

Spontaneous  
processes

First law of  
thermodynamics

# Content last lecture

- 0<sup>th</sup> law of thermodynamic
- Thermal equilibrium
- Temperature
- Reversibility

# Spontaneous processes

System in equilibrium with surroundings will remain unchanged.

If out of equilibrium it will spontaneously drive towards equilibrium

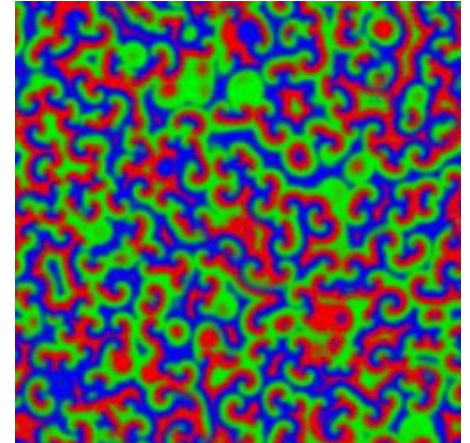
Reverse processes will NEVER occur

Need to apply external "force" to prevent this from happening or to drive system out of equilibrium

Spontaneous = irreversible

not a force  
per se but a "push"

So what happens in a Belousov-Zhabotinsky reaction?  
(see YouTube videos)



# Pitch drop experiment



Spontaneous  $\neq$  Instantaneous

# First law of Thermodynamics

The change in internal energy of a system,  $\Delta U$ , is equal to the work done on the system,  $\Delta W$ , plus the heat supplied to the system,  $\Delta Q$ .

standard  $\rightarrow$   $\Delta U = \Delta W + \Delta Q$  (for finite processes)  
 $dU = dW + dQ$  (infinitesimal processes)

$d \Rightarrow$  ~~func of state~~

This states the conservation of energy.

“Work” for a gas is  $(-p dV)$  but what is the general distinction between heat and work?

Example electrical heating:

the work  $dW = \mathcal{E} dq$  ( $\mathcal{E}$  is electromotive force,  $q$  is charge)

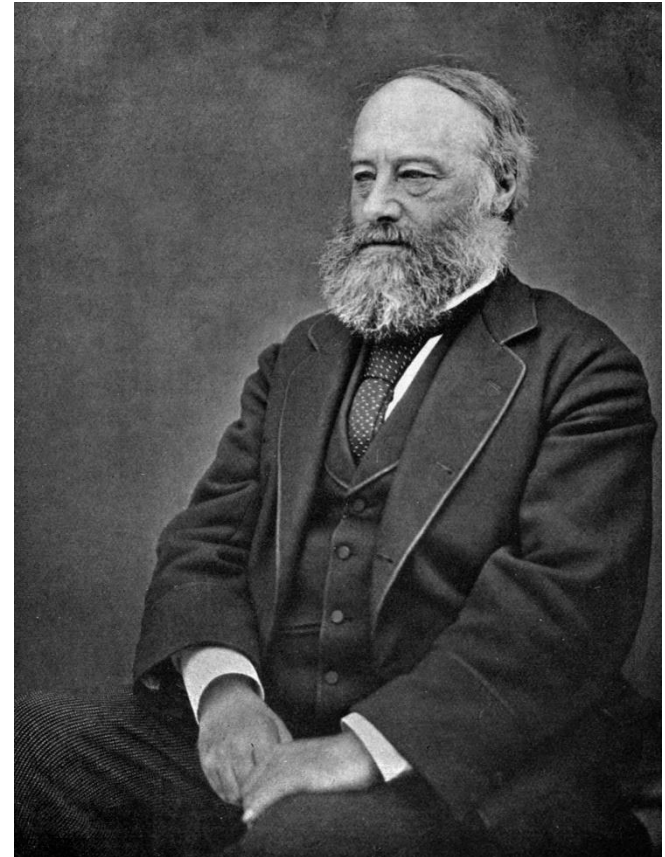
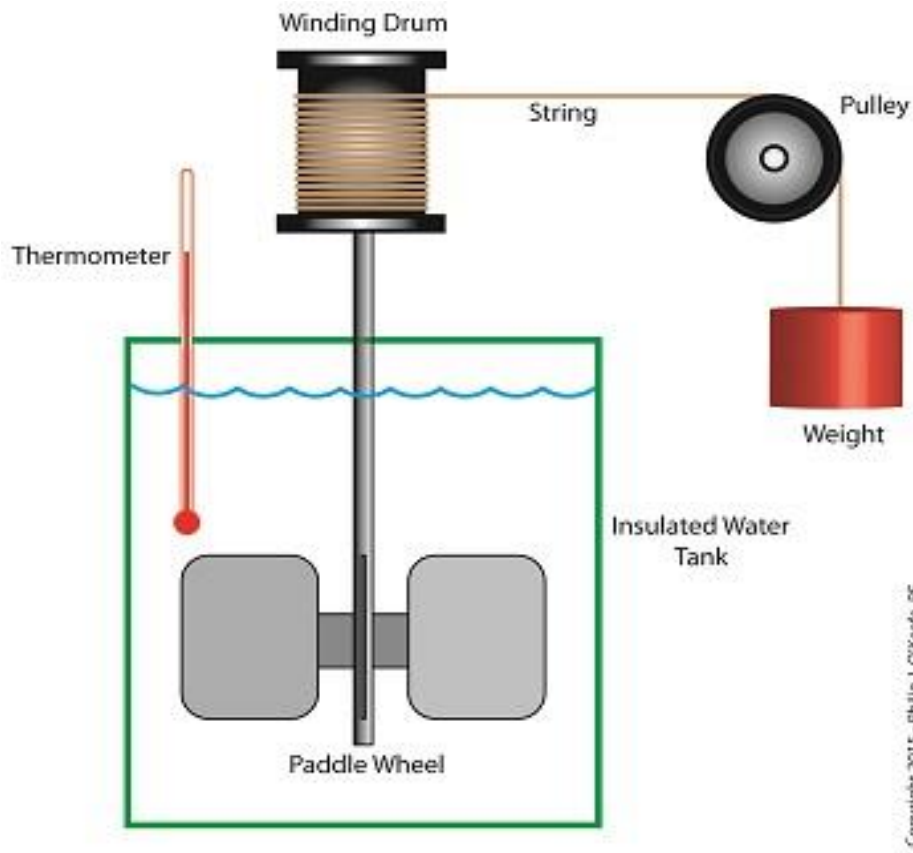
**work** = energy exchanged by transfer between direct macroscopic observables ( $p_1 V_1 \rightarrow p_2 V_2$ );

**heat** = energy exchanged directly between microscopic degrees of freedom of the system (microscopic work).

Pictures taken from Wikipedia

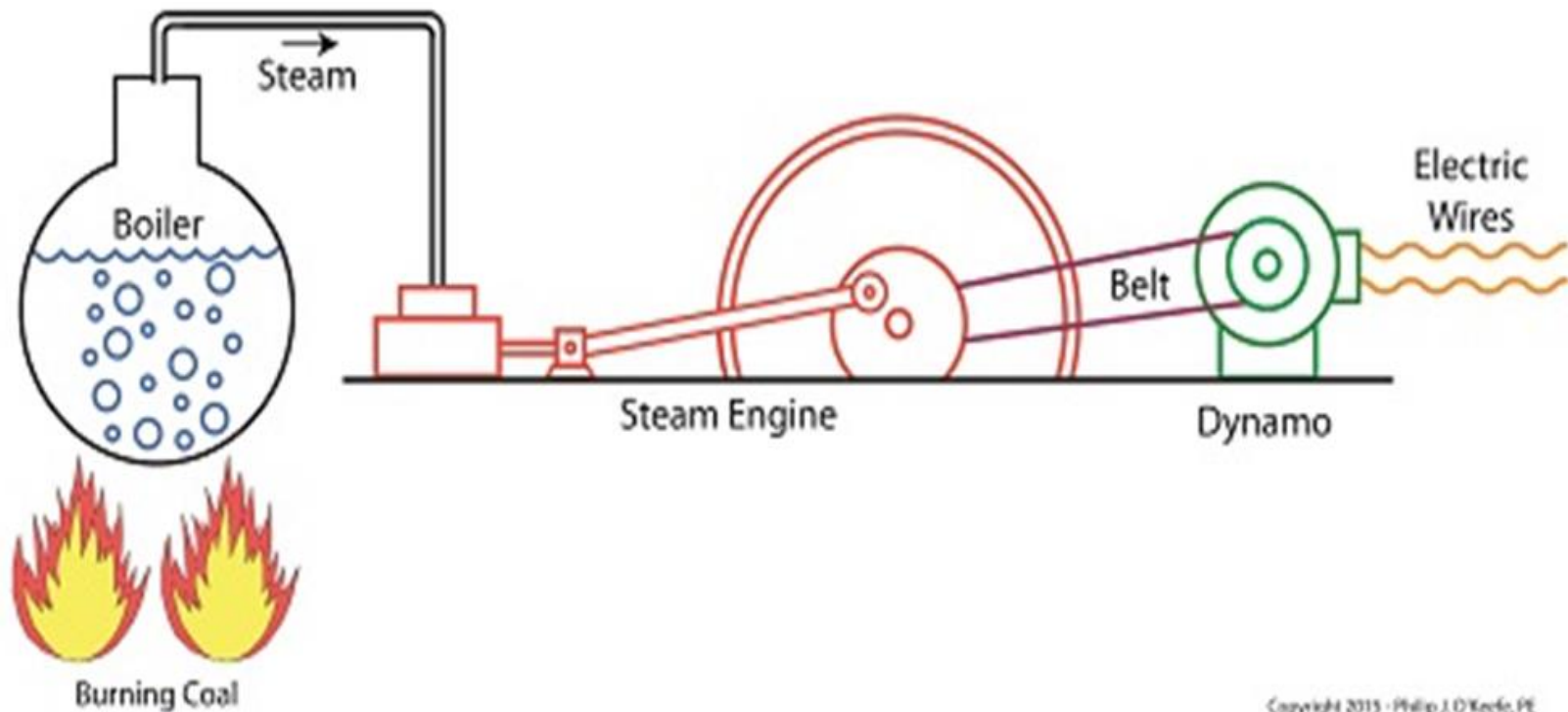
Energy can only be converted from one form into the other. It can never be created or destroyed.

Examples of 1<sup>st</sup> law in action:



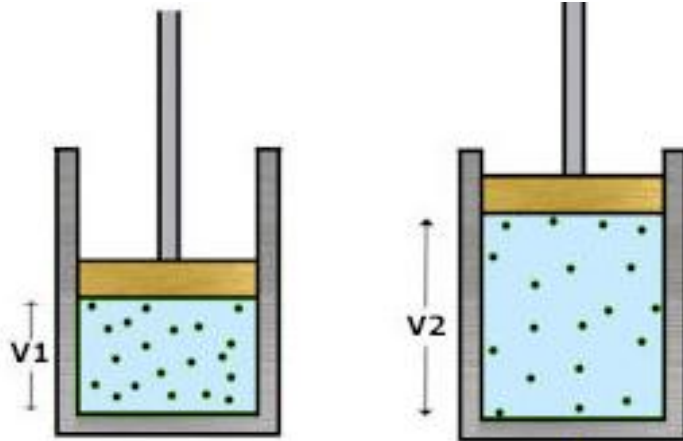
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Examples of 1<sup>st</sup> law in action:



Assume adiabatic work

no charge in heat  
 $\Delta U = \Delta W$

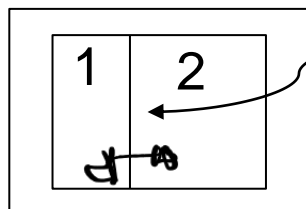


internal energy  $\Delta U = \Delta W + \Delta Q$

$$\Delta U = \Delta W = - \int_{V_1}^{V_2} p dV$$

this is work done by the system

Now assume isolated system



allows heat to pass through  
 (Diathermal, movable wall)

$$\Delta U_1 = \Delta W_{2 \rightarrow 1} + \Delta Q_{2 \rightarrow 1} \quad \Delta U_2 = \Delta W_{1 \rightarrow 2} + \Delta Q_{1 \rightarrow 2}$$

work  $2 \rightarrow 1$  + heat  $2 \rightarrow 1$

work  $1 \rightarrow 2$  + heat  $1 \rightarrow 2$

In a closed system, energy cannot be lost or gained it can only be converted from one form into another.