CLASSICAL THERMODYNAMICS

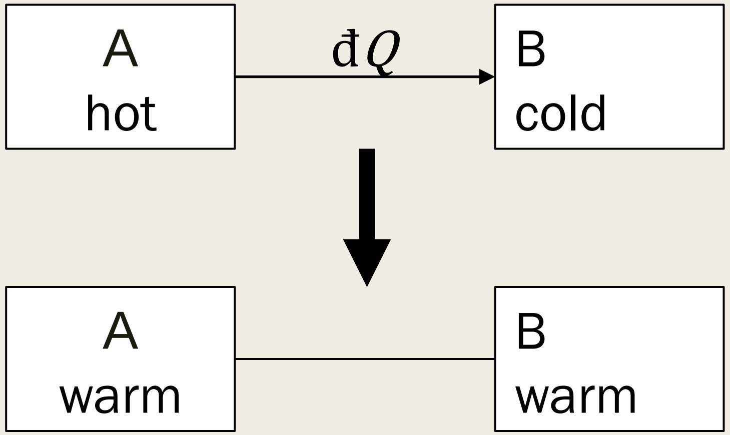
Summary so far

State of a system

- The state of a system is specified once values of all observables are known.
  - *E.g. ideal gas*
  - *Need to know p, V, n, T*
  - *But: $pV=nRT$ (so only need to know 3 and the 4th is defined)*
  - *4 variables - 1 constraint = 3 degrees of freedom*
- Functions of state are variables describing the state of a system

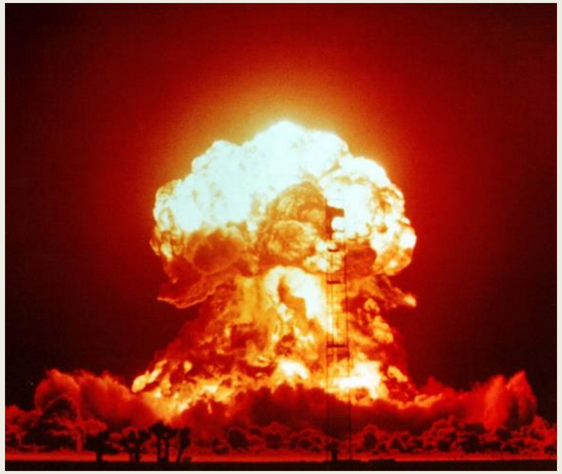
Laws of thermodynamics

- Zeroth Law
  - *If two systems are independently in thermal equilibrium with a third they are also in equilibrium with each other*
  - *“Thermometers work”*
  - *If they are not in thermal equilibrium then heat will flow*



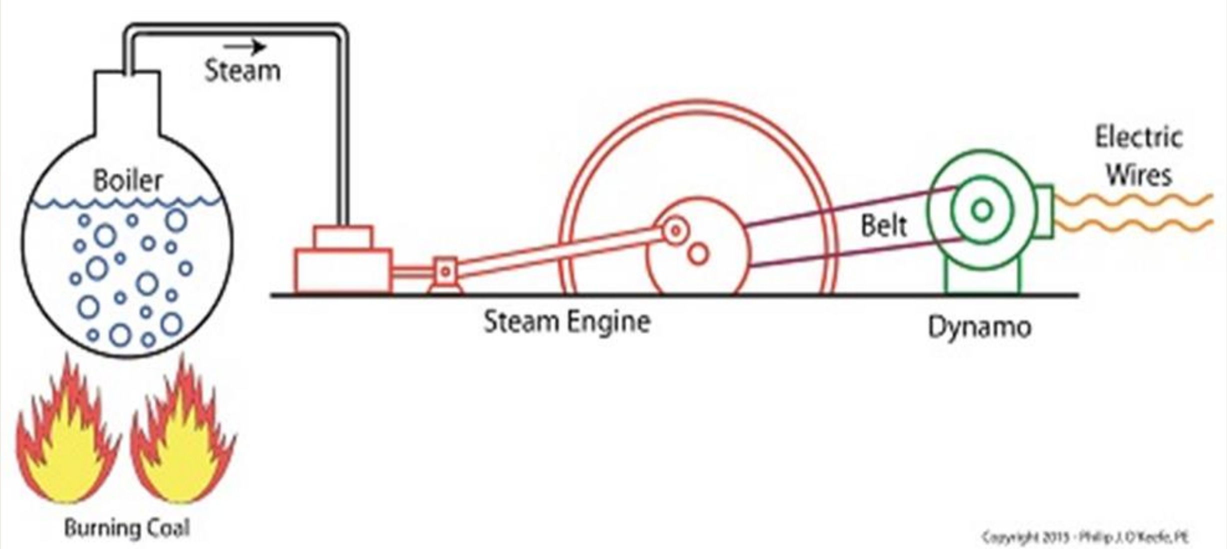
Thermodynamic reversibility

- A thermodynamic process is *reversible* if the process is
  - *quasi-static and*
  - *there is no hysteresis and no memory of the previous state.*
- System in equilibrium with surroundings will remain unchanged.
  - *If out of equilibrium it will spontaneously drive towards equilibrium*
  - *Reverse processes will NEVER occur (spontaneously)*
  - *Need to apply external "force" to prevent this from happening or to drive system out of equilibrium*



Laws of thermodynamics

- First Law
  - *Energy can only be converted from one form into the other. It can never be created or destroyed.*
  - *The change in internal energy of a system, ΔU, is equal to the work done on the system, ΔW, plus the heat supplied to the system, ΔQ.*
  - $dU = đW + đQ$ *(infinitesimal processes)*



Work done in reversible processes

- In general can write

$$đW = X\mathrm{d}x$$

Generalised force (intensive)

Conjugate displacement (extensive)

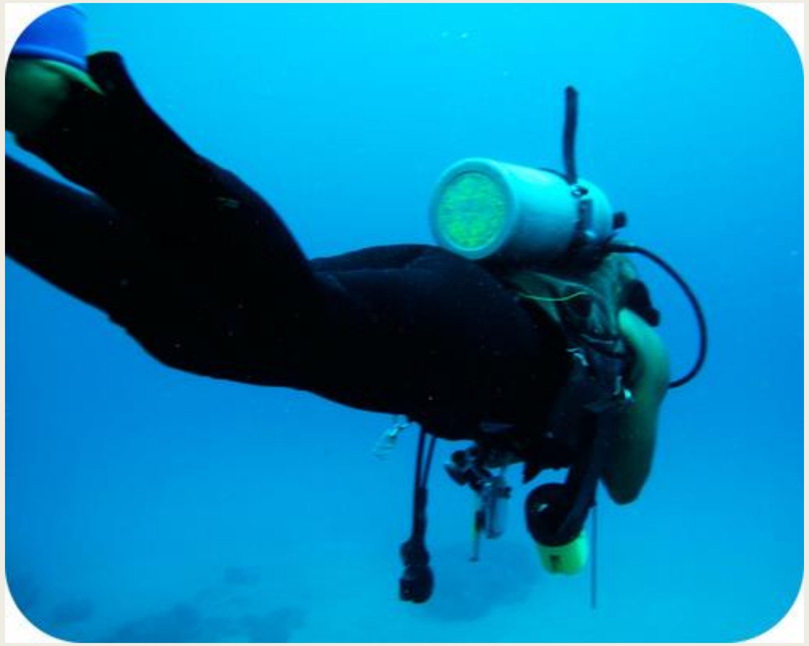
- $\Delta W = \int_i^f X dx$

Pictures taken from https://courses.lumenlearning.com/cheminter/chapter/the-behavior-of-gases/

Some material properties

- κ_T = isothermal compressibility $\equiv -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \equiv \frac{1}{B_T}$

B_T = Bulk modulus



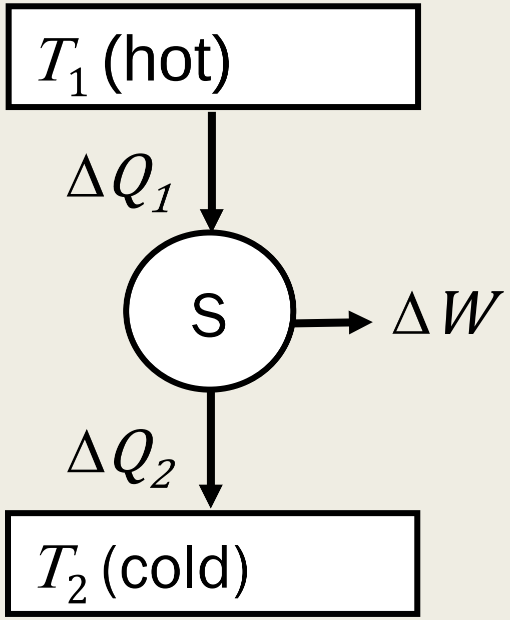
Some material properties

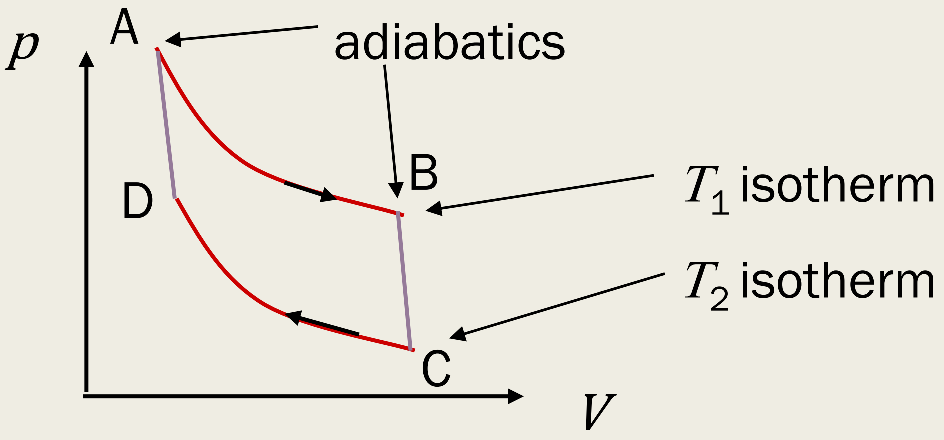
- β_p = thermal expansion coefficient $\equiv +\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Some material properties

- Heat capacity:
  - $C_V = \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$
  - $C_p = \left(\frac{đQ}{dT}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p$

Heat engines





Efficiency:

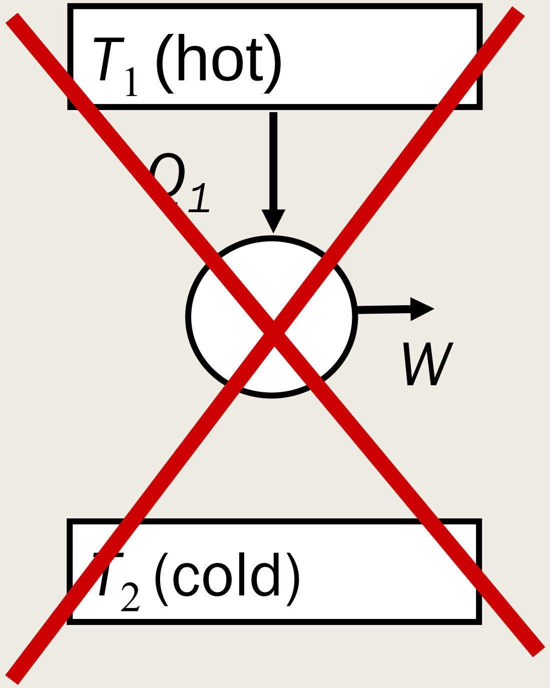
$$\eta = \frac{\text{work out}}{\text{heat in}} = \frac{\Delta Q_1 - |\Delta Q_2|}{\Delta Q_1} = 1 - \frac{|\Delta Q_2|}{\Delta Q_1}$$

Laws of thermodynamics

- Second Law

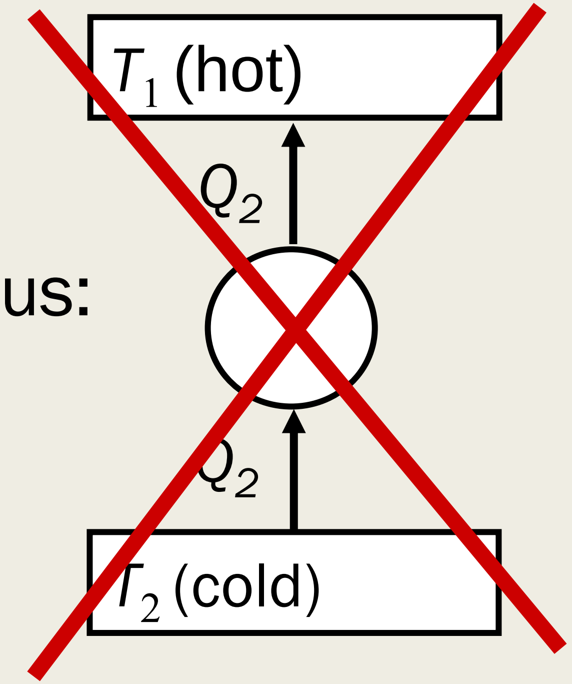
Complete conversion of heat into work

Kelvin:



Only transfer of heat from a colder to a hotter body

Clausius:



Laws of thermodynamics

reversible ⇔ reversed

E E

- Second Law

$$\eta_{\text{Carnot}} \geq \eta_{\text{other}}$$

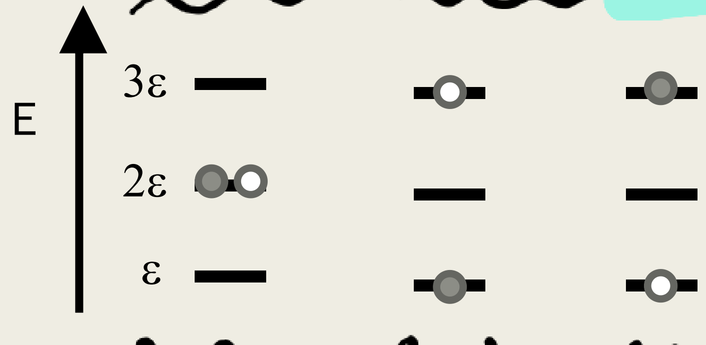
measure of disorder

$$\mathrm{d}S = \frac{đQ_{\text{rev}}}{T}$$

 - *Entropy is function of state*
 - *In irreversible processes total entropy always increases*
 - *This ultimately leads to "Heat Death of the Universe"*

will lead to

 - *From Statistical Mechanics: $S = k \log \Omega$*



$E_{tot} = 4\varepsilon, \underbrace{\Omega = 3}_{\text{ways of arranging}}$

$\underbrace{2+2}_{\text{Opt } 1/3}$ $\underbrace{3+1}_{2/3}$ $\underbrace{3+1}_{3/3}$

$\mathcal{E}_{to}$