

# PHY2009S

## Thermodynamics and statistical models in physics

### Part 3

### Gas Laws

*Matter & Interactions*

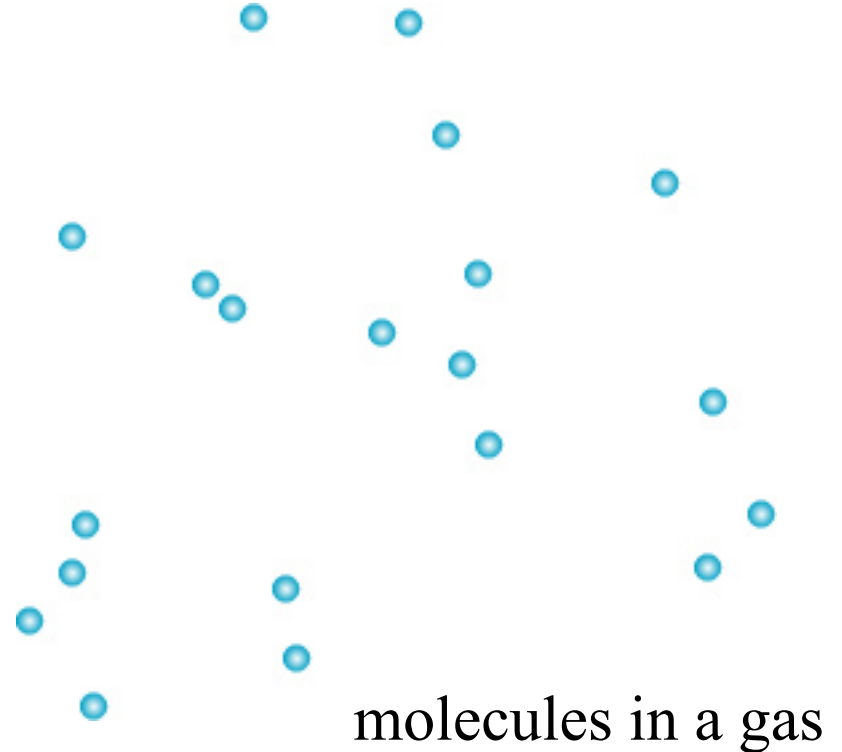
Chapter 12



**Gases:** molecules mostly beyond range of intermolecular forces.

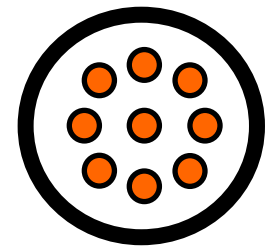
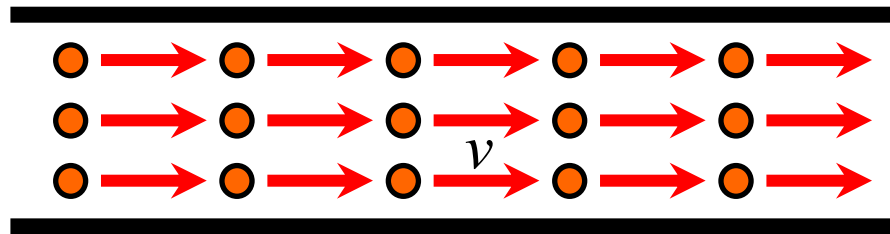
**Solids:** molecules close and cannot move far.

**Liquids:** intermediate case ... molecules always close, but can move.



## 1-d gas leak through hole

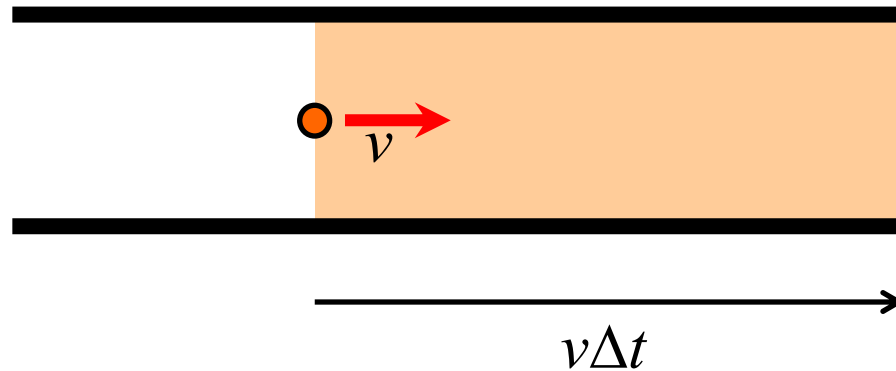
Consider  $N$  molecules travelling to the right with same speed  $v$  inside a tube which has volume  $V$  and cross sectional area  $A$ .



end view

Number density  $n = \frac{N}{V}$

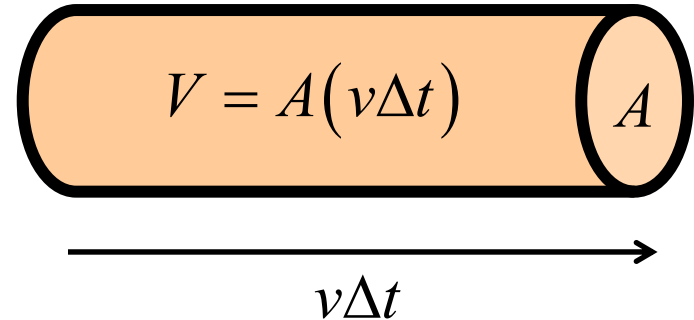
Distance a single molecule travels in time  $\Delta t$  is  $v\Delta t$ .



## 1-d gas leak through tube ...2

Number  $N$  of molecules leaving the tube in  $\Delta t$  is

$$N = nV = nA(v\Delta t)$$



Flux through  $A$  is  $nvA$ .

Real gases move at different speeds, therefore take weighted average:

$$\bar{v} = \frac{n_1 v_1 + n_2 v_2 + n_3 v_3 + \dots}{n}$$

Then flux is  $n\bar{v}A$ .

(one dimensional case, molecules have various speeds)

### 3-d gas leaks through hole

In **3-d** maybe 6 directions ( $x, y, z$  and both ways) gives factor  $1/6$ .  
However, since we must average over angle to wall, etc. ...  
a proper calculation (integration) gives rather a factor  $1/4$ :

$$\text{Then flux is } \frac{1}{4} n A \bar{v} .$$

Consider a 1 mm diameter hole in 1 litre balloon in vacuum at STP.

$$V = 1 \times 10^{-3} \text{ m}^3 \qquad n = \frac{N}{V}$$
$$N = N_A ( V / 22.4 \times 10^{-3} )$$

$$\begin{aligned} \text{Flux} &= \frac{1}{4} n A \bar{v} = \frac{N_A}{22.4 \times 10^{-3}} \left( \frac{\pi d^2}{4} \right) \sqrt{\frac{8}{3\pi}} \sqrt{\frac{3kT}{m}} \\ &= 6.61 \times 10^{21} \text{ atoms s}^{-1} \end{aligned}$$

## Leak causes gas to cool

The faster molecules are more likely to escape ...  
... thus the fraction of slower molecules remaining increases, and the gas in the balloon is colder.

If the gas is a real gas, then escaping gas expands, and molecules must do work against attractive intermolecular forces.

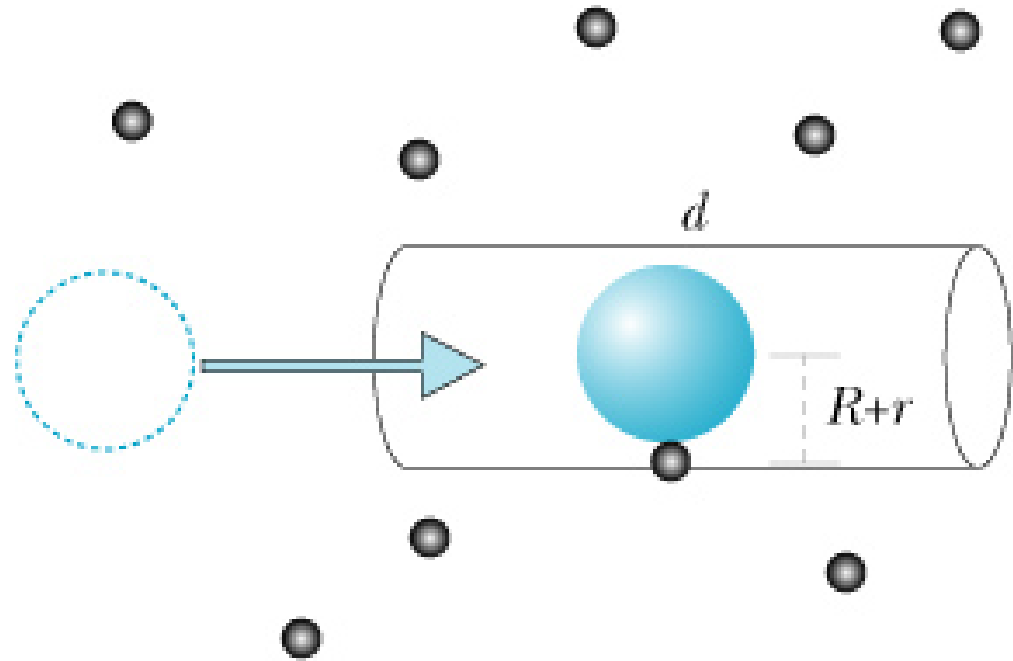
This cools the escaping gas.

*M&I*

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## Mean free path

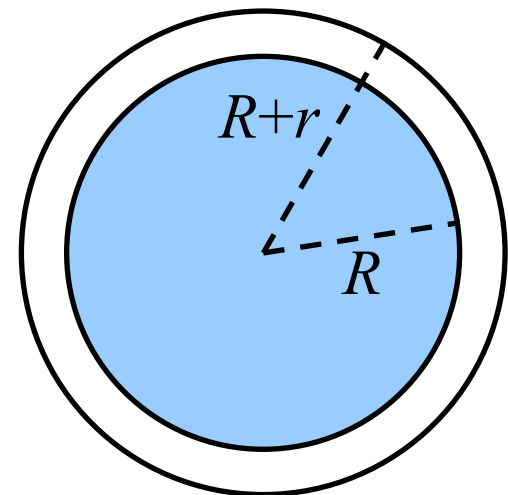
Let  $d$  be the average distance travelled by “special” molecule (dashed circle) in an imaginary cylinder of radius  $R + r$  before it has a collision with a gas molecule (dark).



$$nAd \approx 1$$

$$A = \pi(r + R)^2$$

$$n = \frac{N}{V}$$



## Mean free path in nitrogen at STP

Consider 1 mole of nitrogen at STP

$$n = \frac{N}{V} = \frac{N_A}{22.4 \times 10^{-3} \text{ m}^3} = 2.7 \times 10^{25} \text{ molecules m}^{-3}$$

$$A = \pi \left( 2 \left( 2 \times 10^{-10} \text{ m} \right) \right)^2 = 5 \times 10^{-19} \text{ m}^2$$

$$d = \frac{1}{nA} = \frac{1}{\left( 2.7 \times 10^{25} \text{ molecules m}^{-3} \right) \left( 5 \times 10^{-19} \text{ m}^2 \right)} = 7 \times 10^{-8} \text{ m}$$

Compare average distance between molecules:

$$L = \left( \frac{1}{n} \right)^{\frac{1}{3}} = \left( 2.7 \times 10^{25} \text{ molecules m}^{-3} \right)^{-\frac{1}{3}} = 0.3 \times 10^{-8} \text{ m}$$

Radius of molecule:  $r \approx 2 \times 10^{-10} \text{ m}$

So  $d \gg L \gg r$



## Pressure and temperature

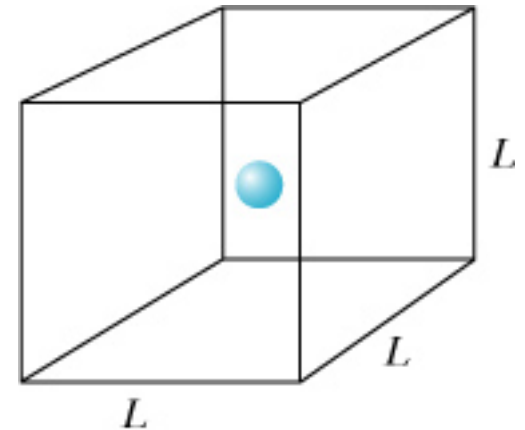
Can we understand the ideal gas law

$$PV = \nu RT$$

for  $\nu$  moles of gas, in terms of kinetic theory?

**Pressure** caused by gas molecules bombarding walls.

**Temperature** related to average kinetic energy of molecules.



## Elastic collisions of helium atom and wall

Consider an elastic collision of a helium atom with a wall.

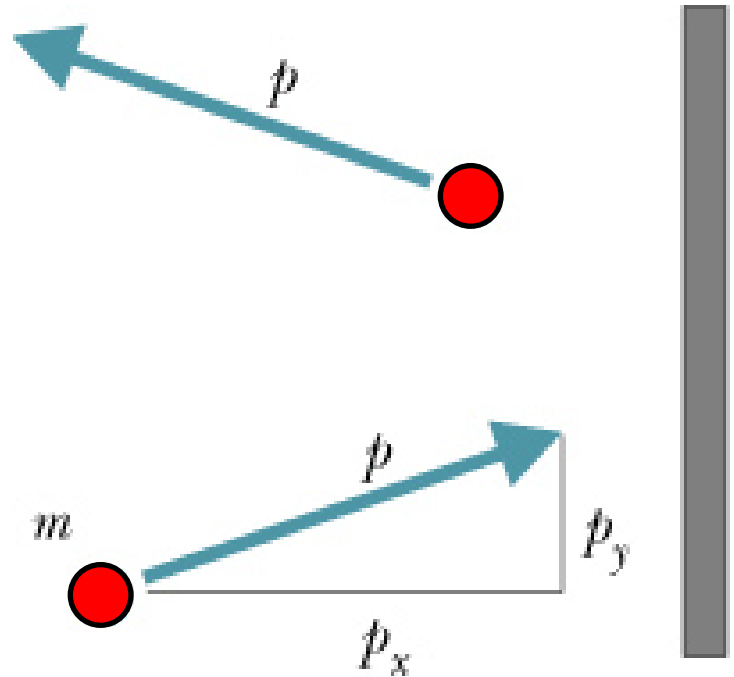
Energy is conserved, but momentum changes.

For the helium atom:

$$\Delta p_x = -2p_x$$

For the wall:  $\Delta p_x = 2p_x$

$$\text{Hence } P = \frac{F}{A} = \frac{1}{A} \frac{\Delta p_x}{\Delta t} = \frac{2p_x}{A\Delta t}$$



## Pressure from collisions: one speed

If  $n_{\text{right}}$  helium atoms per unit volume move with  $+v_x$  then the number of such atoms that hit area  $A$  to their right in time  $\Delta t$  is

$$\Delta t = \frac{1}{n_{\text{right}} A v_x}$$

Then

$$P = \frac{F}{A} = \frac{1}{A} \frac{\Delta p_x}{\Delta t} = \frac{1}{A} \frac{\Delta p_x}{1/(n_{\text{right}} A v_x)} = (n_{\text{right}} v_x) 2 p_x$$
$$= 2 n_{\text{right}} \frac{p_x}{m} p_x$$
$$= 2 n_{\text{right}} \frac{p_x^2}{m}$$

## Pressure from collisions: all speeds (in one dimension)

$$\text{On average: } n_{\text{right}} = n_{\text{left}} = \frac{n}{2}$$

$$\text{Average over all speeds } p_x^2 \rightarrow \overline{p_x^2}$$

If  $n_1$  have  $p_{x,1}$ , and  $n_2$  have  $p_{x,2}$ , ...

$$\text{then } \overline{p_x^2} = \frac{n_1 p_{x,1}^2 + n_2 p_{x,2}^2 + \dots}{n}$$

$$\text{Then the pressure } P = n_1 \left( \frac{p_{x,1}^2}{m} \right) + n_2 \left( \frac{p_{x,2}^2}{m} \right) + \dots$$

$$\text{or } P = n \frac{\overline{p_x^2}}{m}$$

## Pressure from collisions: all directions

Momentum is a vector,  $\vec{p}$  . Magnitude is  $p$ .

Random motion, so average  $\overline{\vec{p}} = 0$

Thus, also  $\overline{p_x} = \overline{p_y} = \overline{p_z} = 0$

But  $p^2 = p_x^2 + p_y^2 + p_z^2$  and  $\overline{p_x^2} = \overline{p_y^2} = \overline{p_z^2}$

Therefore  $\overline{p_x^2} = \frac{\overline{p^2}}{3}$  .

Pressure thus is  $P = \frac{1}{3} n \frac{\overline{p^2}}{m}$  where  $n = \frac{N}{V}$

## Energy of a diatomic gas

Boltzmann distribution also applies to gases.

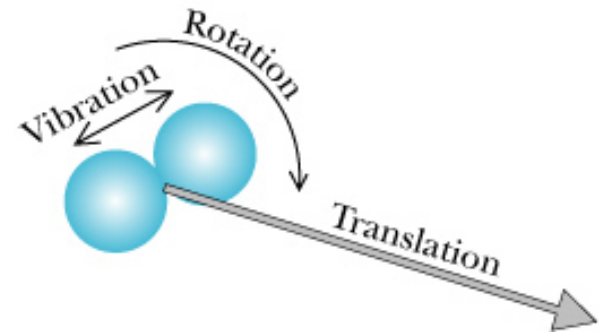
We will focus on ideal gases ... molecules don't interact.

For real gases we assume very dilute,

i.e. low density, few interactions.

Energy of molecule in an ideal gas in the gravitational field near the Earth's surface:

$$E_{\text{molecule}} = K_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}} + Mgy_{\text{cm}}$$



We ignore:

rest energy

nuclear energy

electronic energy

} Reasonable at room temperature

$E_{\text{surroundings}} \ll E_{\text{nuclear/electronic}}$

## Average translational kinetic energy in a gas

Energy depends on a quadratic quantity  $\omega^2$ , e.g.

$$K_{\text{trans}} = \frac{1}{2} M v_{\text{cm}}^2 \quad U_s = \frac{1}{2} k_s x^2 \quad E_{\text{rot}} = \frac{1}{2} I \omega^2$$

Average value of  $\omega^2$  is denoted  $\overline{\omega^2}$

$$\overline{\omega^2} = \frac{\int_0^\infty \omega^2 e^{-\frac{\omega^2}{kT}} d\omega}{\int_0^\infty e^{-\frac{\omega^2}{kT}} d\omega} = \dots = \frac{1}{2} kT \quad (\text{integrate by parts})$$

If  $kT \gg \hbar\omega_0$ , average of a quadratic energy term is  $\frac{1}{2} kT$

The number of quadratic terms in the expression for the energy is often called the “degrees of freedom.”

For an ideal monatomic and diatomic gas:

$$\overline{K}_{\text{trans}} = \frac{1}{2} M \left( \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \right) = 3 \left( \frac{1}{2} kT \right) = \frac{3}{2} kT$$

## Ideal gas law

In terms of  $n = \frac{N}{V}$ , pressure is  $P = \frac{1}{3}n \frac{p^2}{m} = \frac{2}{3}n \frac{\overline{p^2}}{2m} = \frac{2}{3}n \overline{K_{\text{trans}}}$

Previously found that  $\overline{K_{\text{trans}}} = \frac{3}{2}kT$

Therefore  $P = nkT$  molecular version of ideal gas law

For  $\nu$  moles,  $N = \nu N_A$  and  $n = \frac{N}{V}$  and putting  $R = kN_A$

$$PV = \nu RT \quad \text{mole version of ideal gas law}$$

$$\begin{aligned} \text{Gas constant } R = kN_A &= (1.38 \times 10^{-23} \text{ J K}^{-1}) (6.023 \times 10^{23} \text{ mole}^{-1}) \\ &= 8.31 \text{ J K}^{-1} \text{ mole}^{-1} \end{aligned}$$



## Temperature from entropy or ideal gas law

Previously showed that  $\overline{K}_{\text{trans}} = \frac{3}{2}kT$

... based on Boltzmann distribution applied to a low density gas.

... in turn based on **statistical mechanics**:  $\frac{1}{T} = \frac{\partial E}{\partial S}$

Now inserted  $\overline{K}_{\text{trans}} = \frac{3}{2}kT$  into  $P = \frac{1}{3}n\frac{\overline{p^2}}{m}$

... to get ...  $PV = \nu RT$

Thus  $T = \frac{PV}{\nu R}$  Gas thermometer

... same  $T$  is in  $\frac{1}{T} = \frac{\partial E}{\partial S}$

## Real gases

$PV = \nu RT$  “ideal” gas law works well for low density gases

For “real” high density gases ... two problems ...

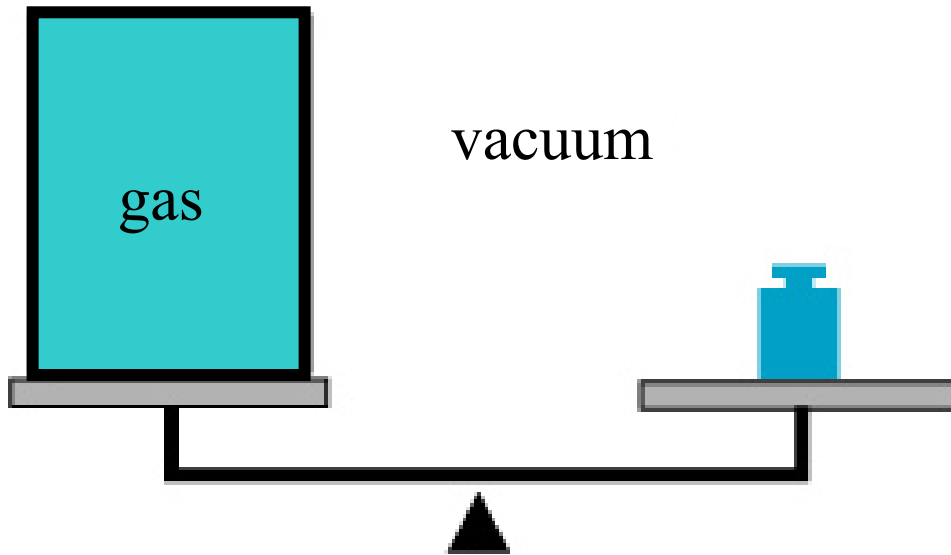
Real gas molecules have volume ... hence  $V$  needs to be smaller  
and short range electric forces ... “van der Waals forces” ...  
... hence  $P$  needs to be smaller

Replace with **van der Waals equation**:

$$\left( P + \frac{\nu^2 a}{V^2} \right) (V - \nu b) = \nu RT$$

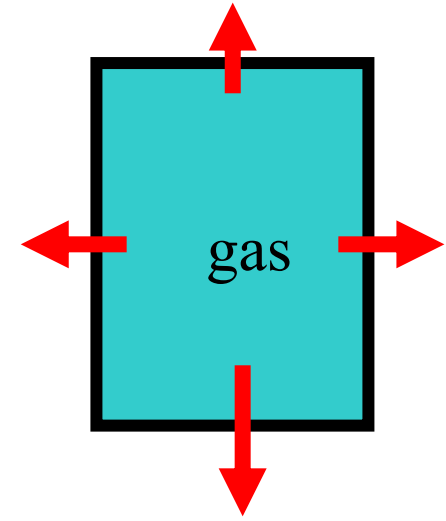
where  $a$  : attraction factor  
 $b$ : volume factor

## Weight of gas in a box



$$F_y = -Mg$$

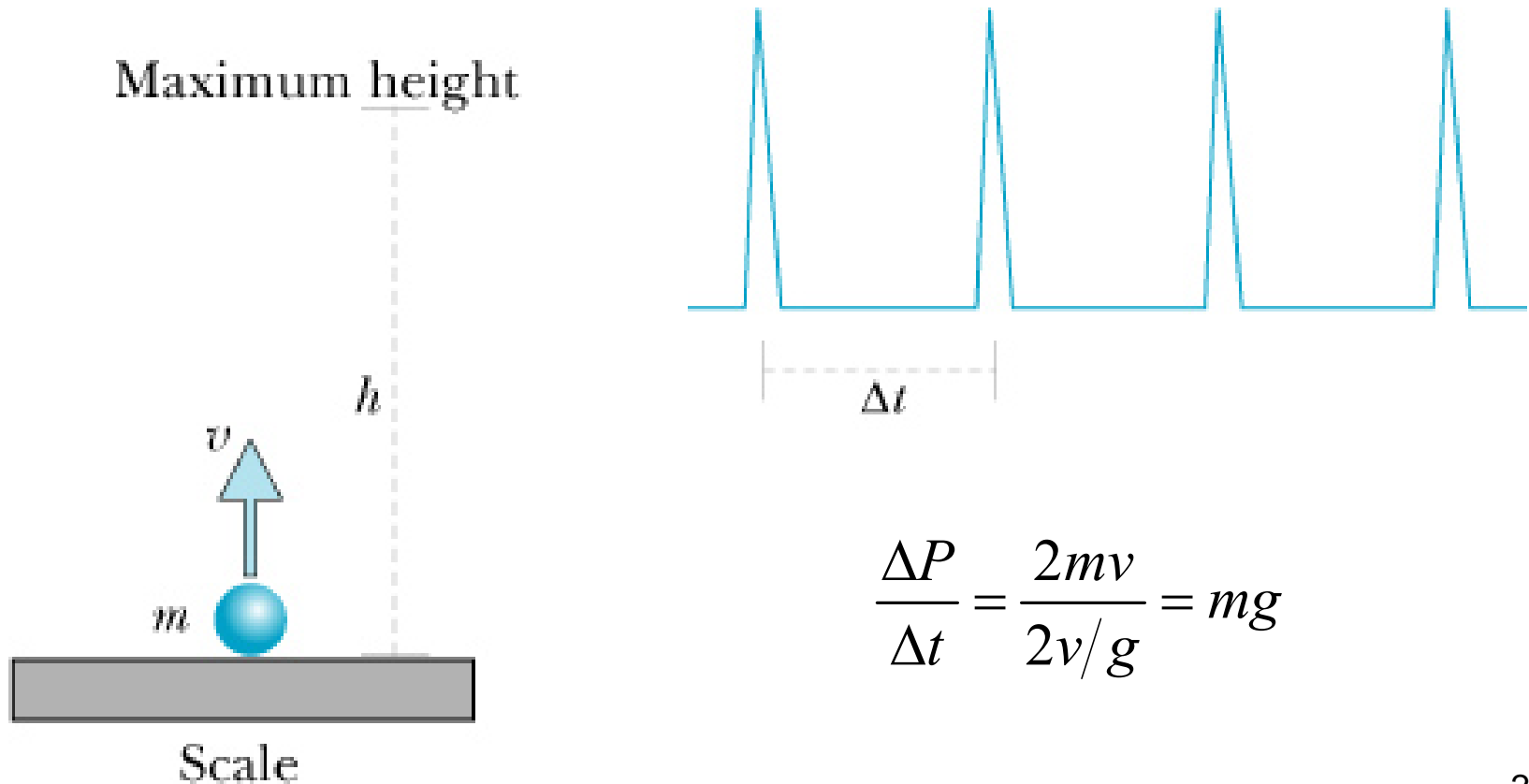
$P$  slightly smaller



$P$  slightly greater

## Weight of a bouncing molecule

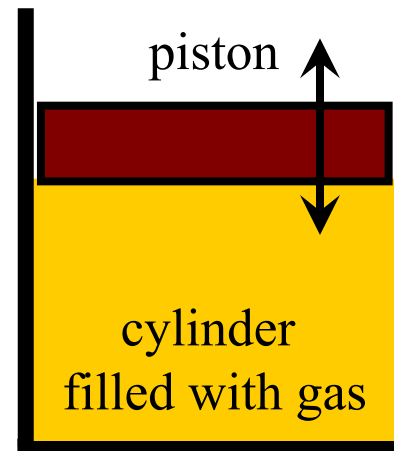
Consider a single molecule that bounces up and down on a scale without losing significant energy.



## Energy transfer between a gas and its surroundings

We need a device that lets us control the flow of energy in and out of a gas, in the form of work done  $W$  or energy transfer  $Q$  ...

... use a system consisting of a cylindrical container of gas that is enclosed by a piston that can move in and out of the cylinder with little friction but which fits tightly enough to keep the gas from leaking out.



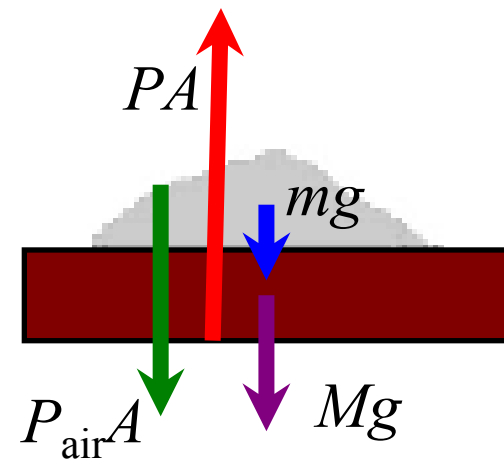
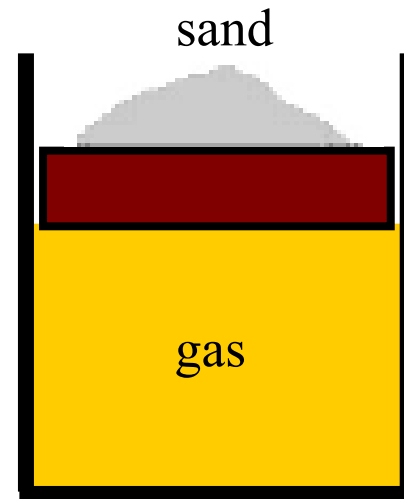
## Energy transfer between a gas and its surroundings ...2

Consider a cylinder of gas with a vertical running piston, on which we can load varying amounts of sand ... in order to control the pressure in the contained gas.

Then the pressure on the gas in the cylinder is

$$P = P_{\text{air}} + \frac{Mg + mg}{A}$$

What will happen if we suddenly dump a whole lot of sand onto the piston?



## Slow compression: a quasistatic process

Instead of dumping a lot of sand, we add (or remove) sand very slowly, one grain at a time ... a new equilibrium is established almost immediately (“quasistatic compression” or “quasistatic expansion” of the gas).

Consider quasistatic compression ...

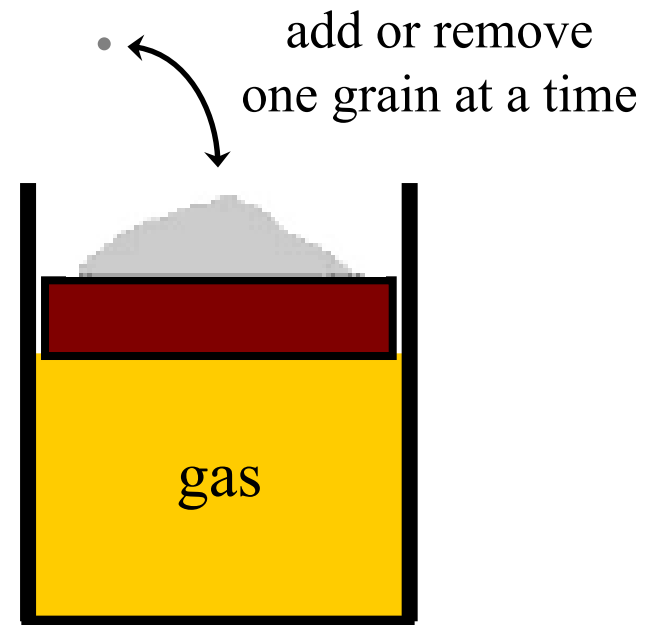
$PV = NkT$  holds ...

... but is  $T$  constant?

... maybe isothermal.

... maybe adiabatic.

... maybe neither.



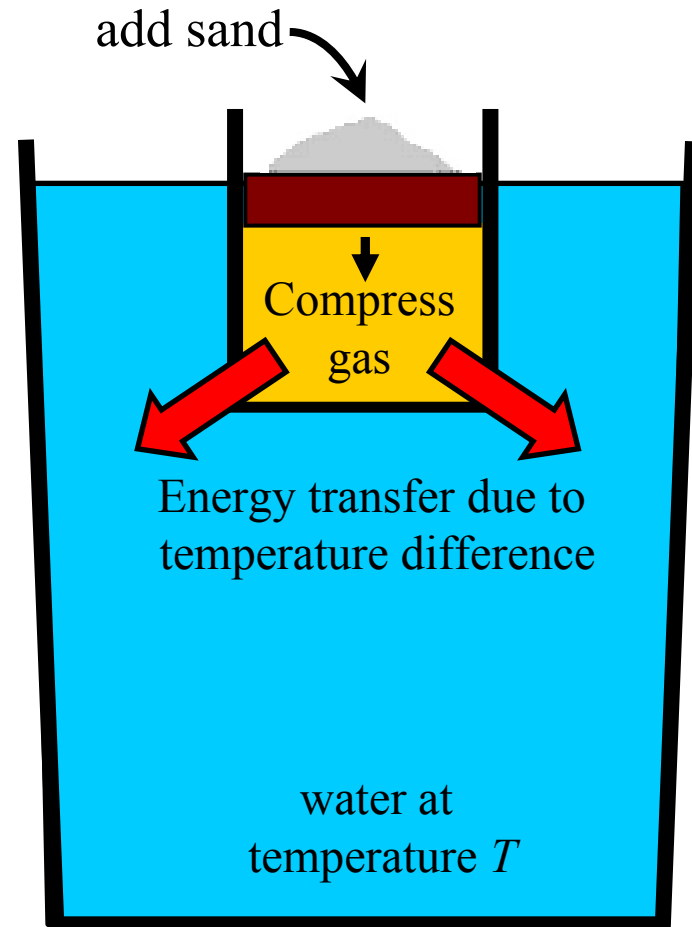
## Isothermal compression

Consider a metal cylinder (good thermal conductor) immersed in a large bath of water.

The big thermal reservoir keeps the temperature of the gas constant as it is compressed.

$$P_1 V_1 = P_2 V_2$$

“Isothermal” or  
constant temperature  
compression.





## Isothermal compression: work and heat

Piston does work on gas.

... and there is thermal transfer of energy out of gas (into the water).

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

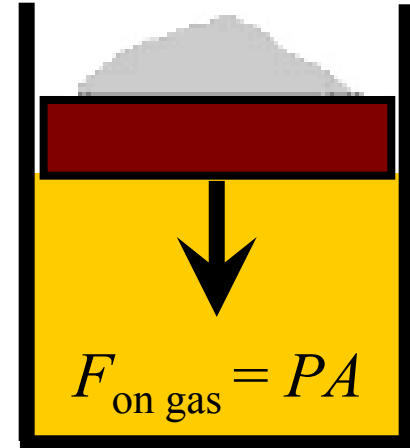
Since  $T = \text{constant}$ ,  $\Delta E_{\text{gas}} = 0$

$$\therefore W + Q = 0$$

Therefore if  $W > 0$ , then  $Q < 0$ , and

$$W = -\int_{V_1}^{V_2} PdV$$

... work done by the piston of the gas.



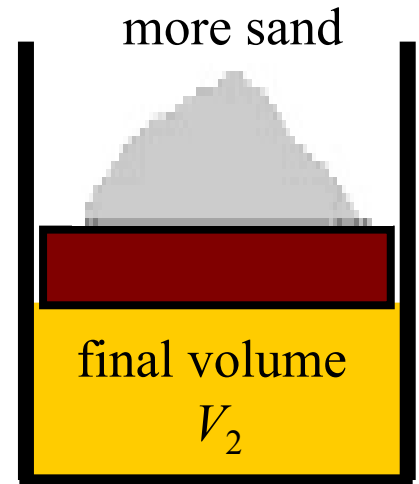
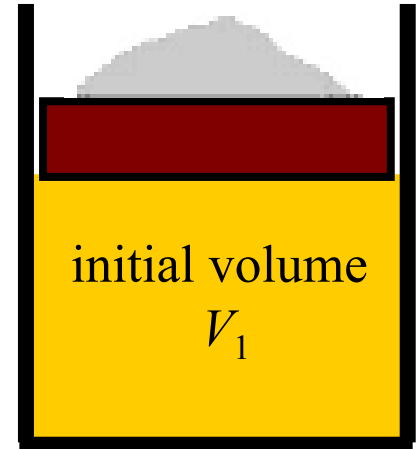
## Isothermal compression: integration

$$\begin{aligned} W &= -\int_{V_1}^{V_2} P dV = -\int_{V_1}^{V_2} \frac{NkT}{V} dV \\ &= -NkT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= -NkT [\ln V]_{V_1}^{V_2} \\ &= -NkT \ln \left( \frac{V_1}{V_2} \right) \end{aligned}$$

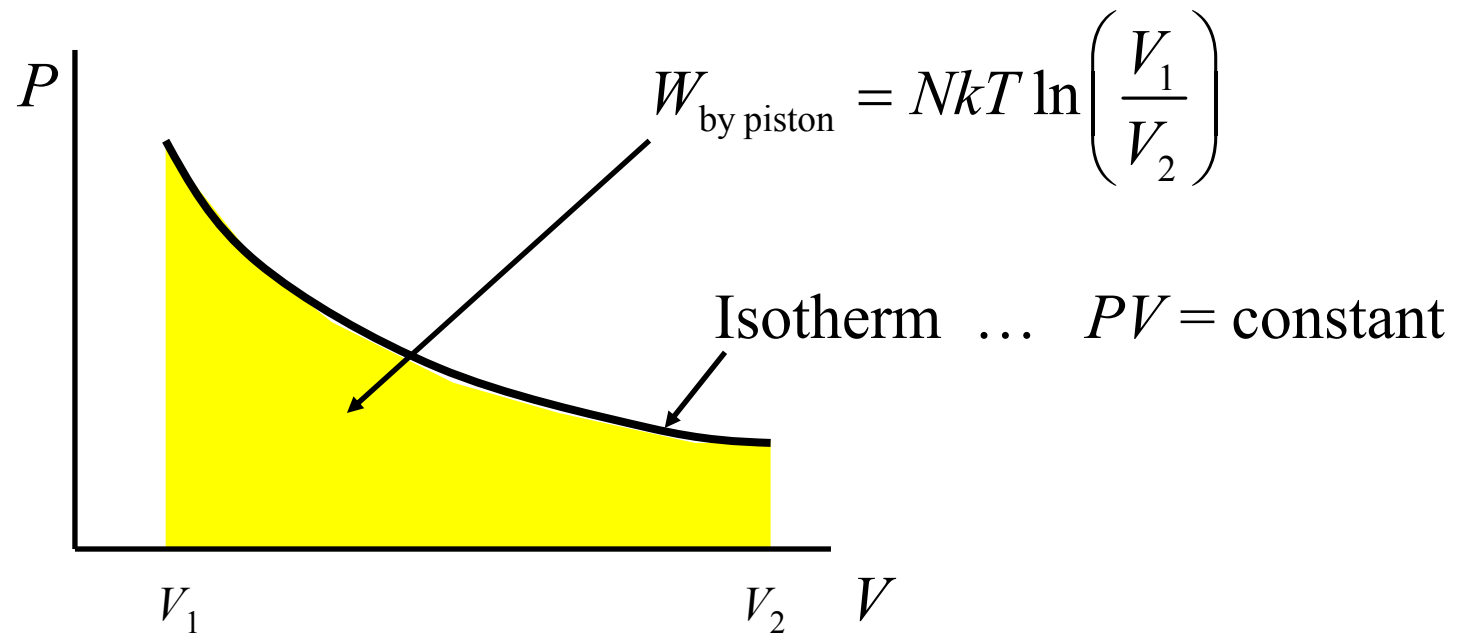
Since the process was a compression  $V_2 < V_1$

$$\text{and since } -\ln \left( \frac{V_2}{V_1} \right) = \ln \left( \frac{V_1}{V_2} \right)$$

$$W_{\text{by piston}} = |Q_{\text{into water}}| = NkT \ln \left( \frac{V_1}{V_2} \right)$$



## Isothermal compression: work done on the gas



## Isothermal compression: first law of thermodynamics

First law of thermodynamics (energy conservation)

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

In this case of isothermal compression of an ideal gas:

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

... where  $E_{\text{int}}$  is the “internal” energy of the gas (the sum of the translational, rotational, vibrational, and other energy terms of all the molecules).

## Heat capacity at constant volume $C_V$

Lock the piston in place ... volume of the gas is constant ... hence no work is done ( $W = 0$ ).

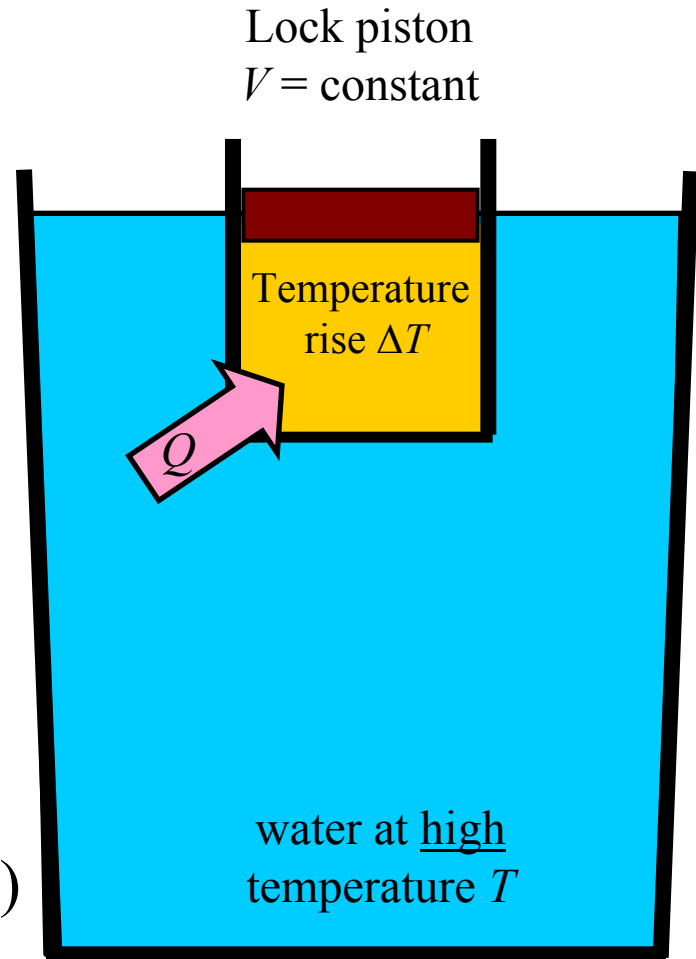
Water hotter than gas, so thermal energy transfer  $Q$  into the gas.

Define the **specific heat capacity at constant volume**  $C_V$  ...

$$\Delta E_{\text{thermal}} = Q = NC_V \Delta T$$

$C_V = \frac{3}{2}k$  for a monatomic gas (He, etc.)

$C_V \geq \frac{3}{2}k$  for other gases ( $\text{N}_2$ , etc.)



## Heat capacity at constant pressure $C_P$

Now piston is movable ... pressure in the gas is constant.

Water hotter than gas, so thermal energy transfer  $Q$  into the gas and the gas does work on piston.

$$Q = NC_P\Delta T = NC_V\Delta T + W$$

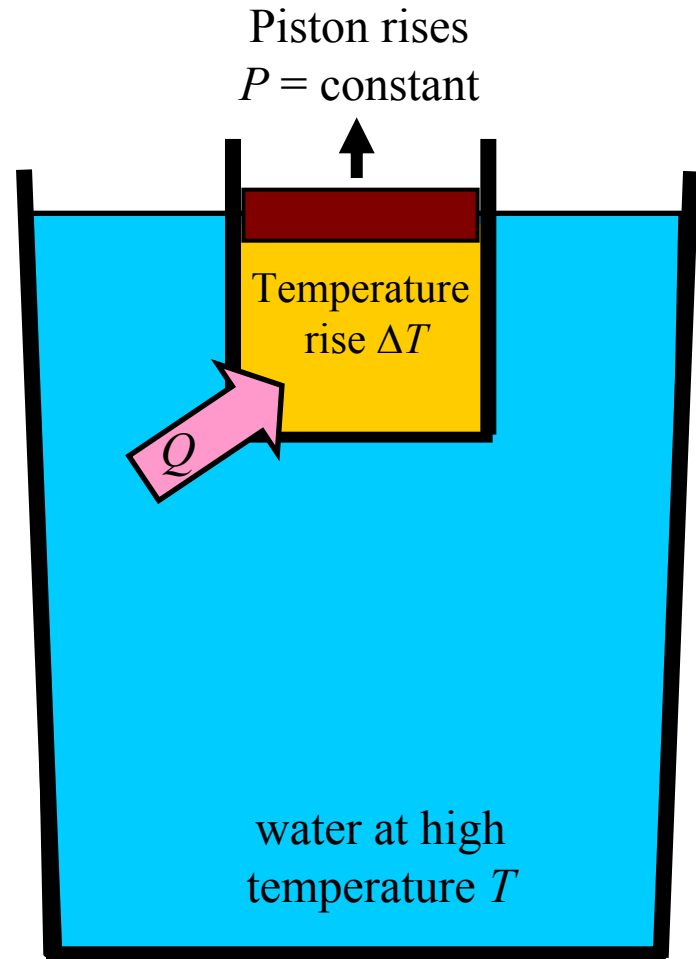
$$\therefore W = -\int_{V_1}^{V_2} PdV = -P\int_{V_1}^{V_2} dV$$

$$= PV_2 - PV_1$$

$$= NkT_2 - NkT_1 = Nk\Delta T$$

$$Q = NC_P\Delta T = NC_V\Delta T + Nk\Delta T$$

$$\therefore C_P = C_V + k$$



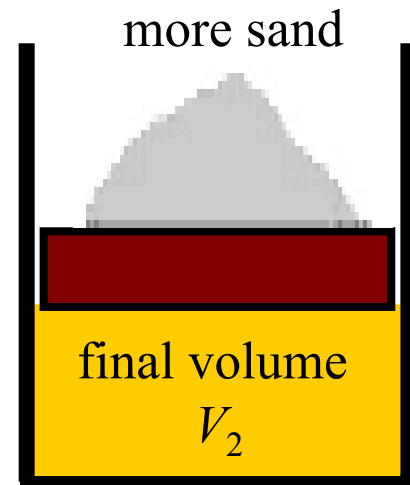
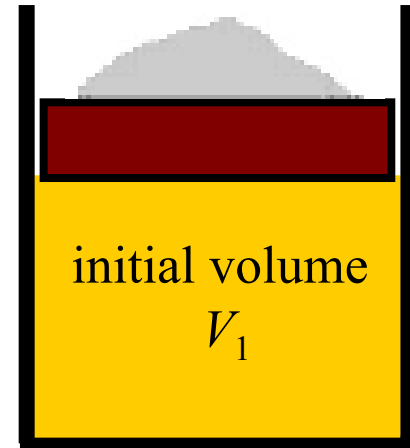
## Adiabatic (No $Q$ ) compression

If the cylinder and piston are made of insulating material, then no thermal energy transfer  $Q$  can occur between the ideal gas and its surroundings ...

... called and **adiabatic compression**.

$$W = -\int_{V_1}^{V_2} PdV = NC_V\Delta T$$

Note that we use  $C_V$  for an ideal gas (although  $V$  is not constant) since the total energy of an ideal gas is entirely determined by the temperature.



## Adiabatic compression: integration

$$W = -\int_{V_1}^{V_2} P dV = NC_V \Delta T \quad \rightarrow \quad -PdV = NC_V dT$$

$$\therefore -NkT \frac{dV}{V} = NC_V dT$$

Then  $\left(\frac{C_V}{k}\right) \int \frac{dT}{T} + \int \frac{dV}{V} = 0$

$$\therefore \left(\frac{C_V}{k}\right) \ln T + \ln V = \text{constant}$$

$$\therefore \ln \left( T^{\frac{C_V}{k}} V \right) = \text{constant}$$

or  $T^{\frac{C_V}{k}} V = \text{constant}$

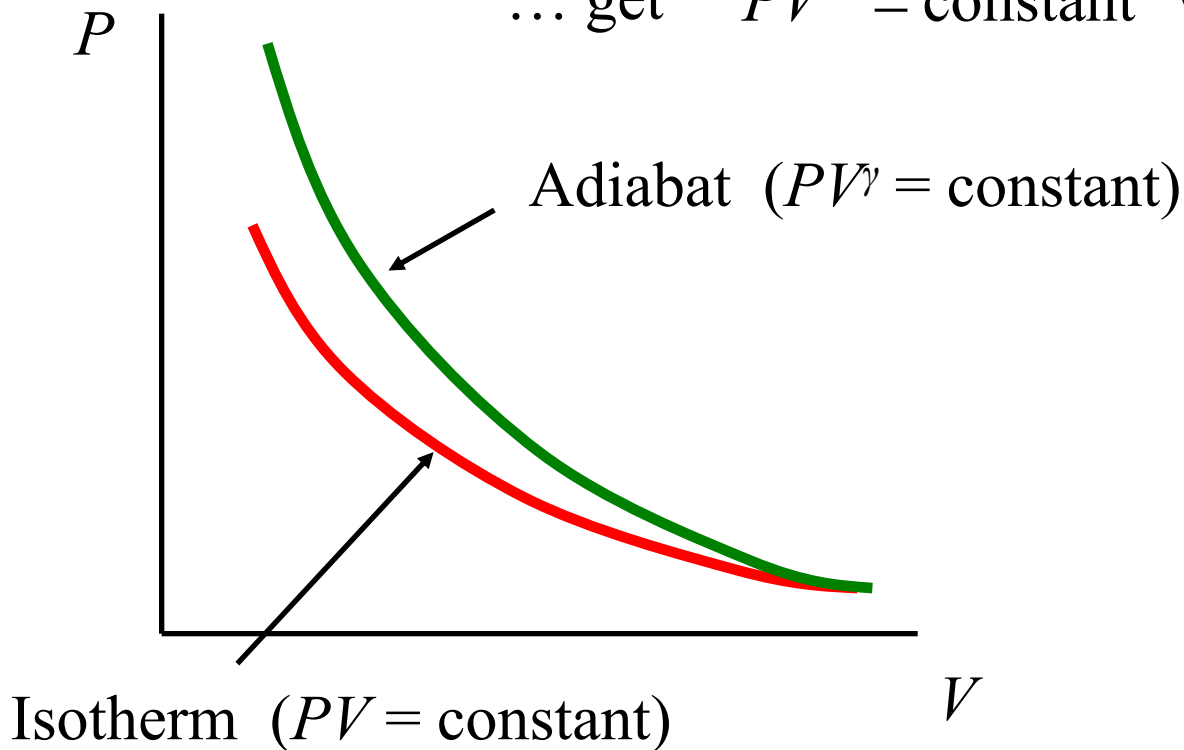


## Adiabatic compression

$$T^{\frac{C_V}{k}} V = \text{constant}$$

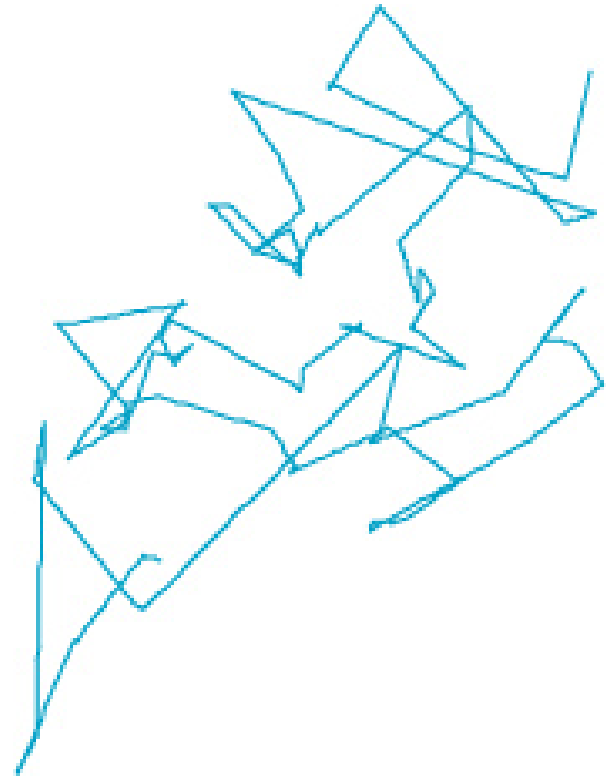
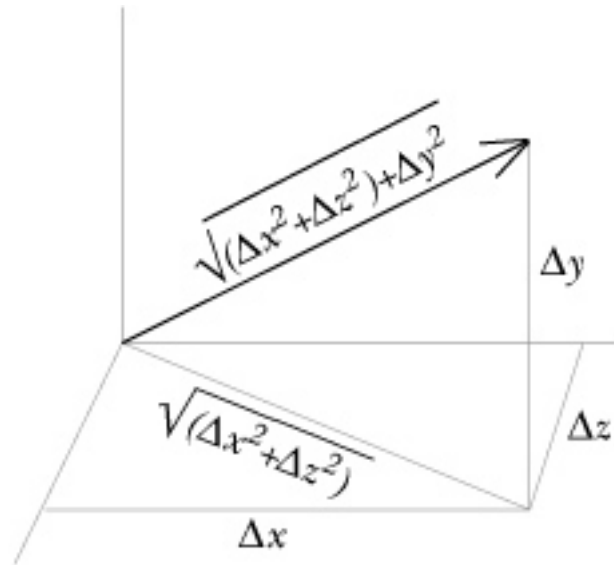
Using  $PV = NkT$  ...

... get  $PV^\gamma = \text{constant}$  where  $\gamma = \frac{C_P}{C_V}$



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## A random walk



## Fundamental limits on efficiency

We have sources of energy in the form of heat ...

.... fossil fuel, hydro, wind, solar, . . . , nuclear.

... industrial societies want machines (engines) to do work.

... need to convert thermal energy transfer to work.

There is a fundamental limitation:

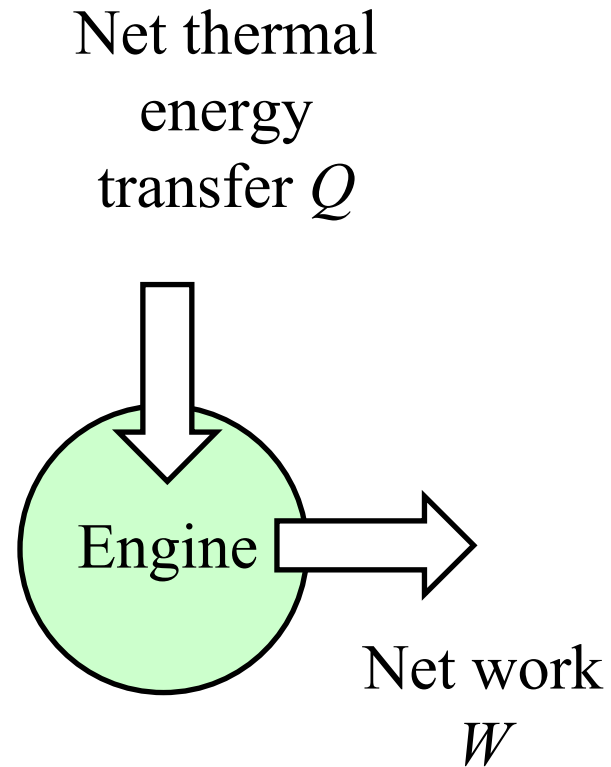
entropy and the second law of thermodynamics.

## An engine converts heat into work

Input to the engine is net thermal energy transfer  $Q$

Output is net work  $W$

Can  $|W| = Q$  ??



... always irreversible processes, e.g. friction.

## Thermal energy transfer and entropy increase

Two blocks connected by a metal bar of length  $L$ , cross sectional area  $A$  and thermal conductivity  $\sigma$ .

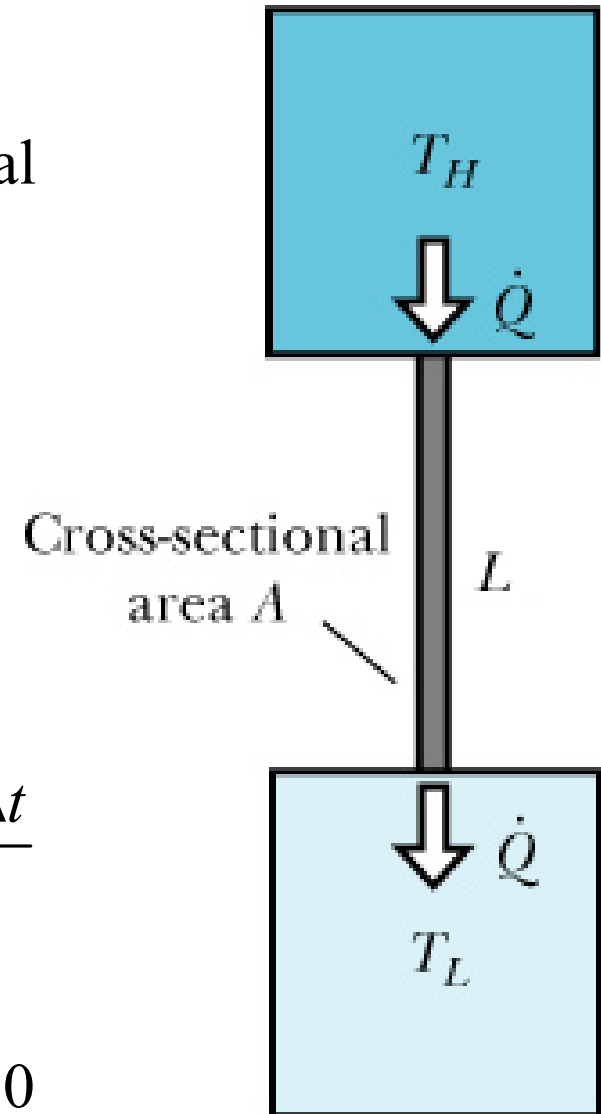
Block at  $T_H$  ... the “source”

Block at  $T_L$  ... the “sink”

$$\frac{dQ}{dt} = \dot{Q} = \sigma A \left( \frac{T_H - T_L}{L} \right) \quad \begin{array}{l} \dot{T}_H \approx 0 \\ \dot{T}_L \approx 0 \end{array}$$

$$\Delta S = \frac{Q}{T} \quad \Delta S_H = -\frac{\dot{Q}\Delta t}{T_H} \quad \Delta S_L = -\frac{\dot{Q}\Delta t}{T_L}$$

$$\Delta S_H + \Delta S_L + 0 = -\frac{\dot{Q}\Delta t}{T_H} - \frac{\dot{Q}\Delta t}{T_L} + 0 \geq 0$$



## Reversible and irreversible processes

Consider entropy of the Universe,  $S_U$ .

$S_U$  increases in irreversible process,  $\Delta S_U \geq 0$

$S_U$  constant in reversible process,  $\Delta S_U = 0$

For a reversible process,  $\Delta S_U = 0$  implies  $Q = 0$  or  $T_H = T_L$ .

Thus  $\dot{Q} \propto T_H - T_L = 0$  and the process is infinitely slow.

Therefore we can carry out (nearly) reversible processes, hardly changing the entropy of the Universe, as long as we transfer energy very slowly ... so as to be of no practical use as a (mechanical) engine.

*M&I*

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## A maximally efficient process

Assume no friction.

Assume a reversible process (slow changes).

Since the process is reversible, we can run engine backwards (i.e. a refrigerator).

Ideas due to Sadi Carnot (1824)

... before the principle of energy conservation was established!

## A cyclic process of a reversible engine

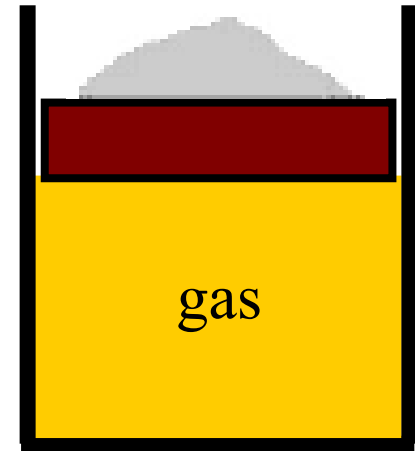
Details of engine do not matter.

Overall principle ... use cylinder of ideal gas, with a piston and some sand on the piston to adjust the pressure on the gas.

... and a hot and cold reservoir.

Four parts to the cycle:

- ... in contact with hot reservoir: isothermal expansion
- ... adiabatic expansion
- ... in contact with cold reservoir: isothermal compression
- ... adiabatic compression





## Isothermal expansion at $T_H$

Engine in contact with the hot reservoir

$$T_{\text{gas}} \approx T_H$$

Lift the piston by sliding some sand off sideways slowly.

Isothermal expansion

... engine gets  $Q_H$  from source.

Source:  $\Delta S_H = -Q_H/T_H$

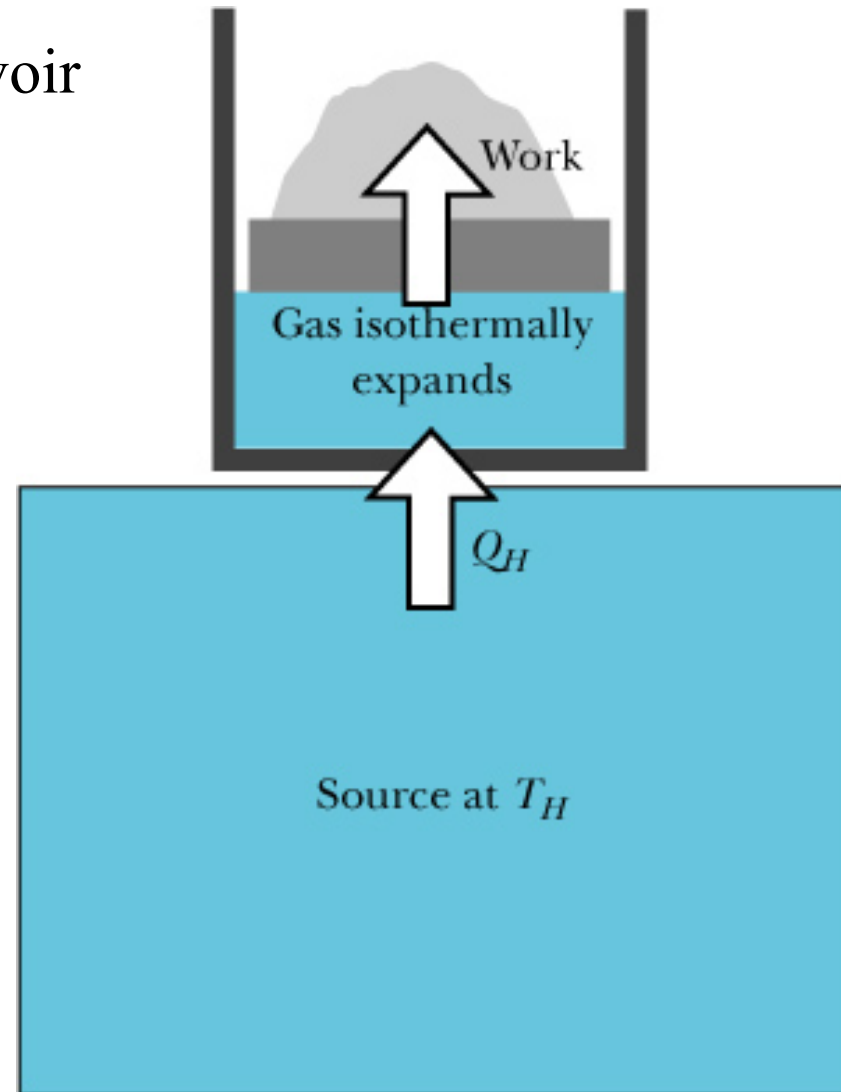
Gas:  $\Delta S_{\text{gas}} = +Q_H/T_{\text{gas}}$

but  $T_H \approx T_{\text{gas}}$

Therefore  $\Delta S_U \approx 0$

No change in gas energy.

All energy went into work  $W_{\text{on gas}} = -Q_H$



## Adiabatic expansion cools gas to $T_L$

No thermal contact with hot reservoir.

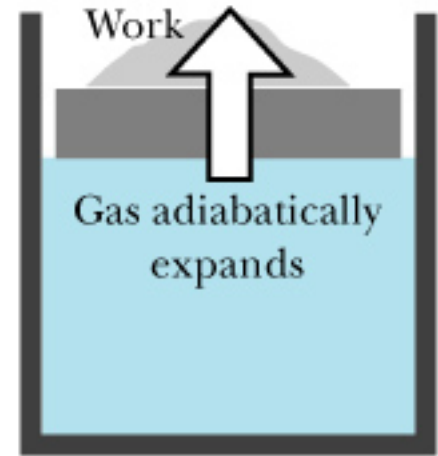
Allow reversible adiabatic expansion ... by slowly moving more weight from the piston.

$$Q = 0 \quad \text{so} \quad \Delta S = 0.$$

Gas does work.

Work done on gas  $W_{\text{on gas}} < 0$

Gas cools to  $T_{\text{gas}} \approx T_L$  .



## Isothermal compression at $T_L$

Engine in contact with the cold reservoir

$$T_{\text{gas}} \approx T_L$$

Lower the piston by sliding some sand on slowly.

Isothermal compression  
... engine gives  $Q_L$  to sink.

$$\text{Sink: } \Delta S_L = +Q_L/T_L$$

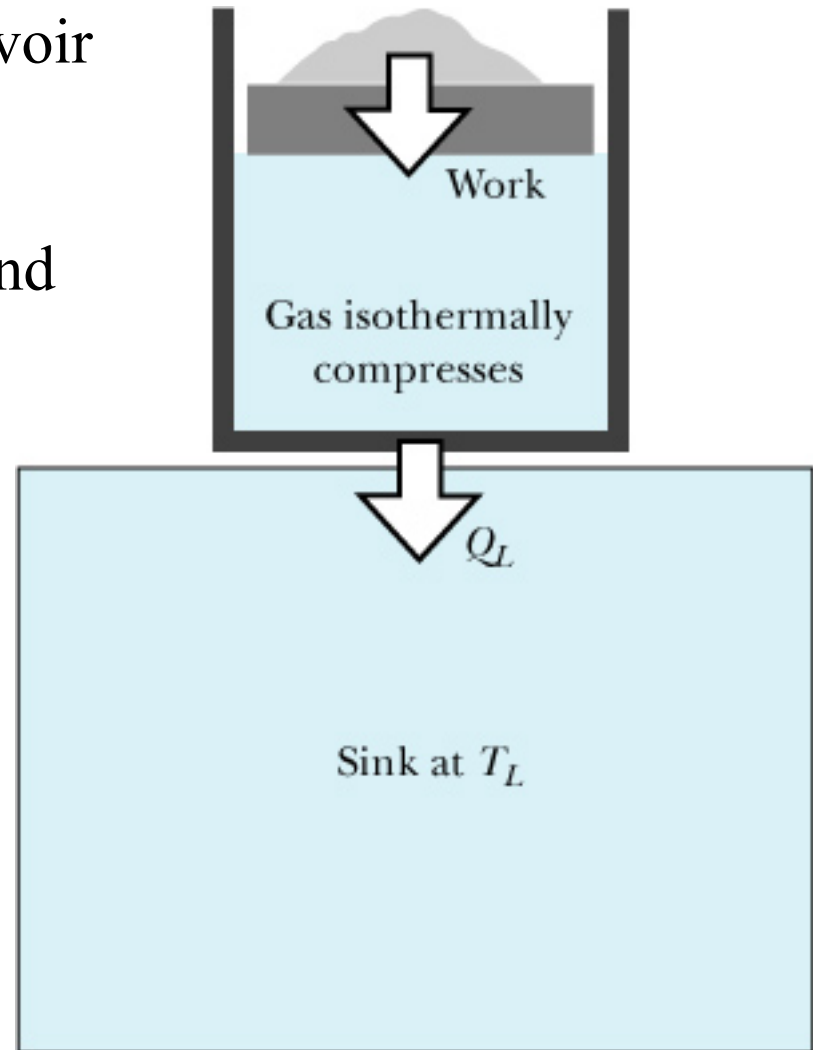
$$\text{Gas: } \Delta S_{\text{gas}} = -Q_H/T_{\text{gas}}$$

$$\text{but } T_L \approx T_{\text{gas}}$$

$$\text{Therefore } \Delta S_U \approx 0$$

No change in energy of the gas.

$$\text{All energy went into work } W_{\text{on gas}} = +Q_L$$



## Adiabatic compression heats gas to $T_H$

No thermal contact with cold reservoir.

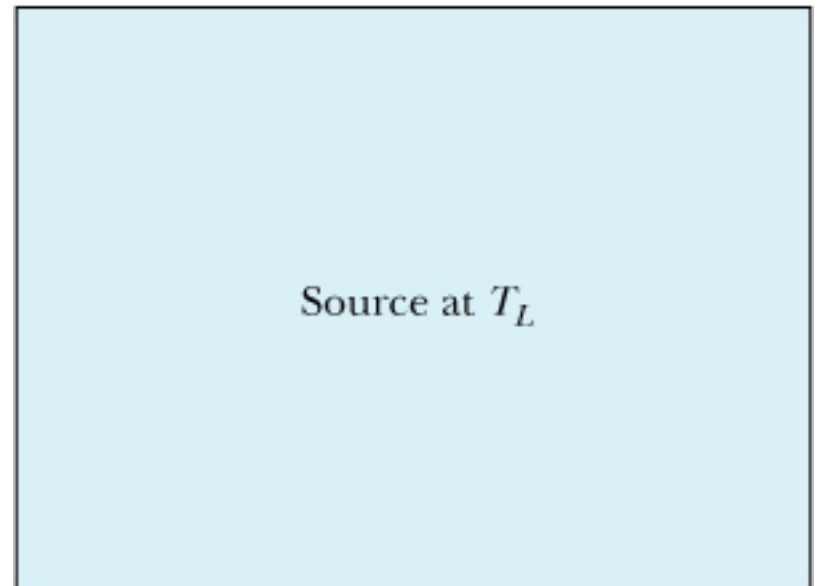
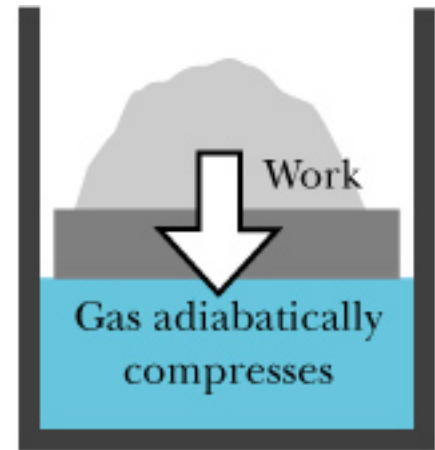
Allow reversible adiabatic compression by sliding some more sand on slowly.

$$Q = 0 \text{ so } \Delta S = 0.$$

Work done on gas  $W_{\text{on gas}} > 0$

Gas warms to  $T_{\text{gas}} \approx T_H$

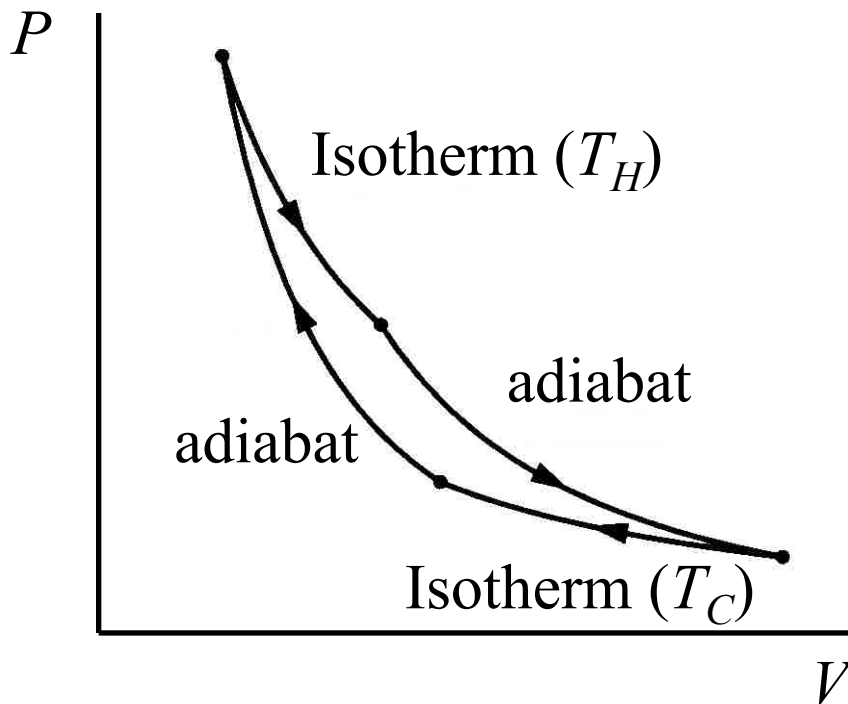
Was there net work done over the whole cycle?



# Carnot Cycle

The four steps of a Carnot cycle:

- ... **isothermal expansion** at  $T_H$  while absorbing heat
- ... **adiabatic expansion** to  $T_C$
- ... **isothermal compression** at  $T_C$  while expelling heat
- ... **adiabatic compression** back to  $T_H$ .



Net work done on gas

$$W_{\text{on gas}} = -\oint P dV$$

Work done by gas  
equals enclosed area.

## Entropy change in one cycle of a reversible engine

Engine is reversible, so  $\Delta S_U = 0$

After one cycle, gas returns to initial state.

Entropy  $S$  is a state function,  $\Delta S_{\text{gas}} = 0$ .

$$\Delta S_U = \Delta S_H + \Delta S_L + \Delta S_{\text{gas}}$$

$$0 = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} + 0$$

$$\therefore \frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

## Energy change in one cycle of a reversible engine

Heat into gas  $Q_H - Q_L$

Work done by surroundings  $W$

Apply conservation of energy

$$\Delta E_{\text{engine}} = Q_H - Q_L + W$$

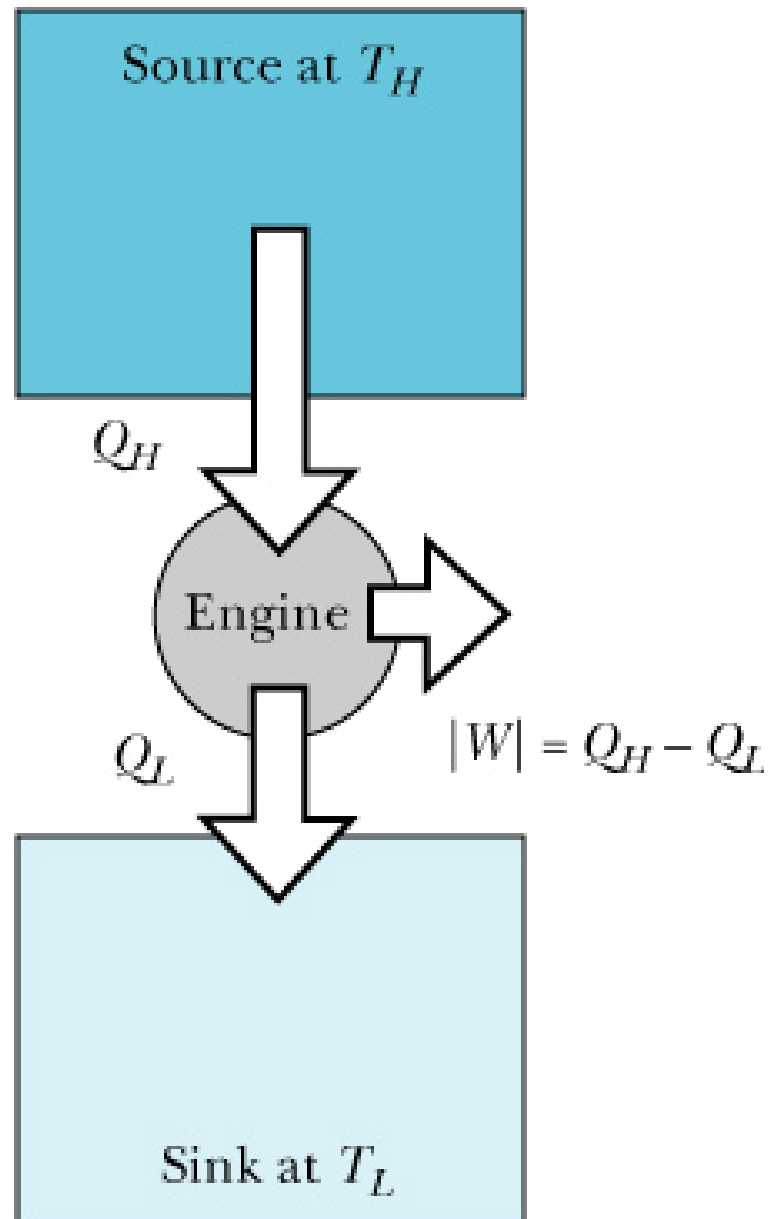
$$Q_H = \left( \frac{T_H}{T_L} \right) Q_L > Q_L$$

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

$$W_{\text{on gas}} = Q_L - Q_H < 0$$

Engine does work

$$W = -W_{\text{on gas}} = Q_H - Q_L$$



## Efficiency of a reversible engine

Define efficiency  $\varepsilon = \frac{|W|}{Q_H} = \frac{Q_H - Q_L}{Q_H}$

$$= 1 - \frac{Q_L}{Q_H} = 1 - \frac{T_L}{T_H}$$

Efficiency does not depend on details, only on input and output temperatures.

Less than 100 % efficient since we have to reject heat.

This wastes heat  $Q_L \propto T_L$  .

Best to use a big  $T_H$ .



## No other engine can be more efficient

Proof by contradiction.

Assume an engine has efficiency more than  $\varepsilon = 1 - \frac{T_L}{T_H}$

Run between  $T_H$  and  $T_L$ .

Then for same  $Q_H$ ,  $Q_L$  is less.

$$\text{Then } \Delta S_U = \frac{-Q_H}{T_H} + \frac{+Q_L}{T_L} < 0$$

... is in violation of second law of thermodynamics.

Thus no engine of greater efficiency than  $\varepsilon$  can exist.

The maximum efficiency is  $\varepsilon_{\max} = 1 - \frac{T_L}{T_H}$

## Real engines are less efficient

Real processes are irreversible, so  $\Delta S_U \rightarrow 0$

$$\Delta S_U = \frac{-Q_H}{T_H} + \frac{+Q_L}{T_L} > 0$$

$$\frac{Q_L}{Q_H} > \frac{T_L}{T_H}$$

$$\varepsilon_{\text{ir}} = \frac{|W|}{Q_H} = \frac{Q_H - Q_L}{Q_H}$$

$$= 1 - \frac{Q_L}{Q_H} < 1 - \frac{T_L}{T_H} < \varepsilon_{\text{max}}$$

## Running engine backwards: refrigerator

Disconnect from hot reservoir at  $T_H$ .

Adiabatic expansion, cooling to  $T_L$ .

Connect to cold reservoir at  $T_L$ .

Isothermal expansion,  $Q_L$  goes in.

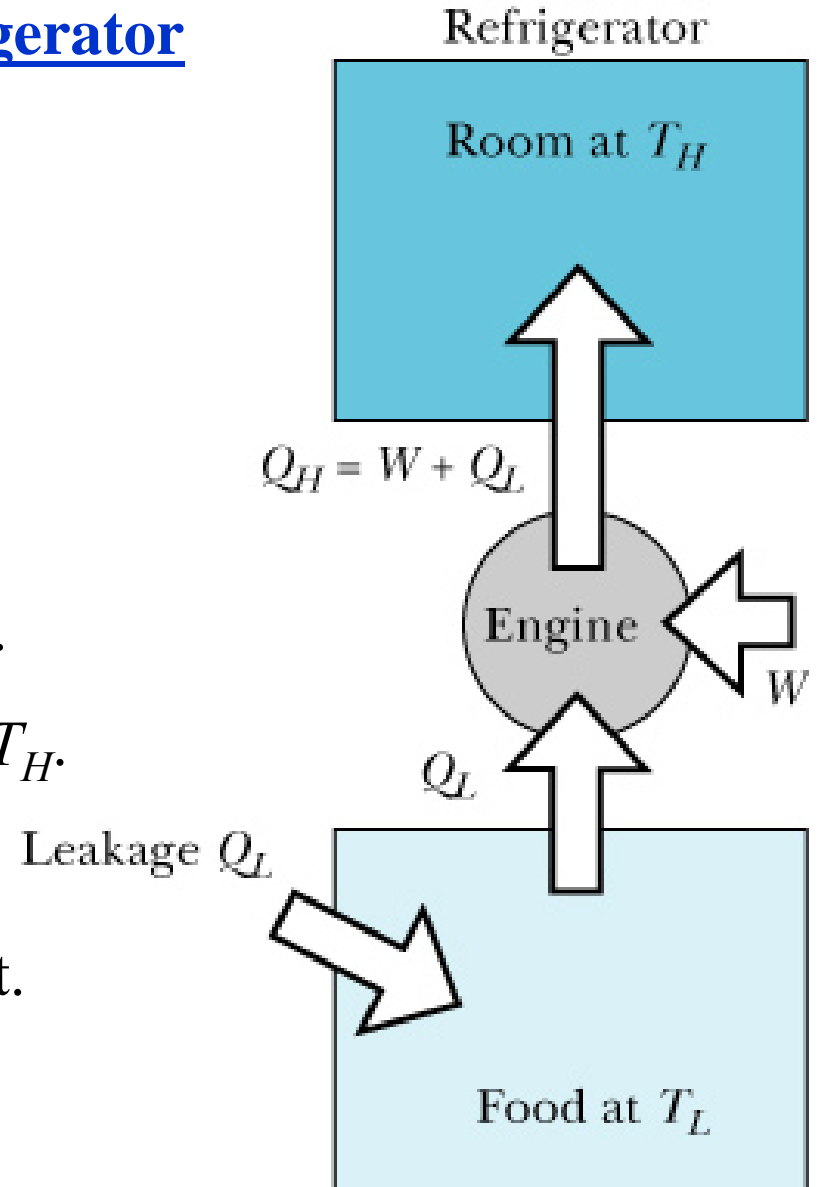
Disconnect from cold reservoir at  $T_L$ .

Adiabatic compression, warming to  $T_H$ .

Connect to hot reservoir at  $T_H$ .

Isothermal compression,  $Q_H$  goes out.

We do work  $W$  on the gas.



## The refrigerator

Energy conservation

$$0 = W + (Q_L - Q_H)$$

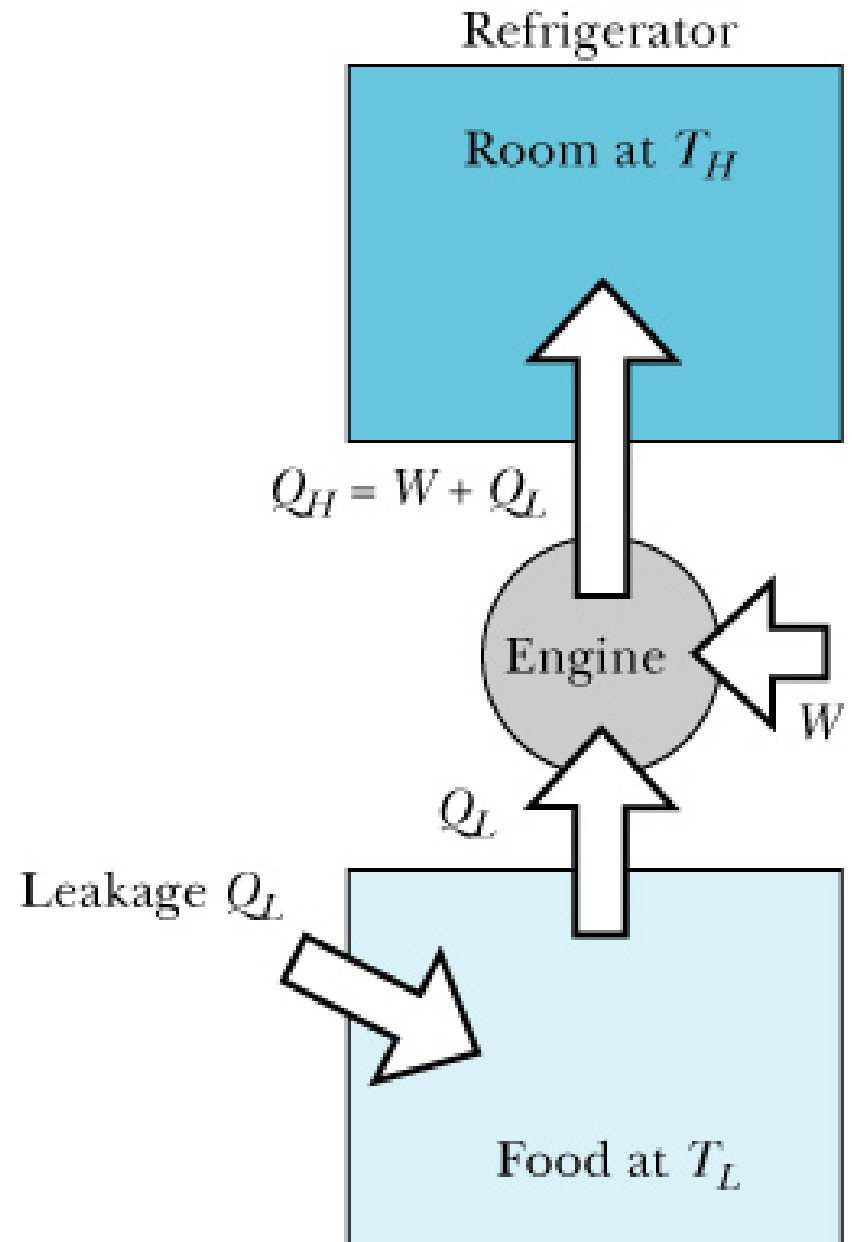
If reversible, so  $\Delta S_U = 0$

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Heat removal “efficiency”

$$\frac{Q_L}{W} = \left( \frac{T_H}{T_L} - 1 \right)^{-1} > 1$$

We simply moved the energy.



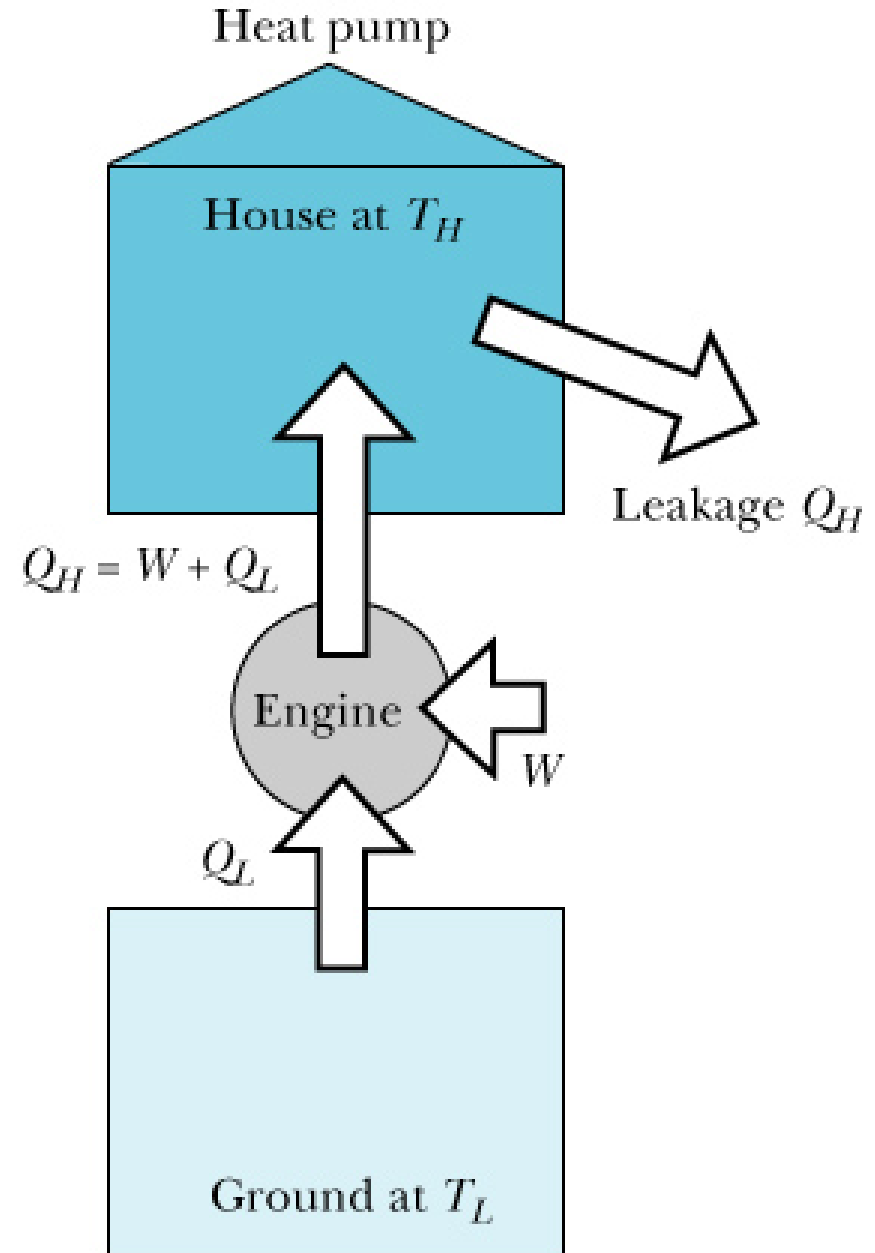
## The heat pump

Same as the refrigerator, but we want to be warm!

Heat arrival “efficiency”

$$\frac{Q_H}{W} = \left(1 - \frac{T_L}{T_H}\right)^{-1} > 1$$

We simply moved the energy.



## Why don't we attain theoretical efficiency?

Friction? No. Minimized by good design, lubrication.

To reduce entropy increase, need small temperature difference between parts of the machine.

Recall:

$$\frac{dQ}{dt} = \dot{Q} = \sigma A \left( \frac{T_H - T_L}{L} \right)$$

... length  $L$ , cross sectional area  $A$  and thermal conductivity  $\sigma$ .

$$\dot{Q} \rightarrow 0 \quad \text{as} \quad (T_H - T_L) \rightarrow 0$$

Machine is slow ...

... in fact, infinitely slow for a perfectly reversible cycle.

## Efficiency of a non-reversible engine

If hot reservoir is connected,  
engine is at  $T_1$ .

If cold reservoir is connected,  
engine is at  $T_2$ .

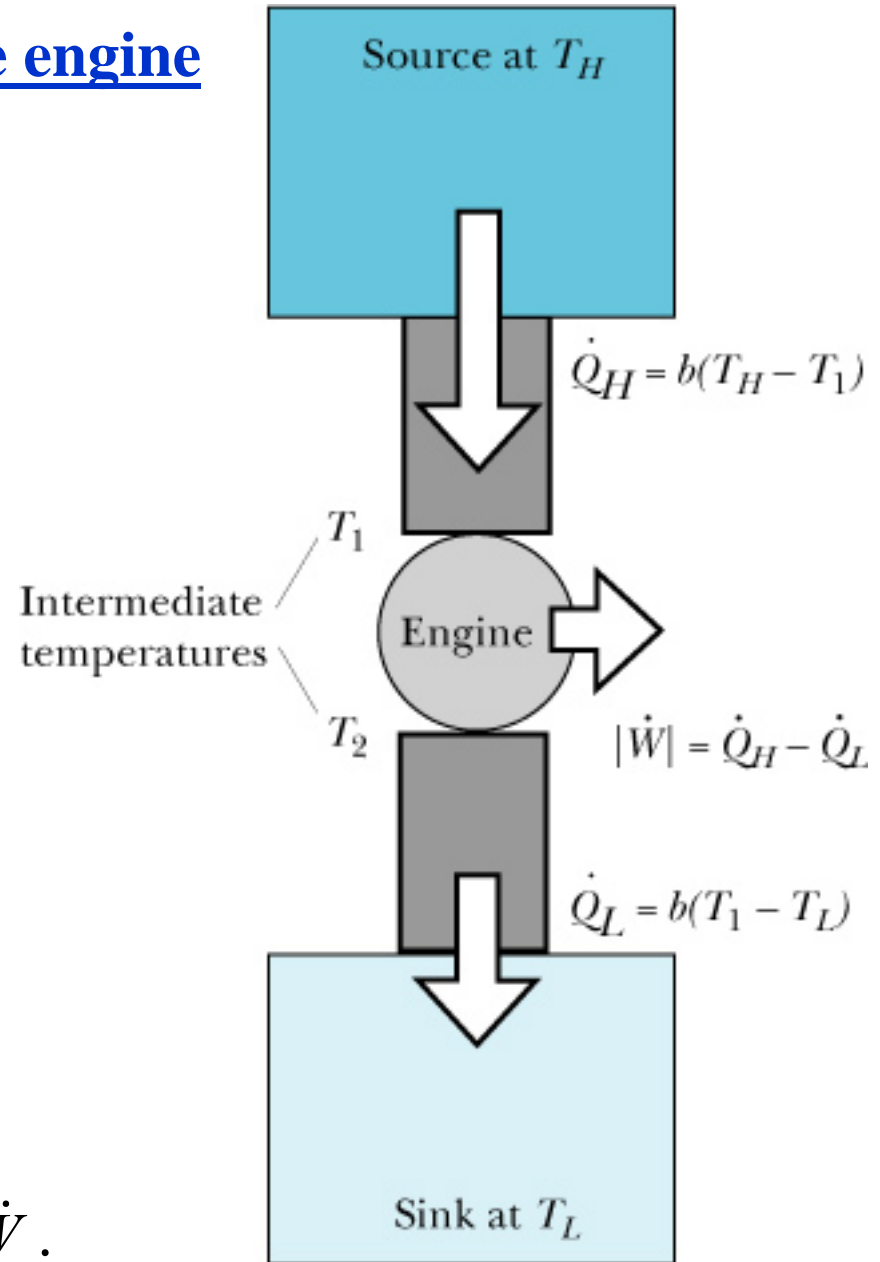
$$\frac{dQ}{dt} = \dot{Q} = \sigma A \left( \frac{T_H - T_L}{L} \right)$$

Write  $\dot{Q}_H = b(T_H - T_1)$   
 $\dot{Q}_L = b(T_2 - T_L)$

Energy conservation gives

$$\dot{Q}_H = \dot{W} + \dot{Q}_L$$

Choose  $b$  to maximize power  $\dot{W}$ .



# There must be maximum power output

(i) Reversible

$$T_1 = T_H \quad \text{and} \quad T_2 = T_L$$

$$\text{Very slow } \dot{W} = 0$$

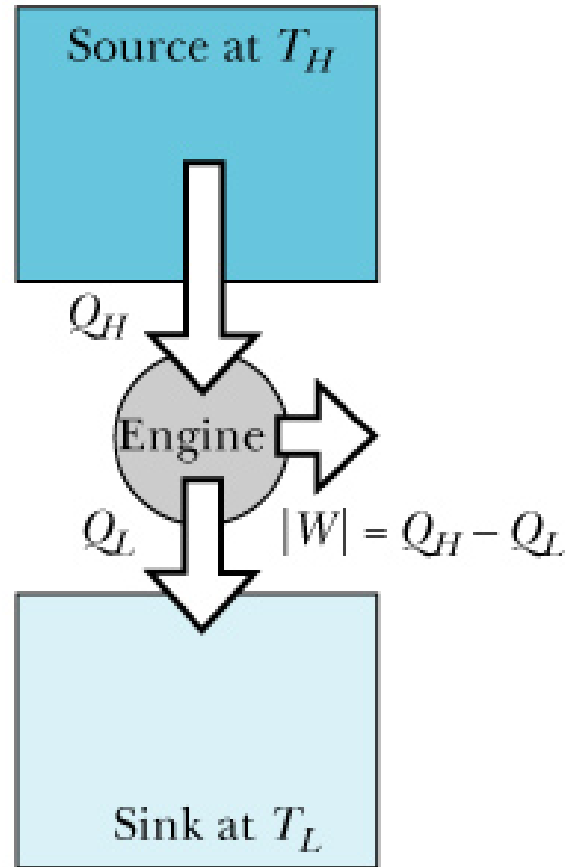
(ii)  $T_1 \approx T_2$  then  $\dot{Q}_H \approx \dot{Q}_L$   
and again  $\dot{W} = 0$

Somewhere between these two extreme designs ... can find the maximum output power.

Can show that the efficiency of a maximum power engine

$$\frac{\dot{W}}{\dot{Q}_H} \leq 1 - \sqrt{\frac{T_L}{T_H}}$$

(i)  
Very slow; no input  
or output power

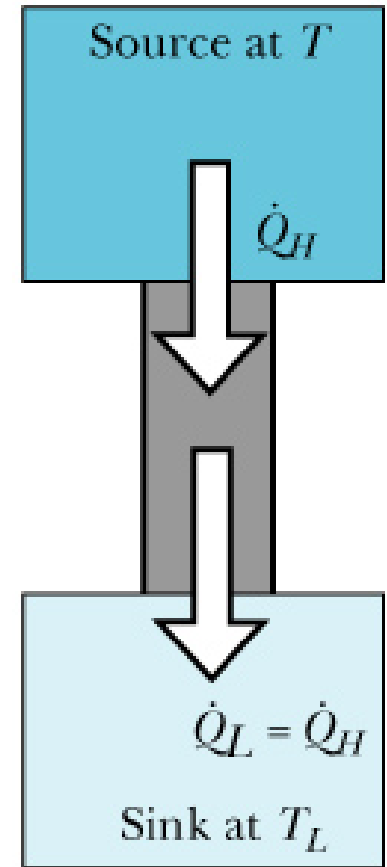


$$\dot{Q}_H = 0$$

$$\dot{Q}_L = 0$$

$$|\dot{W}| = 0$$

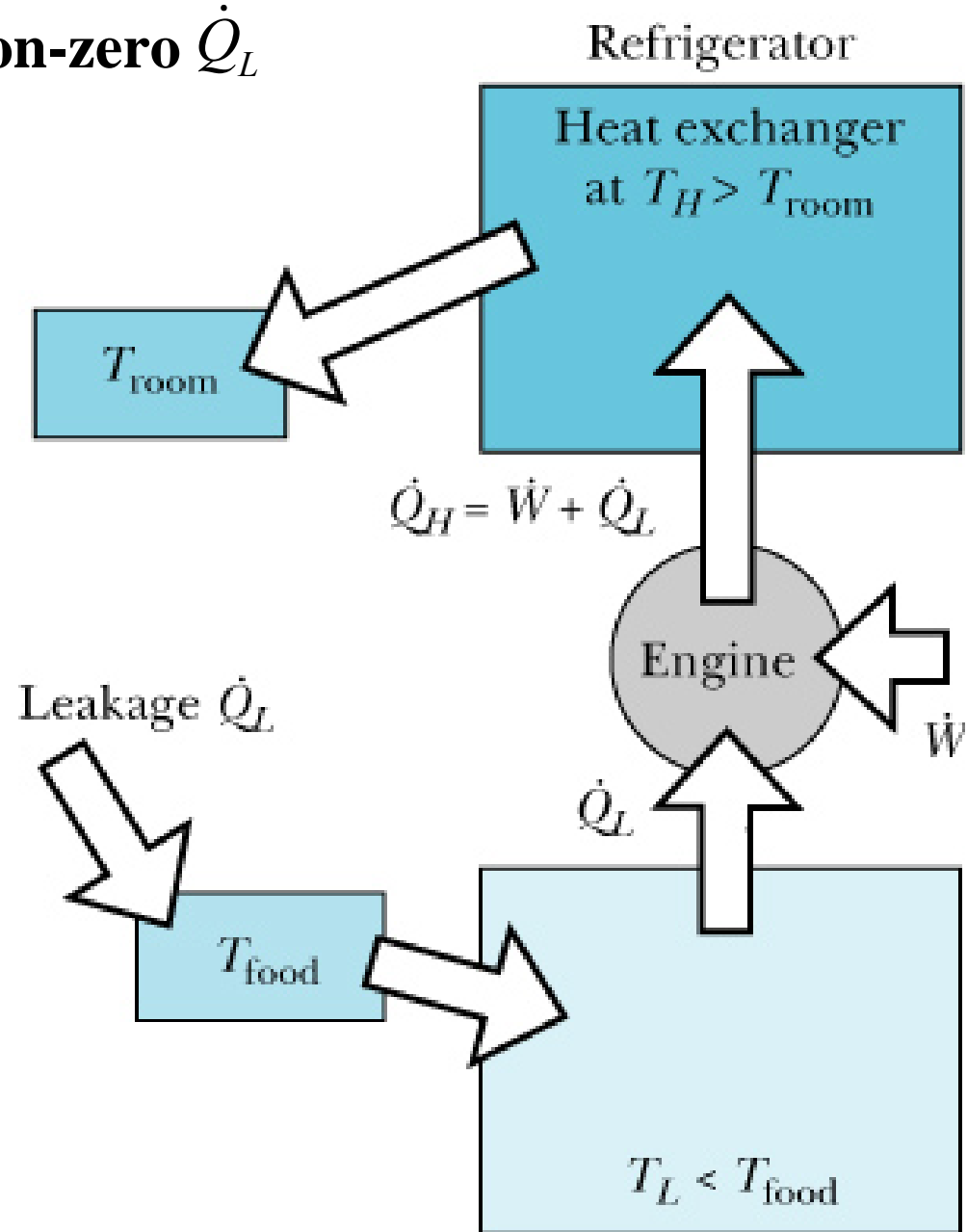
(ii)  
Straight connection;  
no output at all!



$$|\dot{W}| = 0$$



# Refrigerator with non-zero $\dot{Q}_L$



# Heat pump with non-zero $\dot{Q}_H$

