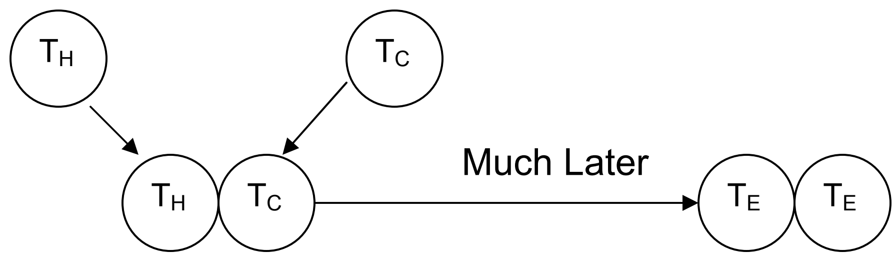
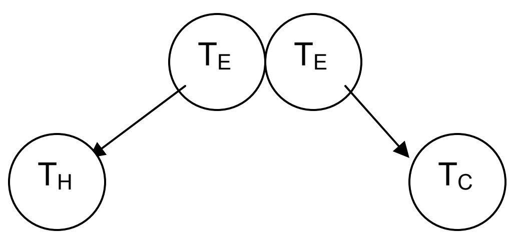
Second Law of Thermodynamics

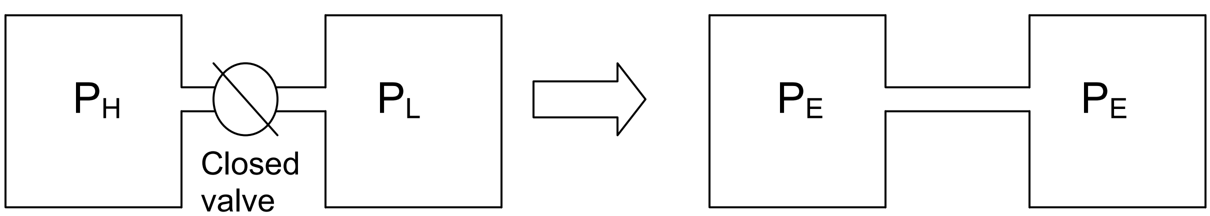
It is an observed fact that certain processes can only proceed spontaneously in one direction (hot coffee gets colder)



The following does not occur

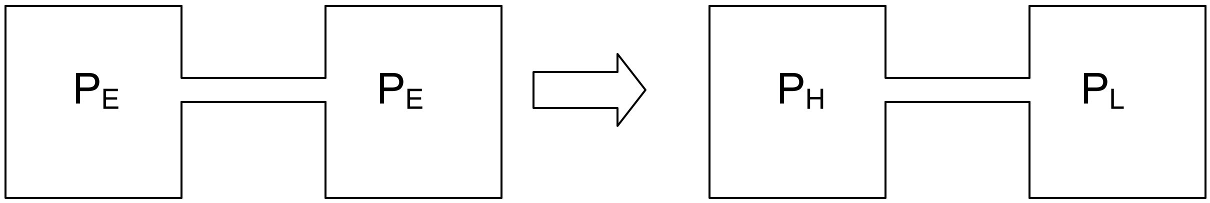


Another example, connecting high pressure tank with a low pressure tank:



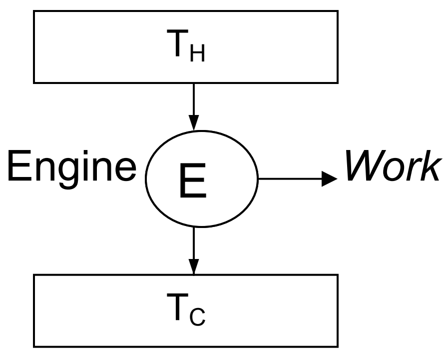
where P_E is the final pressure

The following does not occur:



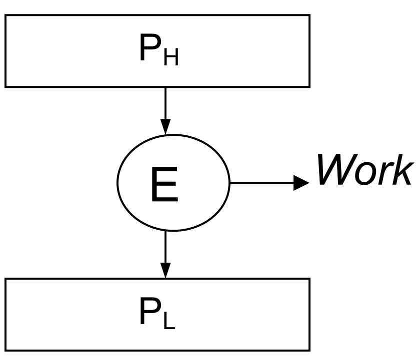
In both cases there is a possibility for doing work using an **engine**.

Example 1:



Such an engine can take heat from the hot body to form steam and then direct the steam through a turbine

Example 2:



Such an engine can direct the gas stream directly through a turbine

The question that arises is how much work can be done, i.e., what is the maximum work produced by the engine?

The evolution of the Second Law

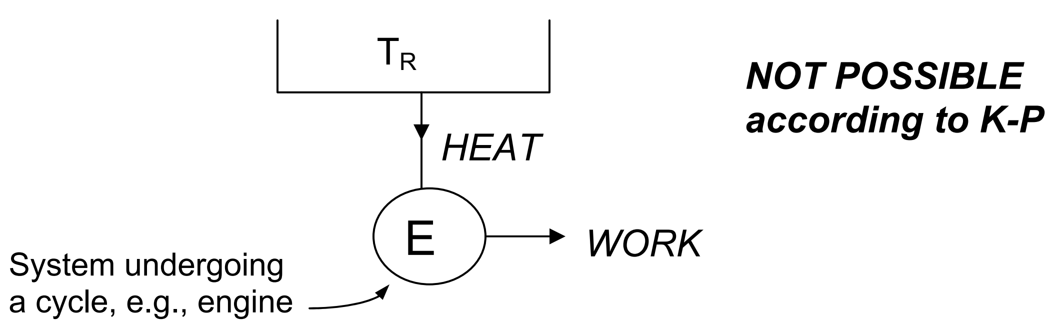
The First Law of Thermodynamics is used to calculate end states of a system as it evolves, it does not answer the following questions:

1) In what direction does a spontaneous process go
2) What is the maximum possible work

The Second Law of Thermodynamics starts with a simple principal concerning the direction of heat flow and evolves into developing a new property called **entropy** (S)

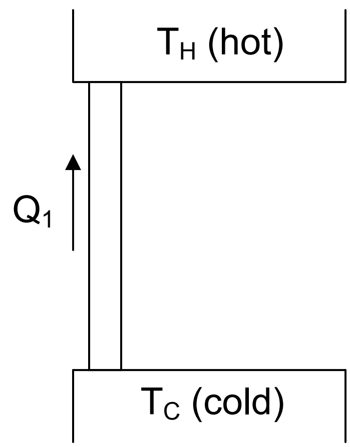
<u>Clausius Statement</u>
It is *impossible* for a system to operate in such a way that the sole result is the transfer of heat from a cold to a hot body

<u>Kelvin Planck Statement</u>
It is *impossible* for a system that operates in a cycle to generate work while transferring heat with a single **reservoir**



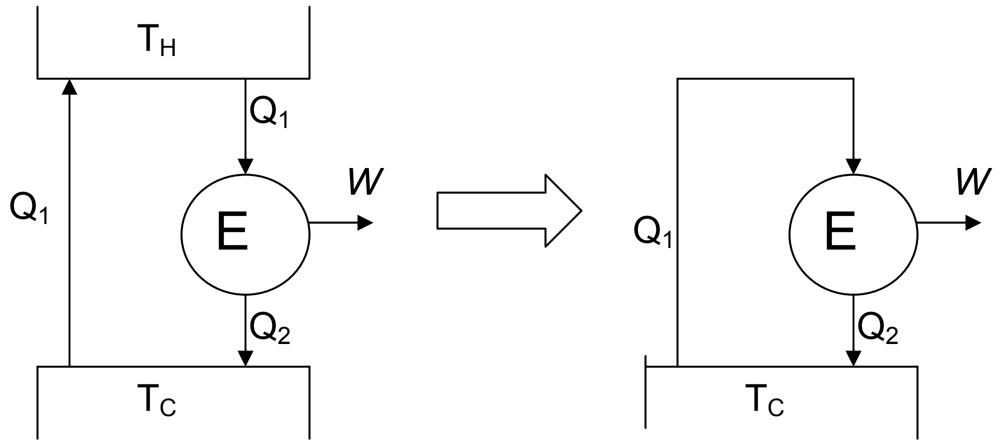
Recall, a reservoir is a body that has so much thermal capacity that its temperature doesn't change when heat transfer occurs

To illustrate the equivalence of the two statements consider the following:

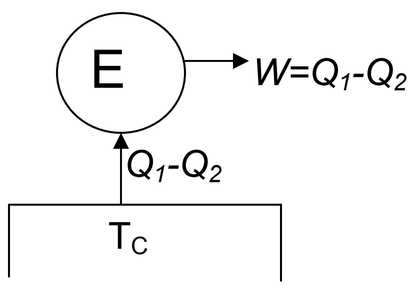


Connect two thermal reservoirs with high thermal conductivity metal and assume Q_1 heat flows from T_C to T_H which according to Clausius is *not* possible

Then place a heat engine between T_H and T_C that draws Q_1 heat from the T_H reservoir and dumps Q_2 heat to the T_C reservoir



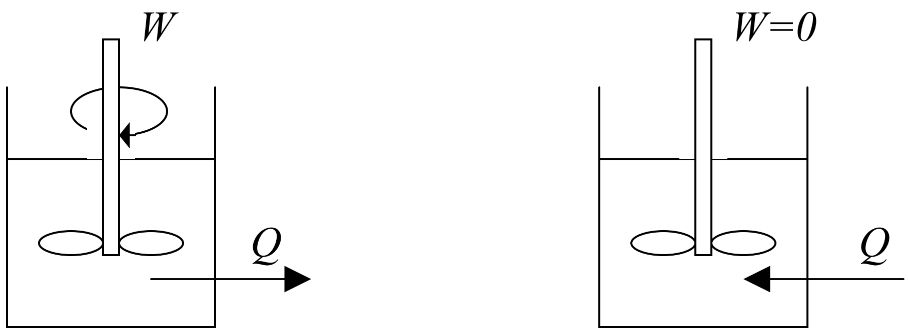
This is quivalent to



This engine takes heat from one reservoir (T_c) to produce work → this is *not* possible according to K-P statement and thus demonstrating the equivalency of the two statements

Heat Engines

Work can easily be converted to heat and other forms of energy, but converting heat into work is not so easy

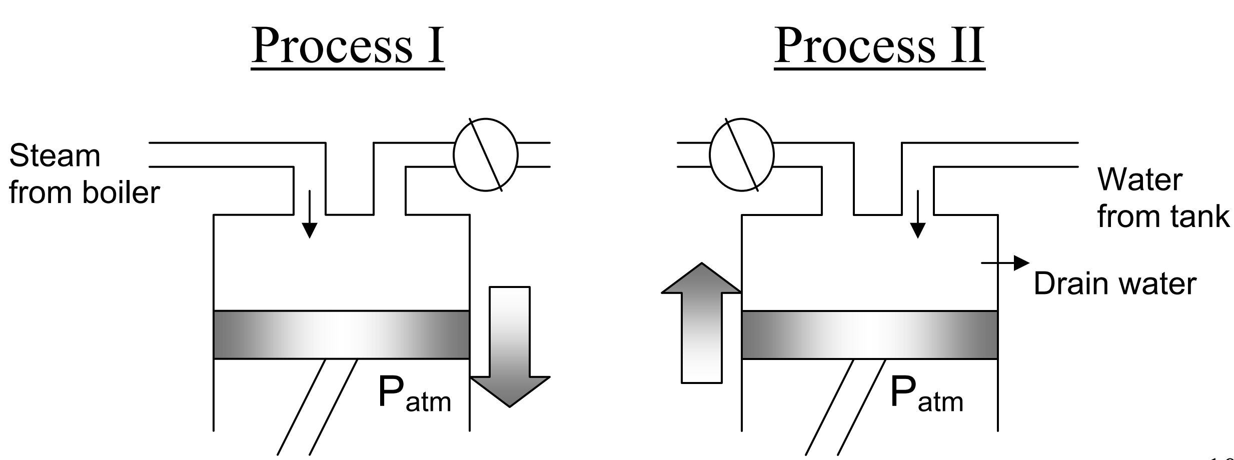


Converting heat into work requires a heat engine

Earliest heat engine operated on steam:

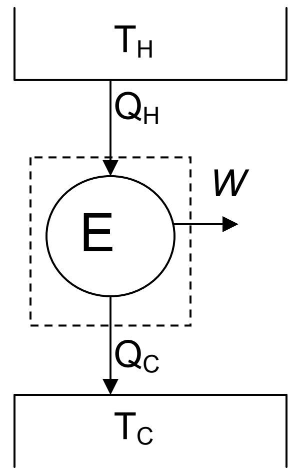
Process I - add steam into the piston-cylinder to raise the pressure above atmospheric pressure and thus push the piston down

Process II - add water to condense the steam and lower the pressure below atmospheric pressure so the piston is "pulled" back up



Thermal Efficiencies

Basic characteristics of heat engine are:



1) Receive heat, Q_H, from a high temperature source

2) Convert part of this heat to work, W

3) Reject the remaining waste heat, Q_C, to a low temperature sink

4) Operate on a cycle

These devices involve a working fluid to and from which heat is transferred

First Law applied to the heat engine cycle yields

$$\cancel{\Delta E} = Q_{net} - W$$
$$0 = (Q_{in} - Q_{out}) - W$$
$$0 = (Q_H - Q_C) - W \qquad \therefore W_{\substack{heat\\engine}} = Q_H - Q_C$$

The efficiency of the cycle is defined as

$$\eta_{\substack{heat\\engine}} = \frac{\text{work done}}{\text{maximum work}} = \frac{W}{W_{MAX}}$$

Maximum possible work corresponds to

$Q_C = 0 \rightarrow \quad W_{MAX} = Q_H$ therefore,

$$\eta_{\substack{heat\\engine}} = \frac{W}{Q_H}$$

Thermal efficiency is the ratio of the work done and the heat input, substituting for W

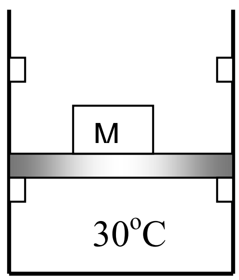
$$\boxed{\eta_{\substack{heat\\engine}} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}}$$

For an internal combustion (IC) engine heat is supplied by combustion Q_H and heat rejected through the exhaust Q_C, typically the thermal efficiency of combustion is around 30%

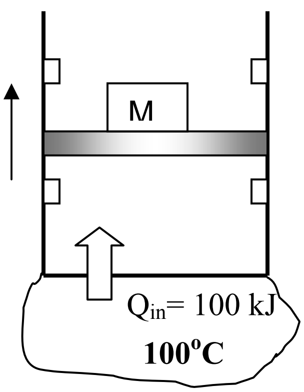
Other engine mechanical inefficiencies translate into an even lower overall efficiency

$$\eta_{\substack{overal\\ICengine}} = \eta_{combustion}\eta_{mechanical}$$

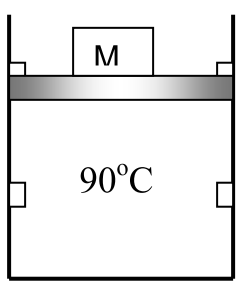
Can we have a 100% thermally efficient engine?
Consider the following simple heat engine designed to lift a weight of mass M



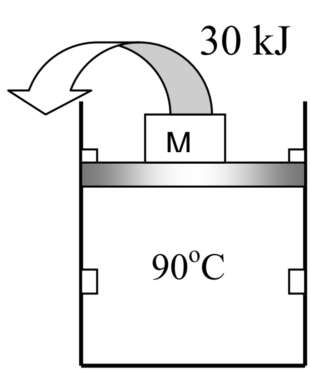
Engine consists of a frictionless, adiabatic piston-cylinder device with two sets of stops and weight placed on the piston. Initial temperature of the gas is 30°C



Add 100 kJ of heat Q to the gas from a source at 100°C
- gas heats up
- gas expands raising the piston

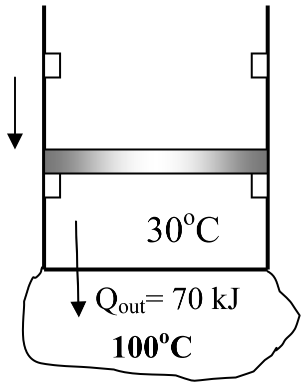


$Q = W + \Delta U$
- heat goes into work done, W, to raise the piston → this results in a PE increase of the mass (say 30 kJ)
- the remaining 70 kJ goes into increasing the temperature of the gas

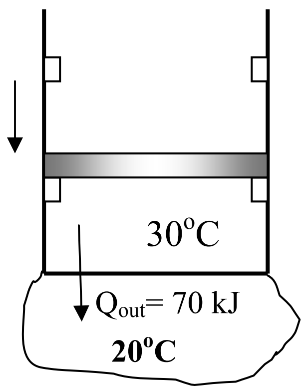


Load is removed and gas temperature is 90°C
* Even under ideal conditions (frictionless and adiabatic) more heat added than work done

To complete the cycle, cool the gas back to 30^{o}C



For 100% efficiency the 70 kJ excess energy added to the gas must be returned to the 100^{o}C source for later use
→ results in heat flow from cold to hot, *Clausius statement says not possible*



Must transfer heat to colder reservoir, say 20^{o}C, to drop temperature back to 30^{o}C
70 kJ excess energy rejected

This energy cannot be re-used in the cycle because the lowest working fluid temperature is 30^{o}C → **waste energy**

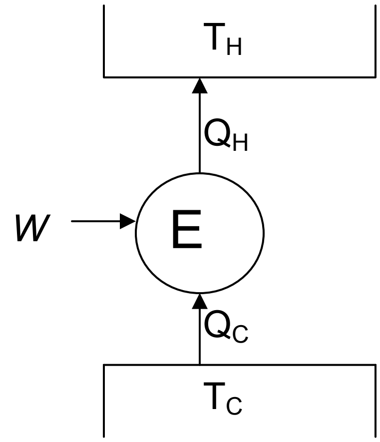
We can conclude that every heat engine must waste some energy by transferring it to a low-temperature reservoir in order to complete the cycle, even under idealized conditions

This is consistent with the Kelvin Planck statement

Refrigerators

A refrigerator takes heat from a hot reservoir (hot room) and dumps it into a cooler reservoir (cooler outdoors).

The refrigeration cycle is the opposite of the heat engine requiring work input



Note: this is *not* inconsistent with Clausius' statement because the heat transfer from the cold to the hot reservoir is not spontaneous.

Applying First Law to the refrigeration cycle

$$\cancel{\Delta E} = Q_{net} - W$$

$$0 = (Q_{in} - Q_{out}) - (-W)$$

$$0 = (Q_C - Q_H) + \mathrm{W} \qquad \therefore W_{refr} = Q_H - Q_C$$

Coefficient of performance (COP) β defined as

$$\beta = \frac{\text{heat removed}}{\text{work done}} = \frac{Q_C}{W_{refr}} = \frac{Q_C}{Q_H - Q_C}$$

Typical values of β are 3-4

Reversible and Irreversible Processes

Have shown that no engine can have 100% efficiency, the question becomes what is the maximum efficiency a heat engine can achieve?

The maximum efficiency will correspond to a cycle consisting of a series of idealized **reversible** processes

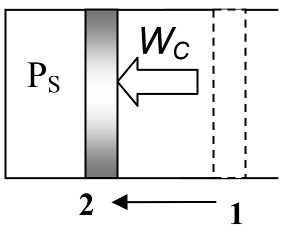
A reversible process is one which the system and its surroundings can be returned to their respective original states at the end of the reverse process

If the system and surroundings cannot be returned to their respective original states the process is termed **irreversible** and the process is said to involve **irreversibilities**.

A process is **internally reversible** if no irreversibilities occur inside the system boundary, irreversibilities may occur outside the system

Demonstrating Irreversibilities via the 2nd Law

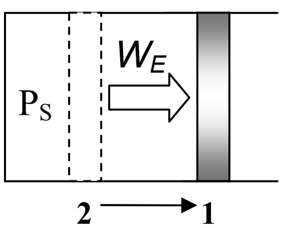
1) Consider quasi-equilibrium adiabatic *compression* (system pressure P_S is uniform and $P_S V^k = const.$)



$$\Delta U_C = \cancel{Q} - W_C$$

$$W_C = \int_1^2 P_S dV = const \int_1^2 \frac{1}{V^k} dV = \frac{P_2V_2 - P_1V_1}{1-k}$$

The reverse quasi-equilibrium adiabatic *expansion* (system pressure P_S is uniform and $P_S V^k = const.$)



$$\Delta U_E = \cancel{Q} - W_E$$

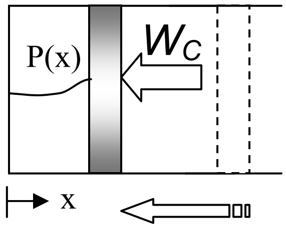
$$W_E = \int_2^1 P_S dV = const \int_2^1 \frac{1}{V^k} dV = \frac{P_1V_1 - P_2V_2}{1-k}$$

$$W_C = -W_E \quad \Rightarrow \quad \Delta U_C = -\Delta U_E$$

When the piston is returned to the initial position:
1) the system IE is recovered, $\Delta U_{1\text{-}2} + \Delta U_{2\text{-}1} = 0$
2) the energy from the surroundings used to compress the gas is returned by the work done by the gas during expansion

Quasi-equilibrium compression and expansion processes are reversible

Consider rapid adiabatic compression (system pressure not uniform and thus $PV^k = const$ does not apply)



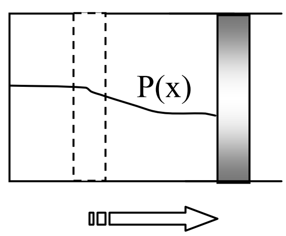
Pressure is higher at the piston face.

$$W_{\substack{rapid \\ compr}} = \int_1^2 P_{\substack{piston \\ face}} dV > W_{rev} = \int_1^2 P_S dV$$

$$\Delta U_C = \cancel{Q} - W_{\substack{rapid \\ compr}}$$

$$\Delta U_C > (\Delta U_C)_{rev}$$

The reverse rapid adiabatic expansion



Pressure is lower at the piston face

$$W_{\substack{rapid \\ \exp an}} = \int_2^1 P_{\substack{piston \\ face}} dV < W_{rev} = \int_2^1 P_S dV$$

$$\Delta U_E = \cancel{Q} - W_{\substack{rapid \\ \exp an}}$$

$$\Delta U_E < (\Delta U_E)_{rev}$$

More work done by the surrounding during rapid compression compared to the work done by the gas during rapid expansion

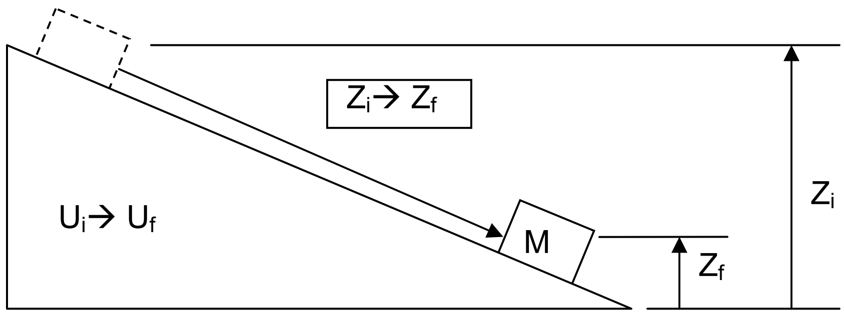
The increase in the gas IE during compression is greater than the gas IE decrease during expansion, $\Delta U_{1\text{-}2} > \Delta U_{2\text{-}1}$

The excess IE is equal to the work deficit of the surroundings

In order to return the system and the surroundings to their original states, 100% of the excess IE of the gas must be transferred to the surroundings in the form of work via a heat engine → *impossible according to K-P*

Rapid compression and expansion processes are irreversible

2) Consider a block sliding down an inclined plane



System includes the block and the inclined plane

Neglect heat transfer to surroundings, Apply First Law

$$(U_f - U_i) + Mg(Z_f - Z_i) + \cancel{(KE_f - KE_i)} = \cancel{Q} - \cancel{W}$$

$$\boxed{U_f - U_i = Mg(Z_i - Z_f)}$$

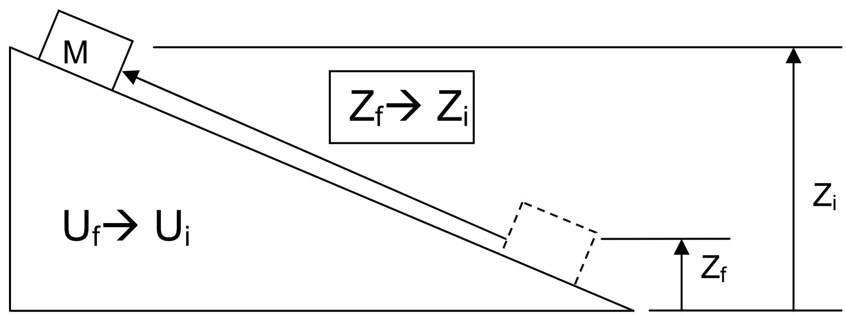
Friction between the block and the plane converts the PE of the block into internal energy of the system

Since there is no interaction between the system and the surroundings (i.e., Q= 0, W= 0) the state of the surroundings remain unchanged

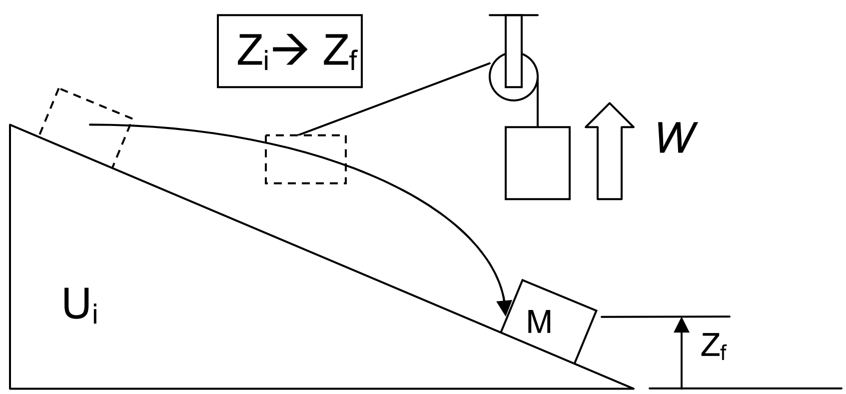
To show reversibility return the system to its initial state

Lets consider a cycle consisting of three processes:

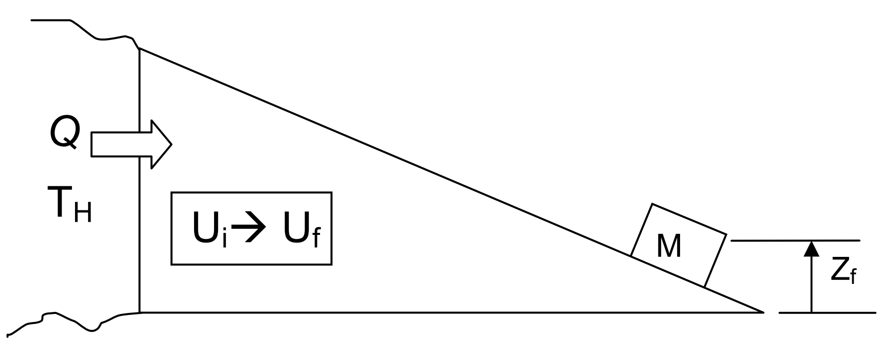
Process I: Reverse process of the original, *assume* it is possible to drag the block back to the initial height Z_i and recover initial internal energy U_i for the system



Process II: Lower the block to Z_f by a frictionless pulley generating work *W* equal to the drop in PE of the mass $Mg(Z_i - Z_f)$



Process III: Add heat *Q* of the amount equal to $U_f - U_i$ by contacting the inclined plane with a hot reservoir



At the conclusion of the cycle consisting of processes I, II, and III

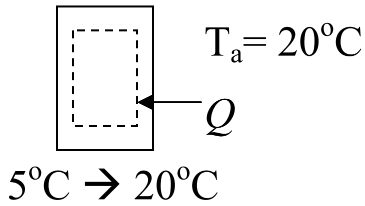
- the block is returned to the initial height Z_f
- the system (block and incline) returned to U_f

The net result of the cycle is to draw heat from a single reservoir and produce an equal amount of work, this is *impossible* according to K-P statement → Process I (assumed) is not possible

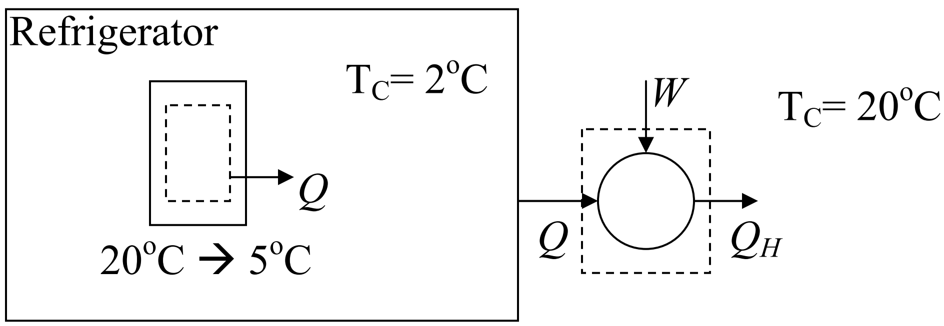
Since we can't return the system to the original state via Process I (reverse of the original process), the original process, from state i to state f, is irreversible

Any process involving friction is irreversible

3) Consider the heating of a soda can in a warm room



To restore the can to its original state of 5°C one needs to refrigerate the can, the refrigerator needs work input



Energy balance of the refrigerator yields $Q_H = Q + W$

The net heat returned to the surroundings Q_H is the heat from the can Q plus the work input to the refrigerator W thus the final IE of the surroundings is higher than the original IE by an amount equal to W

The only way to return the surrounding to the original IE is to use a heat engine to convert 100% of the excess IE into work used by the refrigerator

This is impossible according to K-P statement and thus the original process is irreversible

The source of the irreversibility in this case is the heat transfer across a finite temperature difference

Irreversibilities include:
- dry and fluid friction
- heat transfer through a *finite* temperature difference
- rapid compression and expansion of a fluid
- unrestrained expansion of a fluid
- spontaneous mixing of different gases

* All *real* processes include some irreversibility