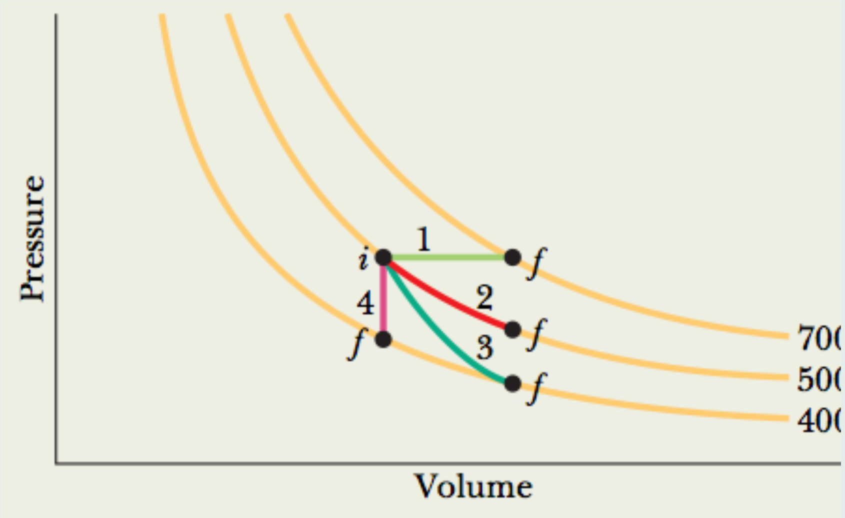
not

$$p_i V_i^{\gamma} = p_f V_f^{\gamma}$$

Ideal gas processes



Constant Quantity	Process Type	Some Special Results ($\Delta E_{\text{int}} = Q - W$ and $\Delta E_{\text{int}} = nC_V \Delta T$ for all paths)
p	Isobaric	$Q = nC_p \Delta T; W = p \Delta V$
T	Isothermal	$Q = W = nRT \ln(V_f/V_i); \Delta E_{\text{int}} = 0$
$pV^\gamma, TV^{\gamma-1}$	Adiabatic	$Q = 0; \quad W = -\Delta E_{\text{int}}$
V	Isochoric	$Q = \Delta E_{\text{int}} = nC_V \Delta T; \quad W = 0$



1. **Isobaric**
2. **Isothermal**
3. **Adiabatic**
4. **Isochoric**

Example: a bubble of $n = 5.00$ mol of helium is submerged at a certain depth in liquid water when the water (and thus the helium) undergoes a temperature increase $\Delta T = 20.0$ C° at constant pressure. As a result, the bubble expands. The helium is monatomic and ideal.

(a) How much energy is added to the helium as heat during the increase and expansion?

$p =$ constant $\Rightarrow$

$$Q = nC_p\Delta T = n(C_V + R)\Delta T$$

For monatomic gases: $C_V = 3R/2$. Hence

$$Q = \frac{5nR\Delta T}{2}.$$

(b) What is the change ΔE_{int} in the internal energy of the helium during the temperature increase?

$$\Delta E_{\text{int}} = nC_V\Delta T = \frac{3nR\Delta T}{2}.$$

(c) How much work W is done by the helium as it expands against the pressure of the surrounding water during the temperature increase?

$$\Delta E_{\text{int}} = Q - W \;\;\Rightarrow\;\; W = Q - \Delta E_{\text{int}} = nR\Delta T$$

Example: adiabatic expansion

$n = 1$ mol of oxygen (assumed to be an ideal gas) has temperature $T_i = 310$ K and volume $V_i = 12$ L.

What would be the final temperature if the gas expands adiabatically to a volume $V_f = 2V_i$? Oxygen (O2) is diatomic.

$$T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1}$$

$$\gamma = \frac{C_p}{C_V} = \frac{1+f/2}{f/2} = \frac{7/2}{5/2} = \frac{7}{5}$$

$$T_f = T_i \left(\frac{V_i}{V_f}\right)^{2/5} = 2^{-2/5} T_i$$

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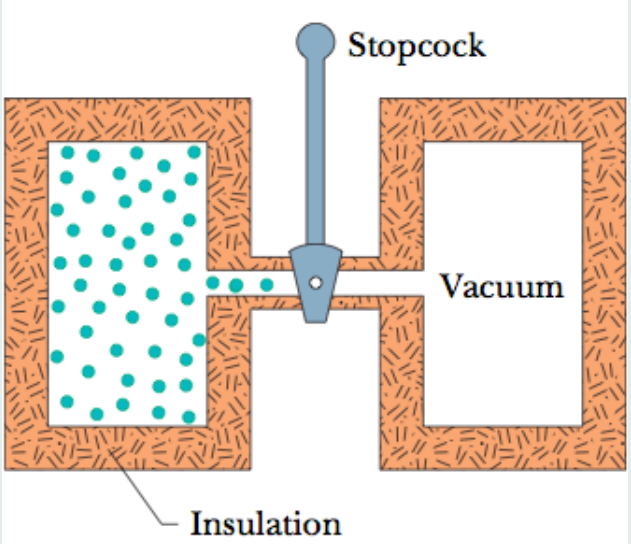
What would be the final pressure if, instead, the gas expands freely to volume $V_f = 2V_i$, from an initial pressure of $p_i = 2.0$ Pa?



$A)\ p_f = p_i$

$B)\ p_f = p_i/2$

$C)\ p_f = 2p_i$

$D)\ p_f = 2^{7/5}p_i$

$E)\ p_f = 2^{-7/5}p_i$

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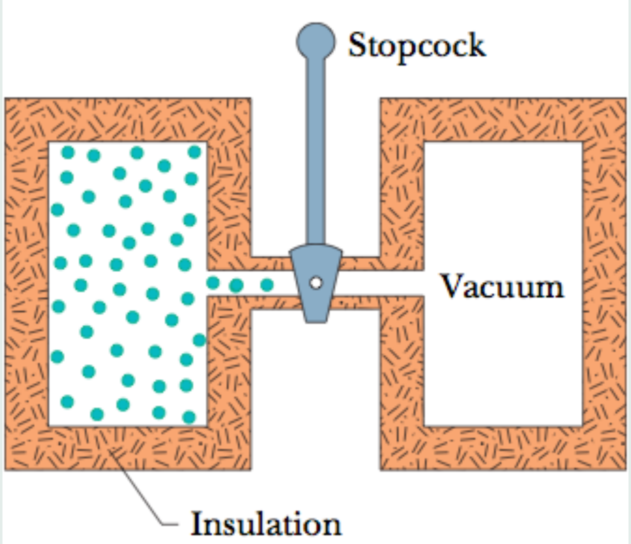
What would be the final pressure if, instead, the gas expands freely to volume $V_f = 2V_i$, from an initial pressure of $p_i = 2.0$ Pa?



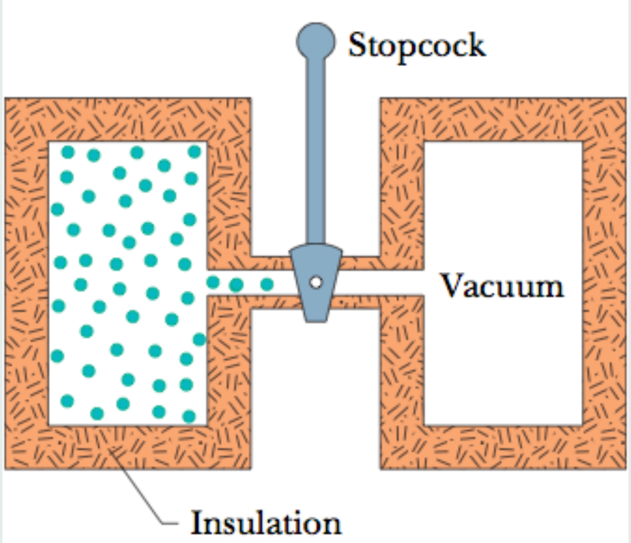
A) $p_f = p_i$

B) $p_f = p_i/2$

C) $p_f = 2p_i$

D) $p_f = 2^{7/5} p_i$

E) $p_f = 2^{-7/5} p_i$



- Insulated containers

$$Q = 0$$

- The total volume of the system does not change

$$W = 0$$

- $\Delta E_{\text{int}} = Q - W = 0$

$$T_i = T_f$$

$$p_i V_i = nRT_i \qquad p_f V_f = nRT_f$$

$$p_f = p_i (V_i / V_f) = p_i / 2$$

20. Entropy and the second law of thermodynamics

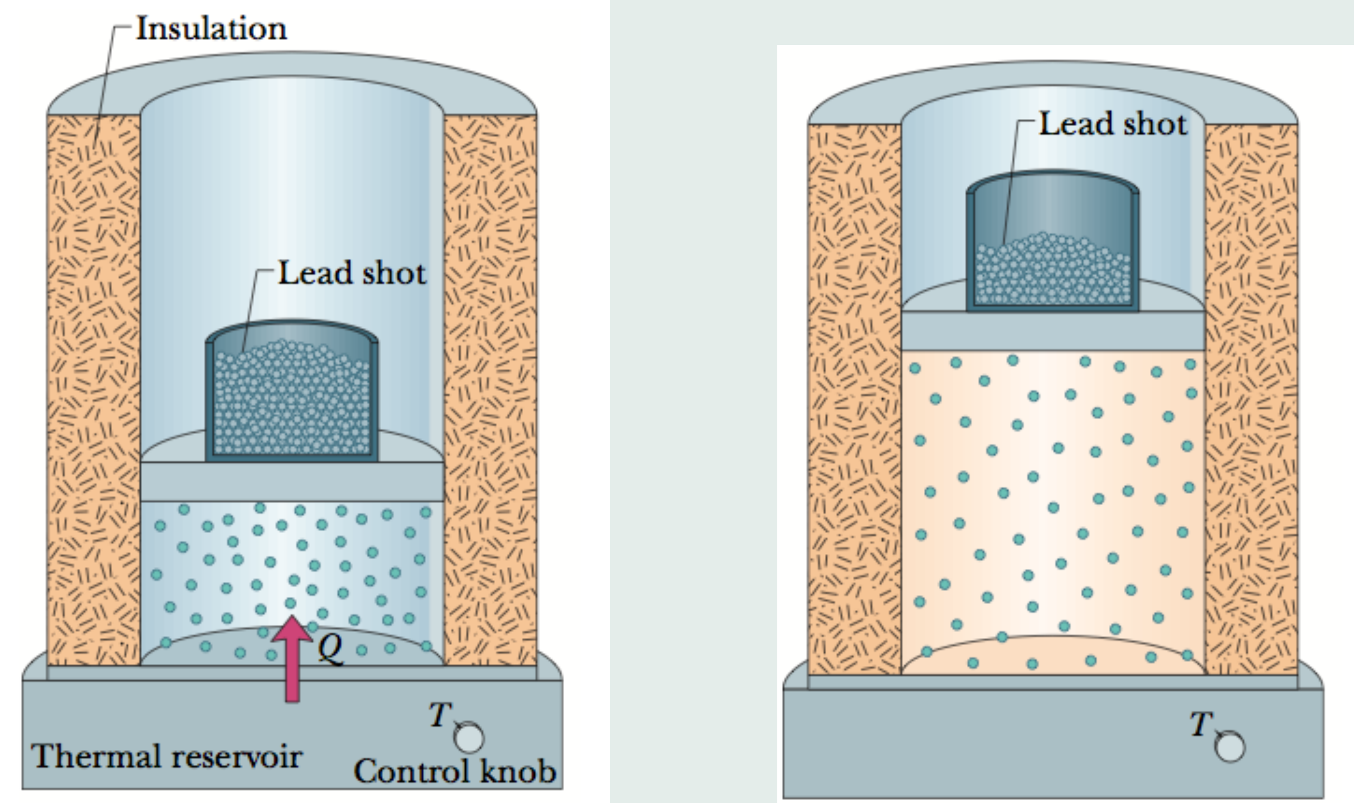
- **Reversible and irreversible processes**

Reversible process: consists of a sequence of well-defined equilibrium states during the intermediate stages of the change from initial state i to final state f.

Each such intermediate state is characterized by some intermediate values (p, V, t)

Reversible processes can be represented by a graph in the (p, v) plane.

Such processes can be reversed, evolving from the final to the initial state through the inverse sequence of equilibrium states.



(*a*) Initial state *i*

(*b*) Final state *f*

The lead shot is **slowly** removed such that the expansion takes place through a sequence of intermediate equilibrium states at constant T.

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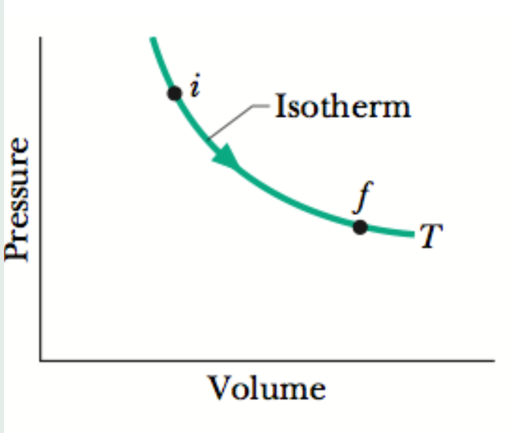
Such a slow process corresponds to an isothermal in the (p, V) plane



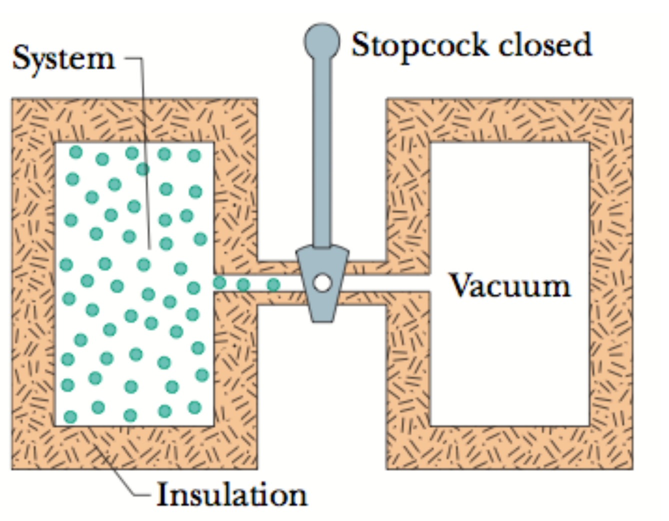
In principle, such a process can be reversed by slowly placing the lead weight back on the piston.

Irreversible process: the evolution from the initial to the final state does **not** consist of a sequence of equilibrium states.

At any given time between the initial and the final state the system is not in thermal equilbrium, hence it cannot be characterized by well defined values of (p, V, T).

For example the temperature and the pressure may not be uniform throughout a sample of ideal gas.

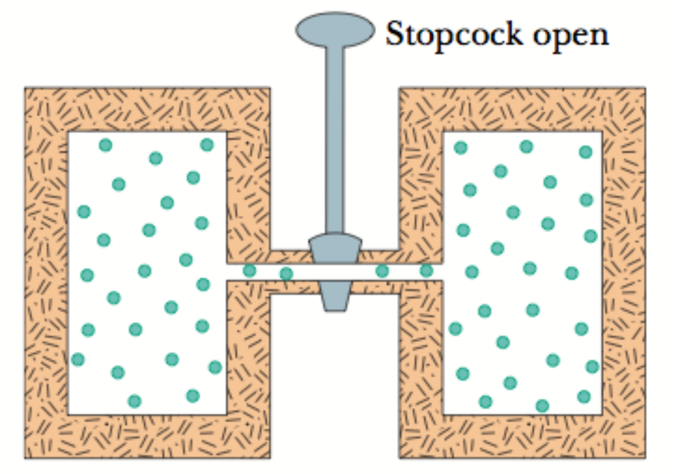
Such processes cannot be reversed. There is no inverse process from the final to the initial state.



(*a*) Initial state *i*

Irreversible process

$\Longrightarrow$



(*b*) Final state *f*

The stopcock is **suddenly** opened. The gas expands **irreversibly** into the second container.

An inverse process is impossible in this case because one cannot confine all the gas molecules back in the first container by closing the stopcock.

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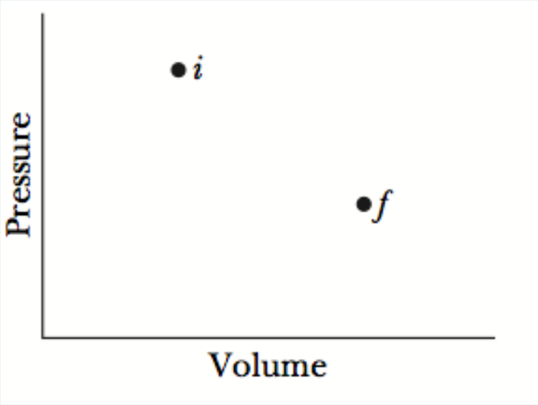
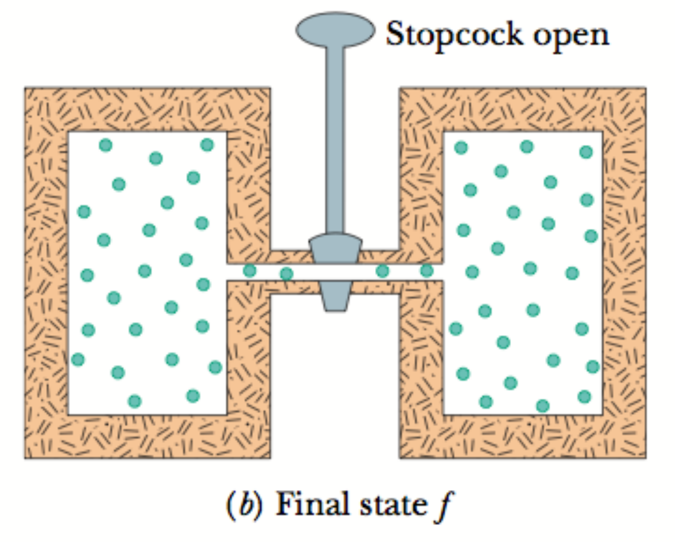
Such a process cannot be represented by a graph in the (p, V) plane.





If we leave the stopcock open, why don't all molecules spontaneously move to the first container, recovering the initial state of the system?

For such a hypothetical process

$$Q = 0 \quad \text{(insulated container)}$$

$$W = 0 \quad \text{(rigid container)}$$

Therefore

$$\Delta E_{\text{int}} = 0$$

The hypothetical inverse process would not contradict energy conservation or the 1st law of thermodynamics.

Need a second principle, or law forbidding such processes.

$$\Downarrow$$

Entropy: a new physical quantity which measures the degree of **disorder** in a physical system. Entropy is denoted by S and it is a function of the state of the system.

Entropy postulate

If an irreversible process occurs in a closed system, the entropy S of the system always increases; it never decreases.

Closed system: no heat or matter exchange with the environement:

$$Q = 0$$

and the number of particles is constant.

For all irreversible processes in closed systems:

$$\Delta S > 0$$

This reflects the natural tendency of physical systems to evolve from **order** to **disorder**.

How do we define and compute the entropy of an ideal gas?

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Key point: for a system in equilibrium entropy is only a function of the state of the system Hence ΔS depends only on the initial and final states (p_i, V_i, T_i), (p_f, V_f, T_f).

$$\Downarrow$$

To find the entropy change for an irreversible process occurring in a closed system, replace that process with any reversible process that connects the same initial and final states.

Change in entropy for a reversible process

- **Isothermal reversible process**

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

- **General reversible process**

$$\boxed{dS = \frac{dQ}{T} \quad \Rightarrow \Delta S = \int_i^f \frac{dQ}{T}}$$

- **Reversible process for n moles of ideal gas**

$$dQ = dE_{\text{int}} + dW$$

$$= pdV + nC_V dT$$

$$= nRT\frac{dV}{V} + nC_V dT$$

$$\Delta S = \int_i^f \frac{dQ}{T} = nR\ln\left(\frac{V_f}{V_i}\right) + nC_V\ln\left(\frac{T_f}{T_i}\right)$$

Note: as expected, ΔS depends only on the initial and final states, not on the process connecting the two states.

$$\Delta S = S_f - S_i$$

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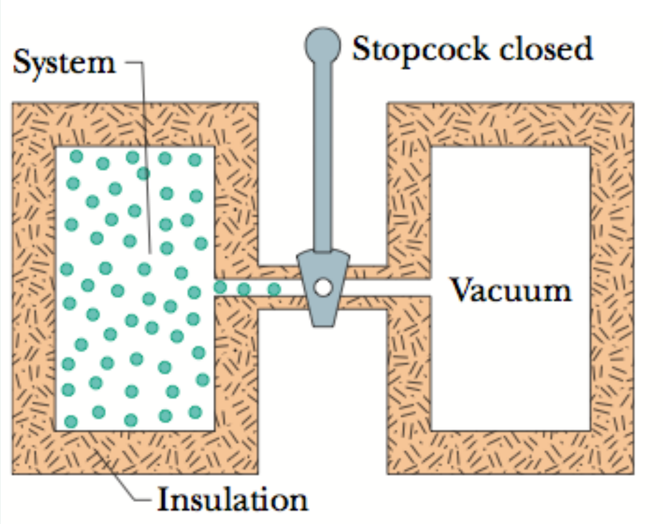
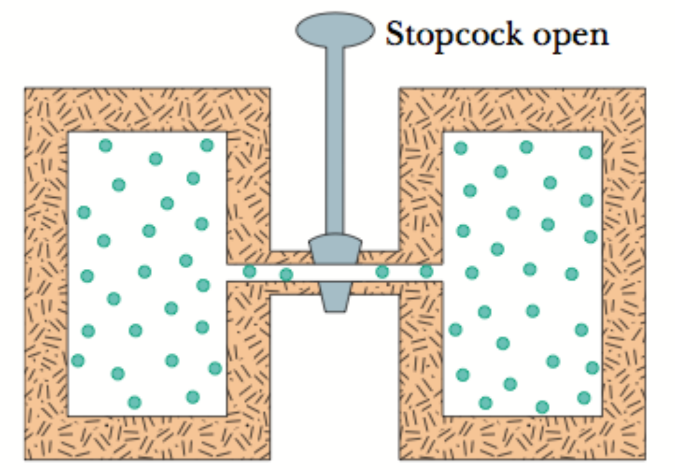
Example: free expansion



(*a*) Initial state *i*

Irreversible process

$\Longrightarrow$



(*b*) Final state *f*

Suppose $n = 1.0$ mol of nitrogen gas is confined to the left side of the container. You open the stopcock, and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process?

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The containers are insulated $\Rightarrow Q = 0$ (closed system).

The **total** volume of the system does not change $\Rightarrow$ $W = 0$.

$$\Delta E_{\text{int}} = Q - W = 0 \Rightarrow T_i = T_f$$

Change in entropy for gas:

$$\Delta S = nR\ln\left(\frac{V_f}{V_i}\right) = nR\ln 2$$

The second law of thermodynamics

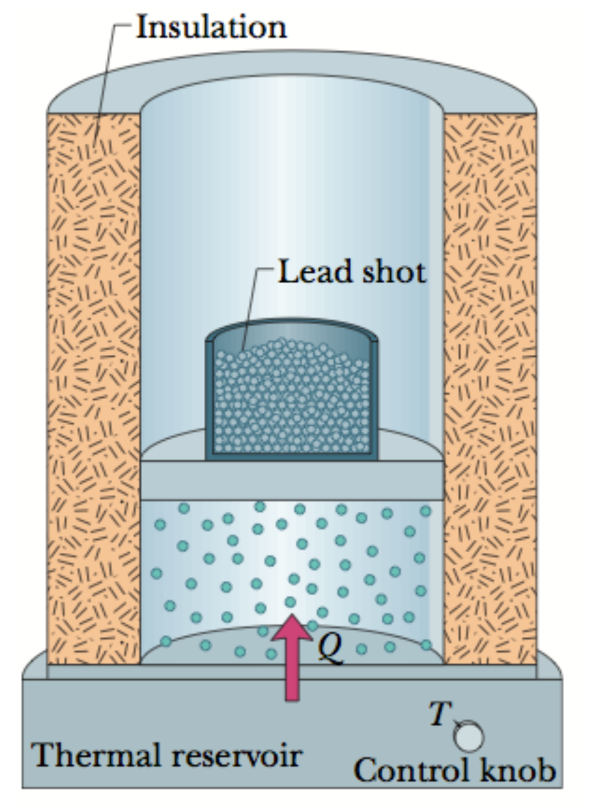
If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

Note: by definition

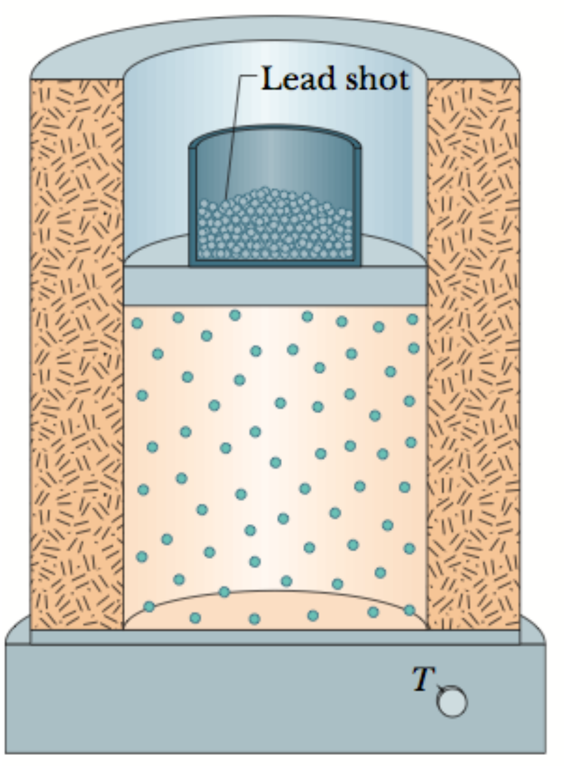
$$dS = \frac{dQ}{T}$$

for **reversible** processes. **Closed system:**

$$dQ = 0 \;\Rightarrow\; dS = 0$$



(*a*) Initial state *i*



(*b*) Final state *f*

The gas itself is **not** a closed system, but the gas **and** the thermal reservoir consitute a closed system.

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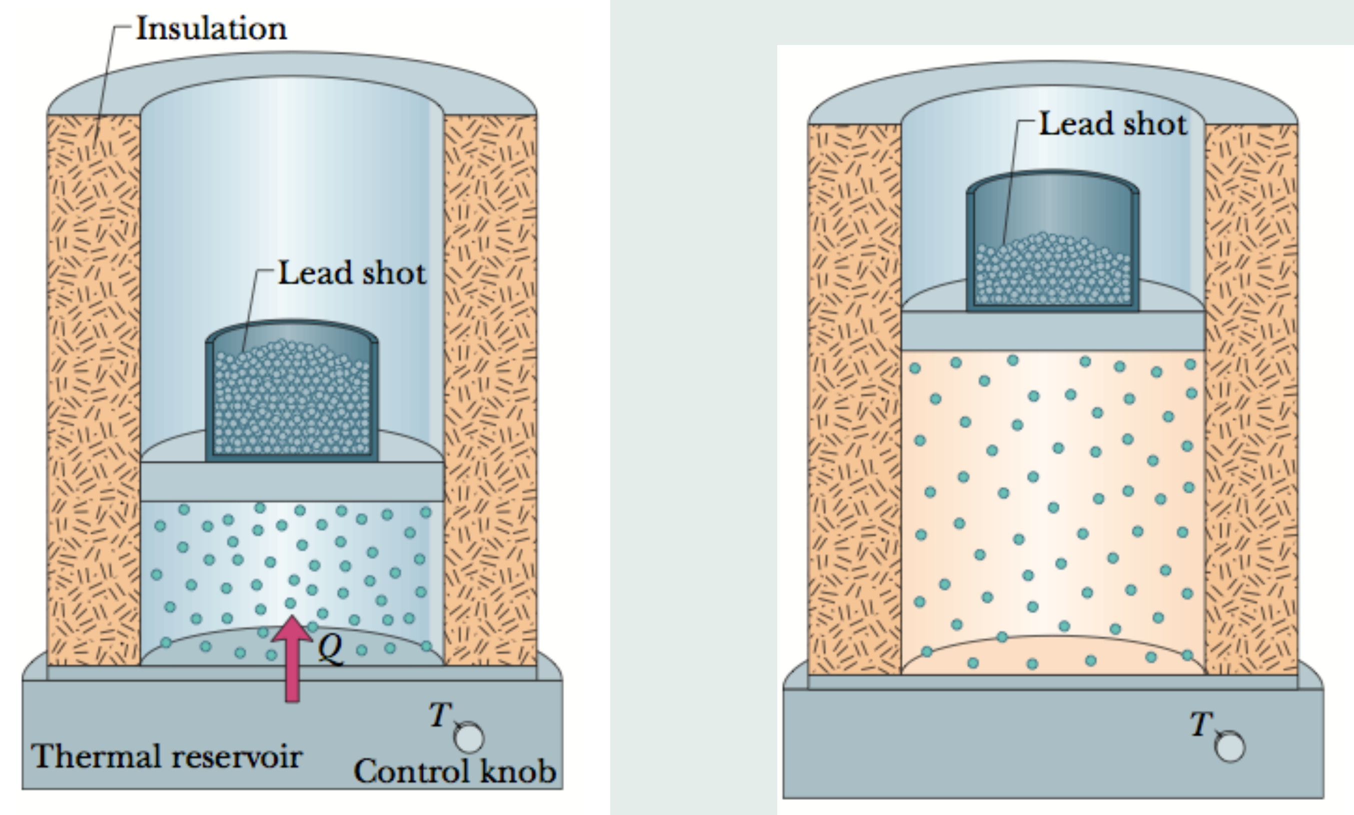

(*a*) Initial state *i*

(*b*) Final state *f*

$$(\Delta S)_{\text{gas}} + (\Delta S)_{\text{reservoir}} = 0$$

$$(\Delta S)_{\text{gas}} \neq 0, \qquad (\Delta S)_{\text{reservoir}} \neq 0$$

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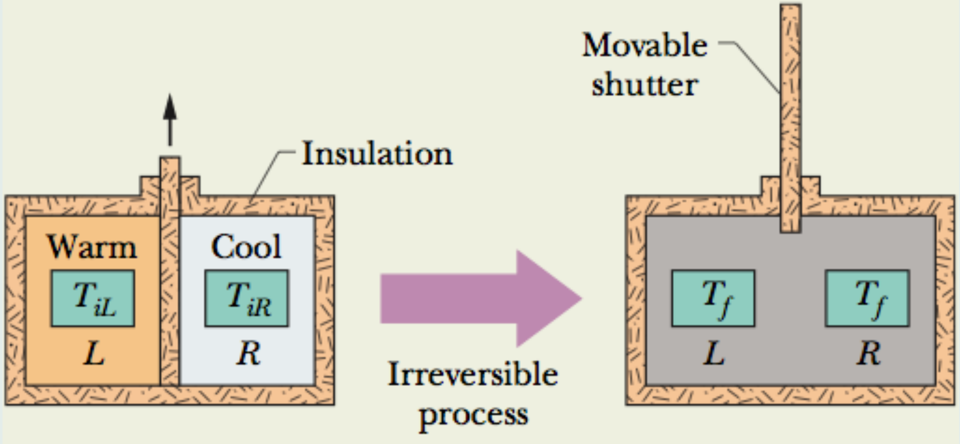
Example:

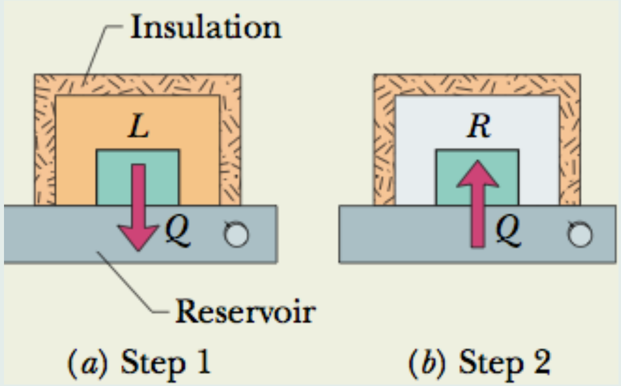


$$\Delta S = ?$$

- two identical copper blocks L, R of mass $m = 1.5$ kg in a thermally insulated box, separated by an insulating shutter.
- $t_{iL} = 60 \ \mathrm{C}^\circ$ and $t_{iR} = 20 \ \mathrm{C}^\circ$.
- Remove the shutter $\Rightarrow$ irreversible process. At the end – thermal equilibrium

$$t_f = 40 \ \mathrm{C}^\circ$$

The final state of equilibrium can be reached by a sequence of reversible processes.



Step 1. Slowly cool down block L from T_L to T_f

$$dQ = mcdT \qquad dS = mc\frac{dT}{T}$$

$$(\Delta S)_L = mc\int_L^f \frac{dT}{T} = mc\ln(T_f/T_L)$$

Step 2. Slowly heat up block R from T_R to T_f

$$(\Delta S)_R = mc\int_R^f \frac{dT}{T} = mc\ln(T_f/T_R)$$

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Total entropy variation:

$$\Delta S = (\Delta S)_L + (\Delta S)_R$$

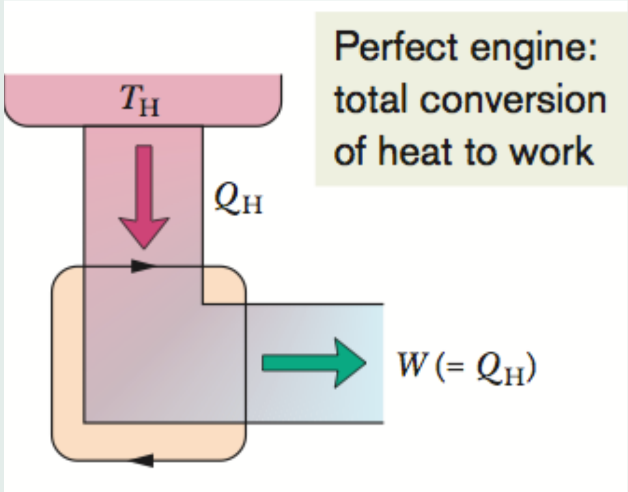
$$= mc[\ln(T_f/T_L) + \ln(T_f/T_R)]$$

Note: In entropy calculations the temperature must be expressed in Kelvins:

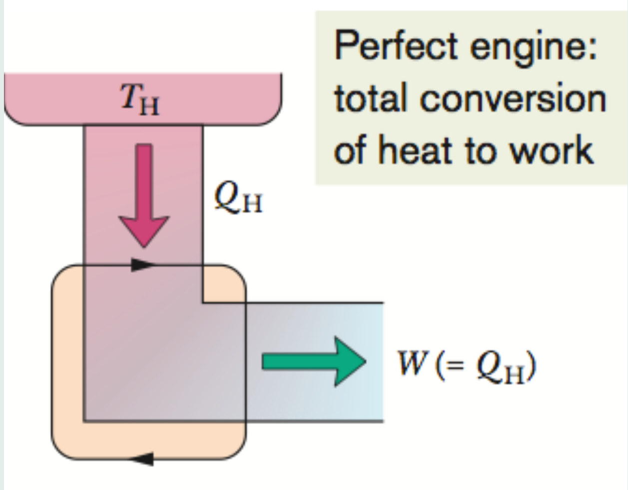
$$T(K) = t(C) + 273.15.$$

Entropy in the real world: Engines

- **Heat engine:** a device that takes in energy by heat and, operating in a cyclic process, expels a fraction of that energy by means of work



- A **perfect** heat engine is a device which converts heat Q_H from a high temperature reservoir to work W with 100% efficiency i.e. $W = Q_H$.



- The cycle cannot close.

- The 2nd law of thermodynamics ⇒ a **perfect** heat engine cannot exist.

- The system can only absorb heat $Q_H > 0$ from the reservoir. Therefore its entropy can only increase

$$\Delta S \geq Q_H/T_H > 0$$

- The system can never spontaneously return to a state with smaller volume at constant T_H since such a process would have

$$\Delta S < 0$$

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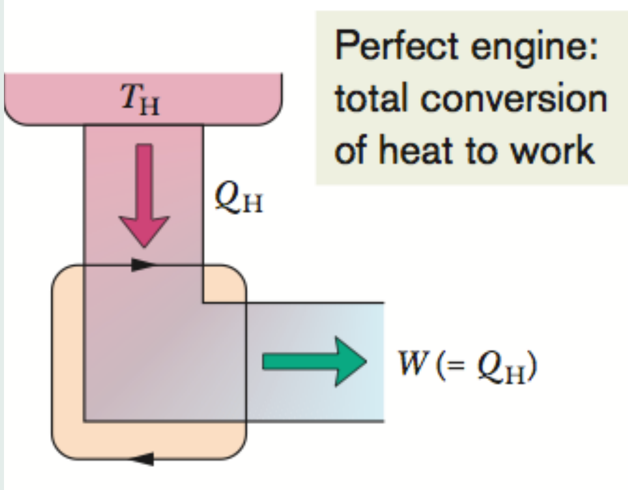
Kelvin-Planck formulation of the 2nd law



Perfect engine: total conversion of heat to work

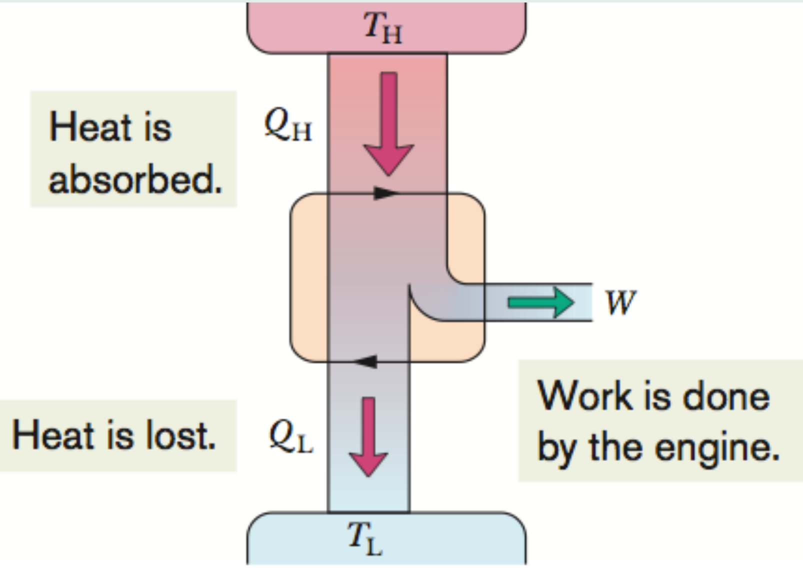
No series of processes is possible whose sole result is the transfer of energy as heat from a thermal reservoir and the complete conversion of this energy to work.

Ideal engine

All processes are reversible and no wasteful energy transfers occur due to, say, friction and turbulence.

Note: ideal engines are **theoretically** possible as opposed to **perfect** engines.

Carnot engine



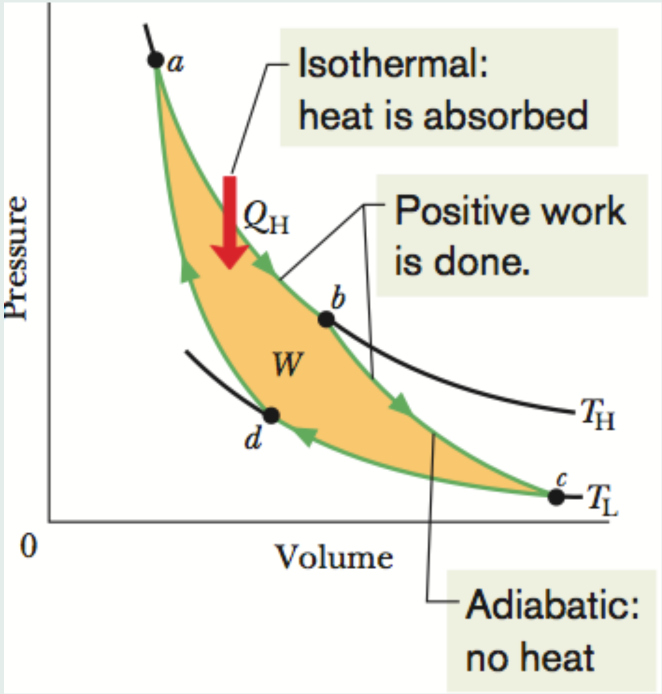
$$W = Q_H + Q_L = Q_H - |Q_L|$$

Q_H = heat absorbed from high temperature reservoir

$|Q_L|$ = heat lost to low temperature reservoir

- **Efficiency**

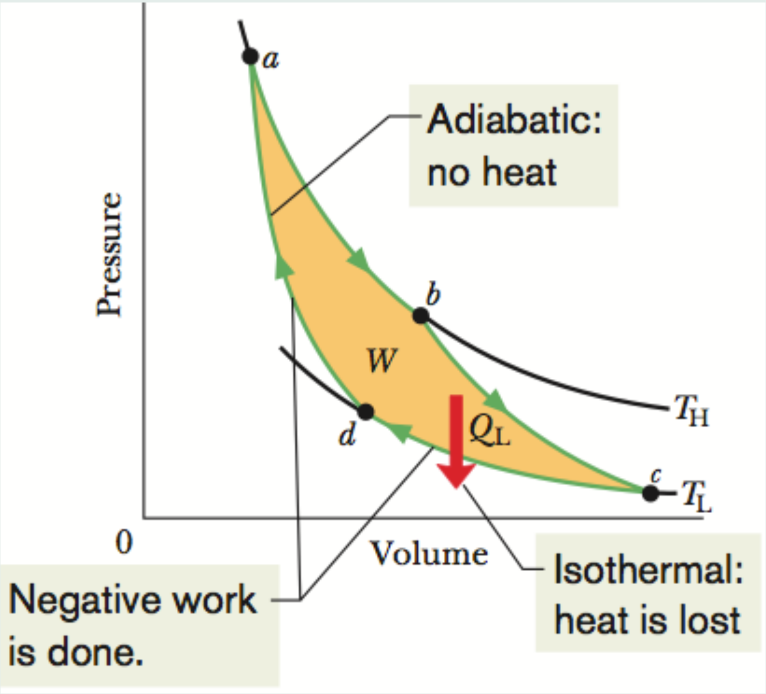
$$\epsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{W}{Q_H}$$



Isothermal: heat is absorbed

Positive work is done.

Adiabatic: no heat



Adiabatic: no heat

Negative work is done.

Isothermal: heat is lost

- **Gas** in a cylinder closed by a piston.
- All processes assumed ∼ **reversible.**
- **1st Law** for the **cycle**:

$$0 = \Delta E_{\text{int}} = Q_H + Q_L - W = Q_H - |Q_L| - W$$

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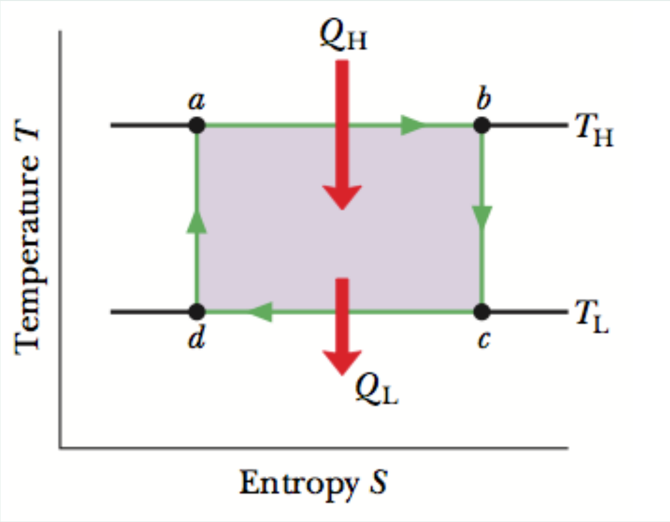
The Carnot cycle in the (S, T) plane



$$(\Delta S)_{\text{cycle}} = 0 \;\Rightarrow\; \frac{Q_H}{T_H} - \frac{|Q_L|}{T_L} = 0$$

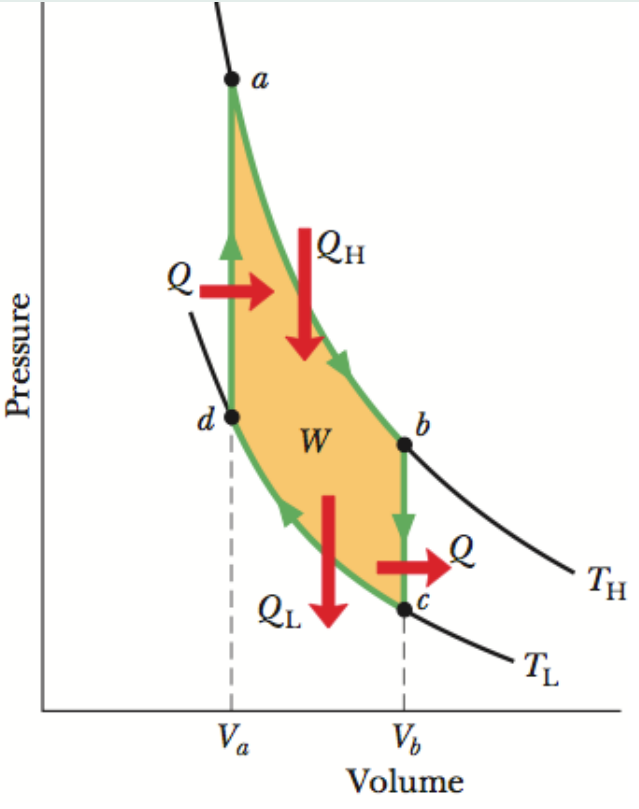
- **Efficiency of Carnot engine**

$$W = Q_H - |Q_L| \qquad \frac{Q_H}{T_H} = \frac{|Q_L|}{T_L} \qquad \epsilon = \frac{W}{Q_H} = 1 - \frac{|Q_L|}{Q_H}$$

$$\boxed{\epsilon = 1 - \frac{T_L}{T_H}}$$

Note: In real world the efficiency of a Carnot engine would be much smaller than its theoretical value because all processes involved are not really reversible and the adiabatic processes cannot be perfectly adiabatic.

Other engines: Stirling engine



- Total absorbed heat:

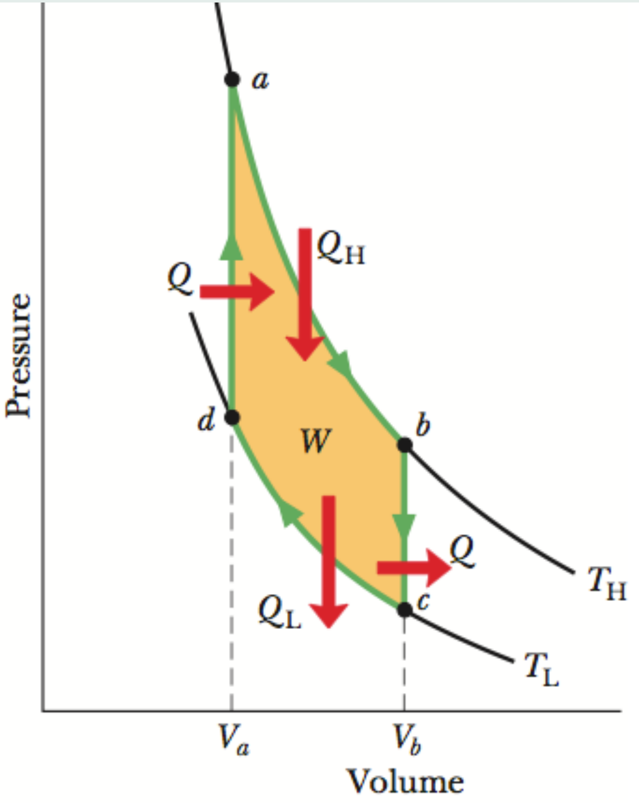
$$Q_H + Q_{ad}$$

- Total heat lost:

$$|Q_L| + |Q_{bc}|$$

- 1st Law for cycle:

$$W = Q_H + Q_{ad} - |Q_L| - |Q_{bc}|$$



- Efficiency:

$$\epsilon_S = \frac{W}{Q_H + Q_{ad}}$$
$$= 1 - \frac{|Q_L| + |Q_{bc}|}{Q_H + Q_{ad}}$$

- If E_{int} depends **only** on temperature and amount of gas $\Rightarrow$

$$\Delta E_{ad} = |\Delta E_{bc}|$$

- 1st Law for $a \to d$ and $b \to c$

$$Q_{ad} = \Delta E_{ad} \qquad |Q_{bc}| = |\Delta E_{bc}|$$

since $W_{ad} = W_{bc} = 0.$

$$Q_{ad} = |Q_{bc}|$$

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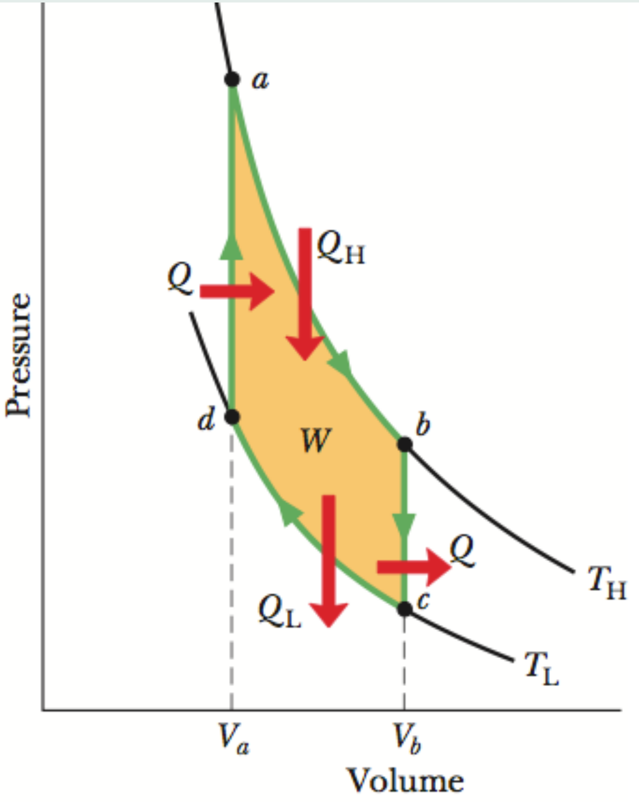


$$\epsilon_S = 1 - \frac{|Q_L| + |Q_{bc}|}{Q_H + |Q_{bc}|}$$

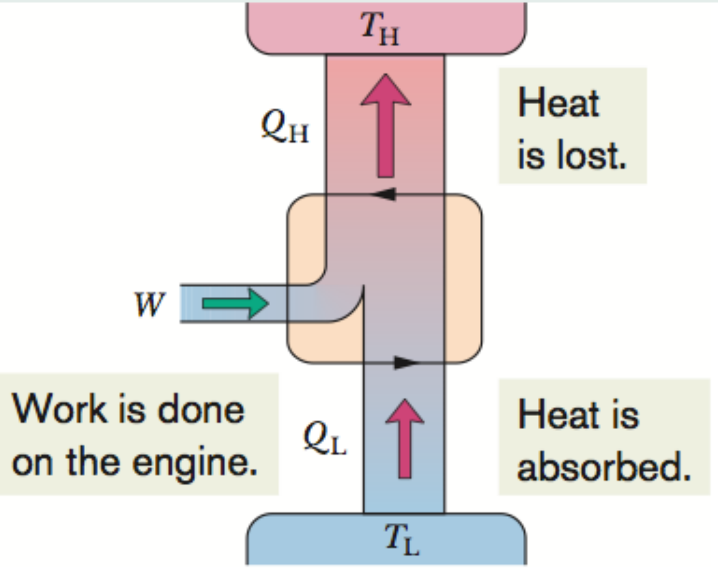
$$\begin{aligned}\epsilon_S - \epsilon_C &= \frac{|Q_L|}{Q_H} - \frac{|Q_L| + |Q_{bc}|}{Q_H + |Q_{bc}|} \\ &= -\frac{(Q_H - |Q_L|)|Q_{bc}|}{|Q_L|(Q_H + |Q_{bc}|)} > 0\end{aligned}$$

The efficiency of the Stirling engine is smaller that the efficiency of a Carnot cycle working within the same temperature range.

Carnot's Theorem

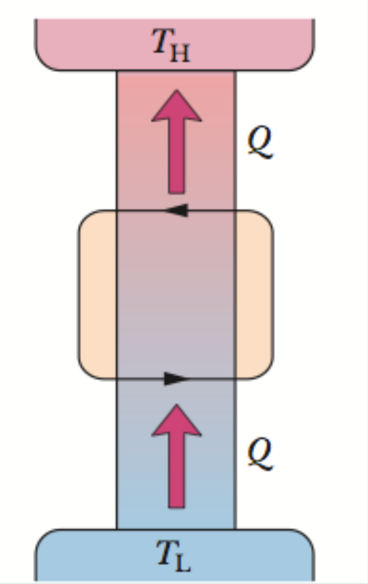
All heat engines between two heat reservoirs are less efficient than a Carnot engine operating between the same reservoirs.

Refrigerators



- **Refrigerator:** a device that uses work in order to transfer energy from a low temperature reservoir to a high temperature reservoir through a thermodynamic cycle.

- **Ideal refrigerator:** **all processes are reversible and no wasteful energy transfers occur as a result of, say, friction and turbulence.**



Perfect refrigerator: total transfer of heat from cold to hot without any work

- **Perfect Refrigerator:** transfers energy as heat Q from a cold reservoir to a warm reservoir without the need for work.
- **2nd Law** ⇒ perfect refrigerators cannot exist

No series of processes is possible whose sole result is the transfer of energy as heat from a reservoir at a given temperature to a reservoir at a higher temperature.

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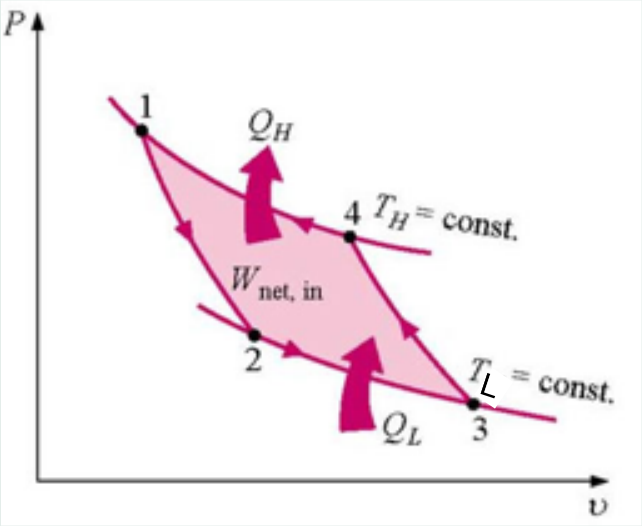
Carnot Refrigerator



Reversed Carnot cycle

- **Coefficient of Performance**

$$K = \frac{\text{what we want}}{\text{what we pay for}} = \frac{Q_L}{W}$$

$$K = \frac{Q_L}{|Q_H| - Q_L}$$

$$\boxed{K = \frac{T_L}{T_H - T_L}}$$