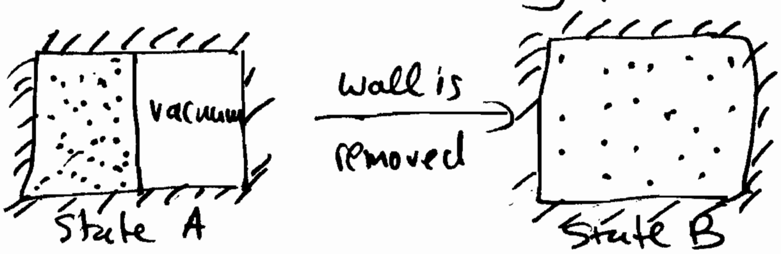
Reversible and Irreversible Processes

A process $A \to B$ is called <u>reversible</u> if the system can be brought back to the initial state A from the final state B with <u>no change</u> to any part of the universe.

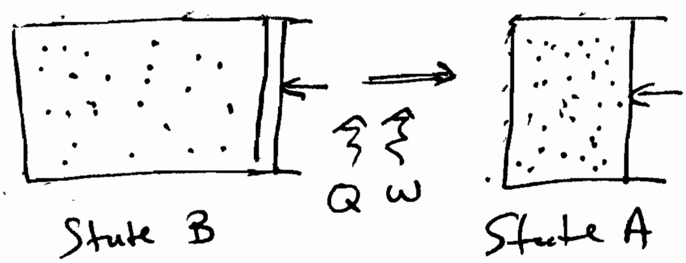
Consider the following process in a closed, isolated system:



$\Delta U = \cancel{Q} + \cancel{W} = 0 \Rightarrow$

$\Delta T = 0$ (for <u>ideal gases</u>)

Is this process reversible? We could attempt to reverse it by compressing the gas back to state A:



$\Delta U = Q + W = 0 \Rightarrow$

$Q = -W$

$\therefore$ need to remove heat equal to $-$(work input)

Clearly, this "reverse" process results in changes outside the system. However, if we could convert <u>all</u> the heat released back into work, the net change would be zero.

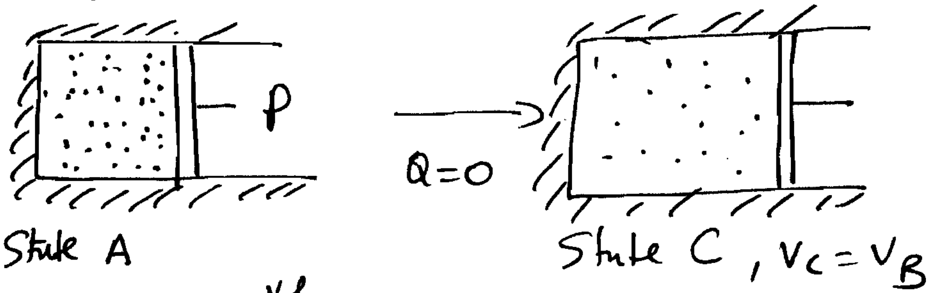
Many, many experiments have shown such complete conversion of heat into work to be <u>impossible.</u>

The original $A \to B$ process is <u>Irreversible</u>

<u>All</u> naturally occuring (spontaneous) processes

are irreversible.

Now consider a different process starting from the same state A, to state C, with $V_C = V_B$, using a well-lubricated, frictionless piston:



$\Delta U = W$

$dU = -PdV \Rightarrow$

$$\Rightarrow W = -\int_{V_i}^{V_f} PdV < 0 \quad \text{[work produced]}$$

For the reverse process from $C \to A$, exactly as much work is needed as that produced from $A \to C$.

The process is <u>reversible</u>.

In general, reversible processes require:

* no internal or external gradients of T, P, μ [$\mu \equiv$ chemical potential, to be defined later]
* no conversion of mechanical work into heat
* no friction
* infinite time and infinite patience

Irreversibilities in natural processes define a <u>direction</u> in time. Consider the three movies linked from the course web page:

m1 : breaking glass
m2 : protein-drug interaction
m3 : mixing/separation(?) of LJ fluids

} Can you tell when time is running backwards?

Second Law

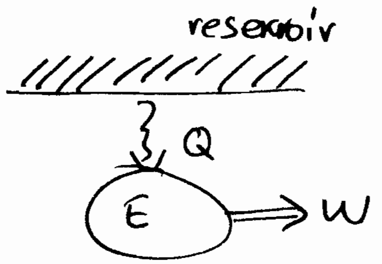
Makes the notion of spontaneous change rigorous, allowing predictions of processes that can/cannot occur naturally.

<u>Definitions</u> A "<u>heat reservoir</u>" is a large mass that can exchange heat with no change in T

<u>Heat Engines</u> are devices that exchange heat and work with their surroundings with no internal changes (e.g. a complete cycle of an int. comb. engine)

<u>Kelvin-Planck Postulate</u> (2nd Law)

It is not possible for a heat engine interacting with a <u>single</u> heat reservoir to convert <u>all</u> the heat transferred from the reservoir into work.



An impossible process "Perpetual Motion Machine of the 2nd kind"

[A Perp. Motion Machine of the 1st kind violates the first Law - e.g. (E) $\Longrightarrow$ w , also impossible]

One of several equivalent statements; cannot be proven but is confirmed by innumerable experiments.

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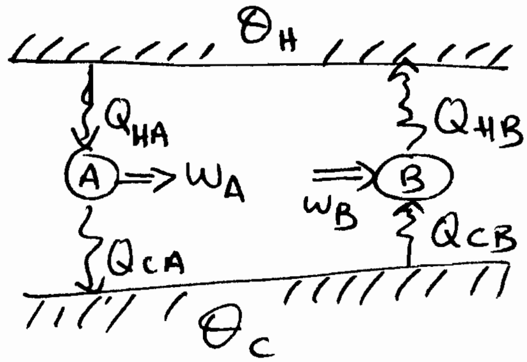
<u>What are the consequences?</u> Consider two engines:



A transfers heat from hot → cold, producing work

B transfers heat from cold → hot, requiring work

Both - in principle - permitted.

But some combinations of the two types could land us into trouble -

* Set $|Q_{CA}| = |Q_{CB}|$ by adjusting # of cycles or engine size

* Couple A to B

* Net process A+B: $W = |W_B| - |W_A|$

  $Q = |Q_{HA}| - |Q_{HB}| = -W$

If $W < 0$ (work produced)
$\Rightarrow Q > 0$ (heat absorbed) } impossible, violates postulate

$\therefore W \geq 0$ (work required)
$Q \leq 0$ (heat produced) } for <u>any</u> engines A and B

Now consider <u>reversible</u> engines A + B

$W = |W_B| - |W_A| \geq 0 \Rightarrow |W_B| \geq |W_A|$

Change labels, run in reverse

$\Rightarrow |W_A| \geq |W_B|$

$|W_A| = |W_B| \Rightarrow |Q_{HA}| = |Q_{HB}|$