Lecture 2

First Law for Closed Systems

- Internal energy, heat, work
- 1^{st} law for closed system (energy conservation)
- P-V diagram
- Illustration using piston, weight, friction
  - different components of work
  - recoverable vs. lost work
  - shaft (useful) work
  - quasistatic process is reversible

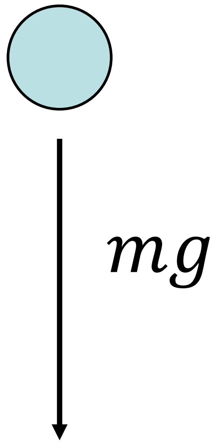
Objectives

- Use P-V diagram
- Identify different components of work

Energy Conservation

In purely mechanical world:

- Kinetic energy $K = \frac{1}{2}mv^2$
- Potential energy
  - gravitation $U = mgh$
  - electric field $U = q\psi$



e.g., ball dropping under gravity

In the absence of work, total energy is conserved

$$\Delta E = \Delta K + \Delta U = 0$$

Energy conservation is consequence of time translation symmetry
– Noether theorem (1915)

Work

$$work = force \times distance\ in\ the\ direction\ of\ force$$

$$W = \int \vec{f} \cdot d\vec{\xi}$$

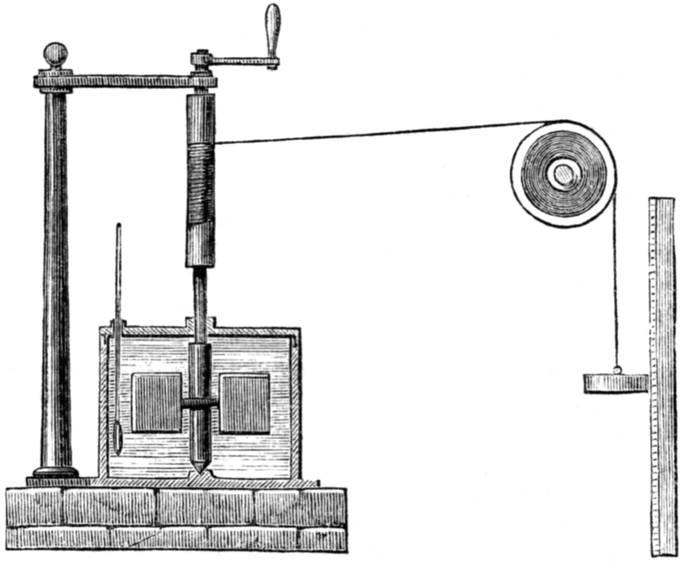
$$\delta W = \vec{f} \cdot d\vec{\xi}$$

- pV work: $\delta W = -pdV$
- tensile work: $\delta W = \tau dL$
- charging work: $\delta W = \psi dq$

Heat

The recognition of heat as a form of energy in transient was a major conceptual advance that took many generations

Mechanical equivalence of heat (James Joule 1840)



1 cal = 4.184 J

Internal Energy

An additional form of energy to the macroscopic kinetic and potential energy

Kinetic energy due to random thermal motion + potential energy of microscopic interactions

Total system energy includes both the macroscopic kinetic and potential energy as well as internal energy

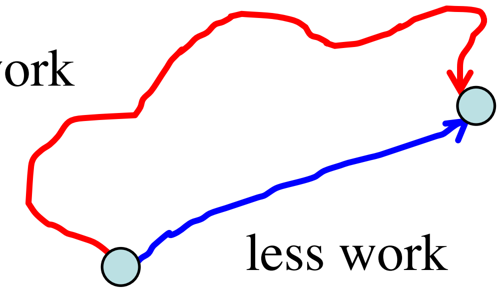
Internal energy is a state function, usually denoted by U

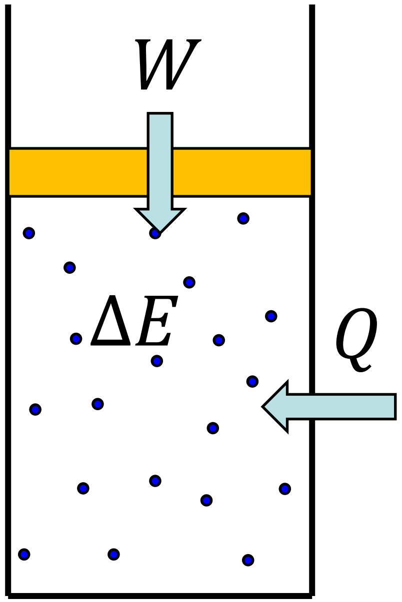
First Law for Closed Systems

$$\Delta E = Q + W$$

Differential form:

Heat and work path dependent





In the absence of overall kinetic and potential energy

$$\Delta U = Q + W$$

$$dU = \delta Q + \delta W$$

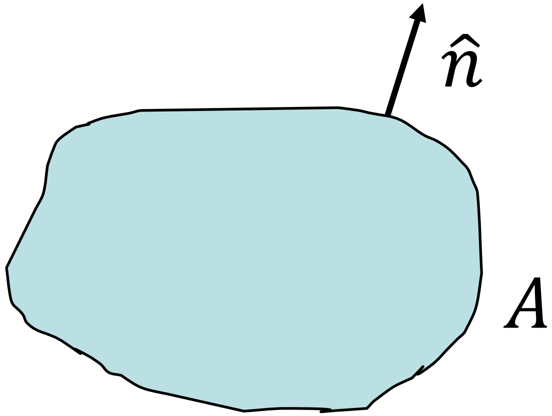
W: net work

Q: net heat

Heat Transfer

General expression

$$Q = -\int \vec{J} \cdot \hat{n} dAdt$$



Modes of heat transfer

- Conduction
- Convection
- Radiation

Phenomenological description: e.g., Newton's law of cooling

$$J = -K(T - T_r)$$

In equilibrium thermodynamics, we almost never have to specify the exact mode of heat transfer, but always relate heat to entropy change

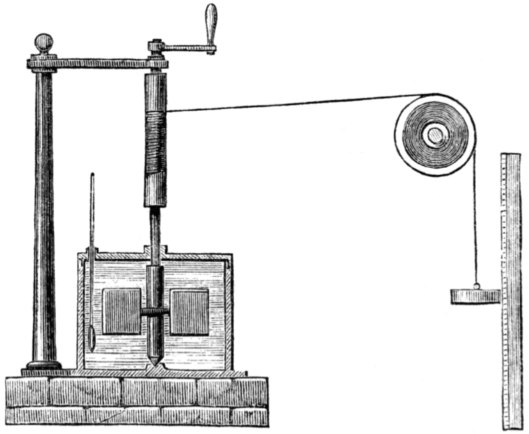
Shaft Work

The work term in first law includes all net work done by the surrounding to the system

Some work can be written in terms of system variables, e.g., pV work

Other work involves some shaft device; this type of work can't be written using system variables. We'll call it shaft work.

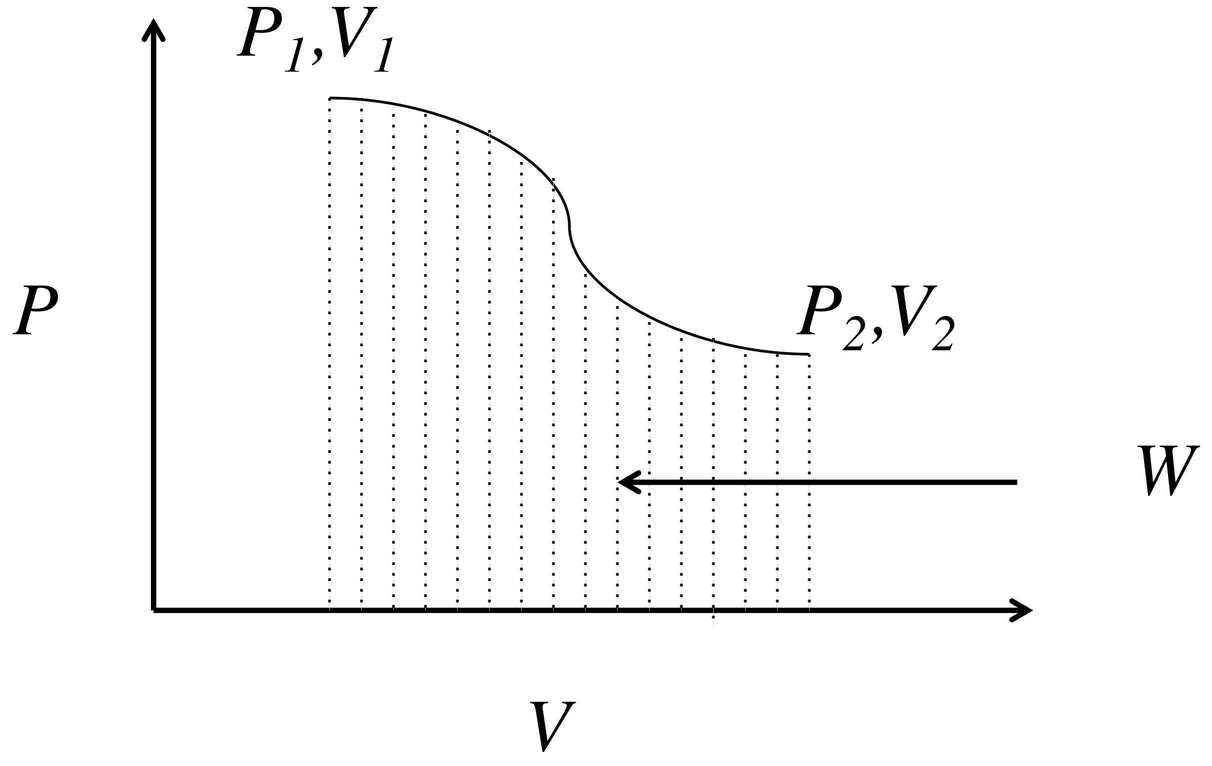
Sometimes it's useful to separate shaft work from work related to system variables



PV Work

$$\delta W = -PdV$$

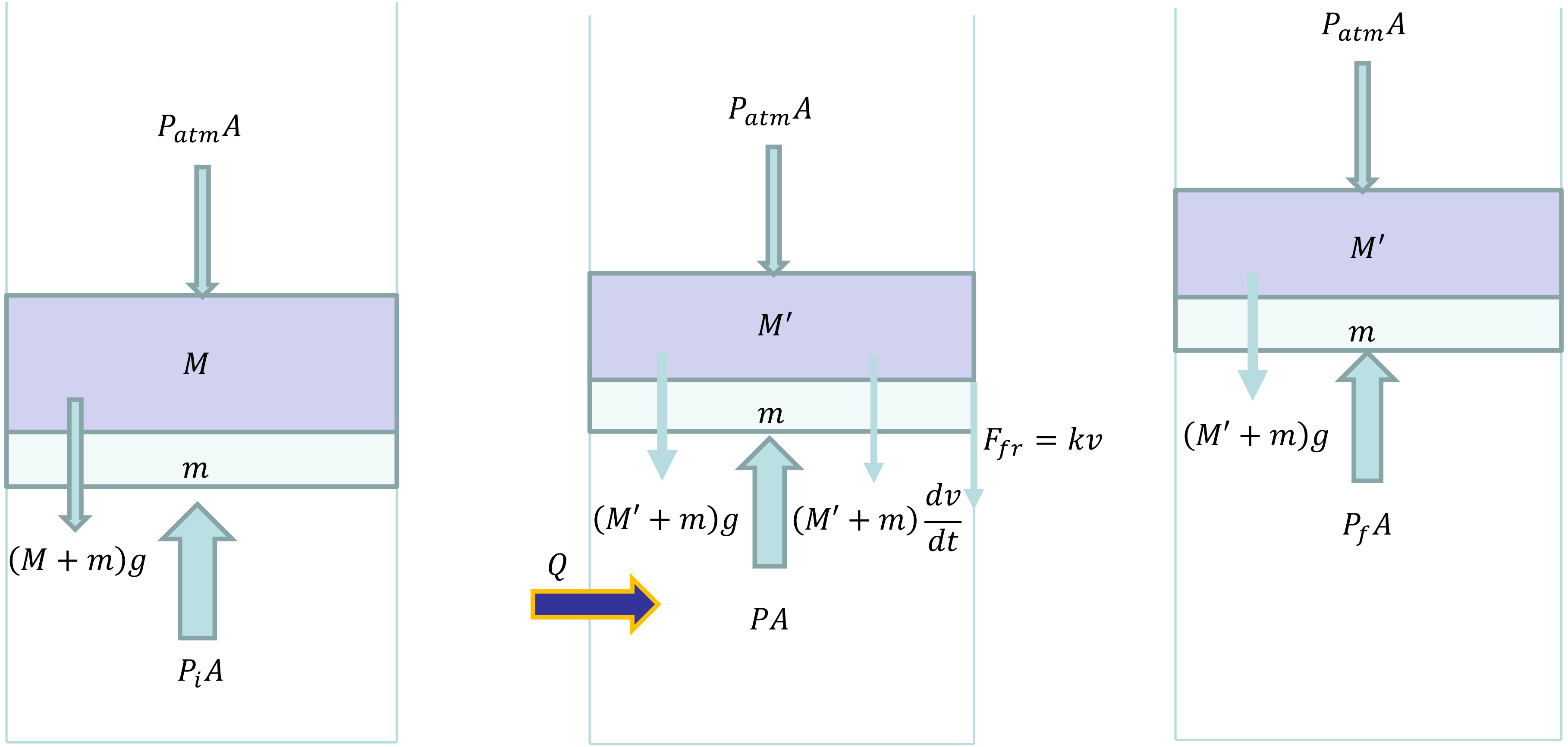
$$W = -\int_{V_1}^{V_2} PdV$$



Recoverable Work, Lost Work, Dissipation

Isothermal expansion after sudden decrease of mass from *M* to *M'*

Example 3.4-7 Sandler



initial

final

Analysis

Ideal gas + isothermal $\Delta U = 0$ internal energy only depends on T for ideal gas

$\Longrightarrow$ $Q = -W$ heat absorbed by system equal work done by system

Assuming internal equilibrium during expansion, i.e, gas satisfies equation of state at every point during the expansion

Work done by gas $$-W = \int_{V_i}^{V_f} PdV = RTln\,\frac{V_f}{V_i}$$

Where does this work go? Not all of it is received by the surrounding, so in general this not the net work exchange between system and surr.

Components of Work

Force balance

$$PA = P_{atm}A + (M' + m)g + (M' + m)\frac{dv}{dt} + F_{fr}$$

Integrating over height change

$$\int PdV = \underbrace{P_{atm}\Delta V}_{\text{work against ambient pressure}} + \underbrace{(M' + m)g\Delta h}_{\text{work against gravity}} + \underbrace{(M' + m)\int \frac{dv}{dt}dh}_{\text{work against inertia}} + \underbrace{\int F_{fr}dh}_{\text{work against friction}}$$

Components of Work

Final pressure $P_f = P_{atm} + (M' + m)/A$

Inertial term $\int \frac{dv}{dt} dh = \int \frac{dv}{dt} v dt = \int v dv = \frac{1}{2}\left(v_f^2 - v_i^2\right)$

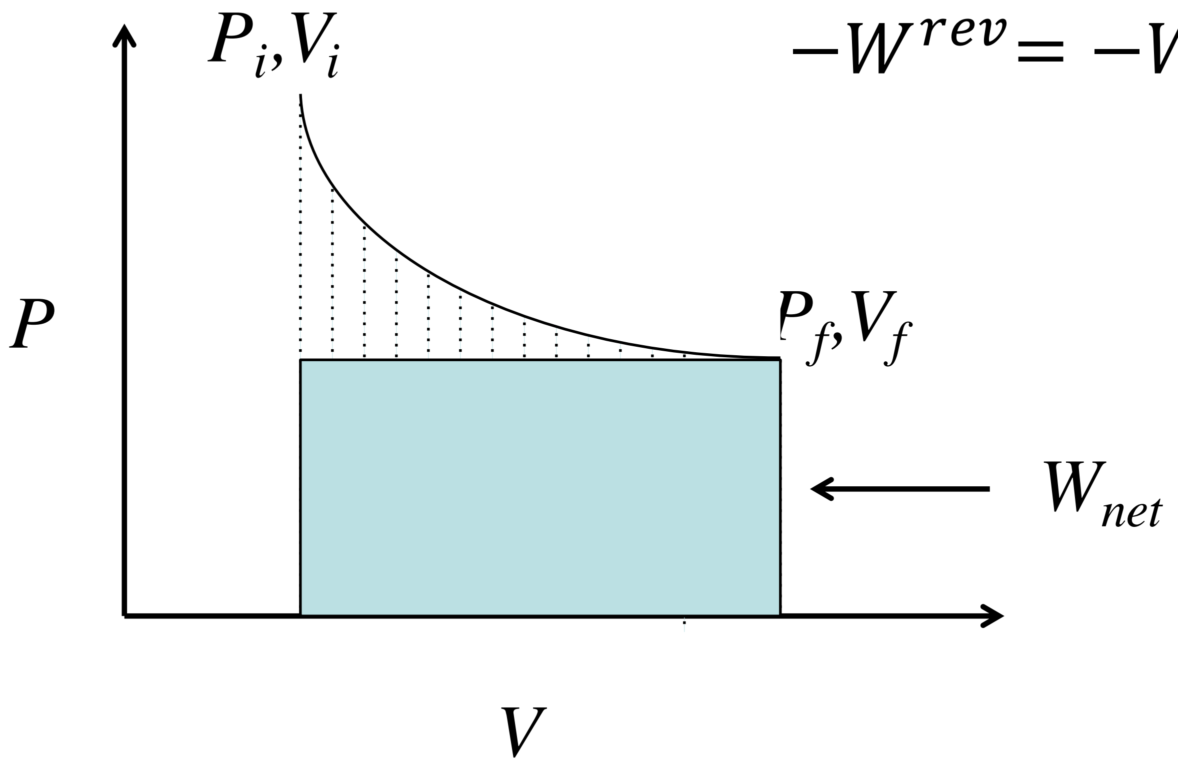
vanishes if wait until system comes to rest

Assuming linear friction $F_{fr} = kv$

Inertial term $\int F_{fr} dh = k \int v^2 dt > 0$

$$RT\ln\frac{V_f}{V_i} = P_f\Delta V + k\int v^2 dt$$

work done by gas (reversible work) | net work received by surrounding | lost work (dissipated work)



$$-W^{rev} = -W^{net} + W^{dis}$$

Effects of Dissipation

Since $$W^{dis} \geq 0$$

$$-W^{rev} \geq -W^{net}$$ less work is received by surrounding in irreversible expansion

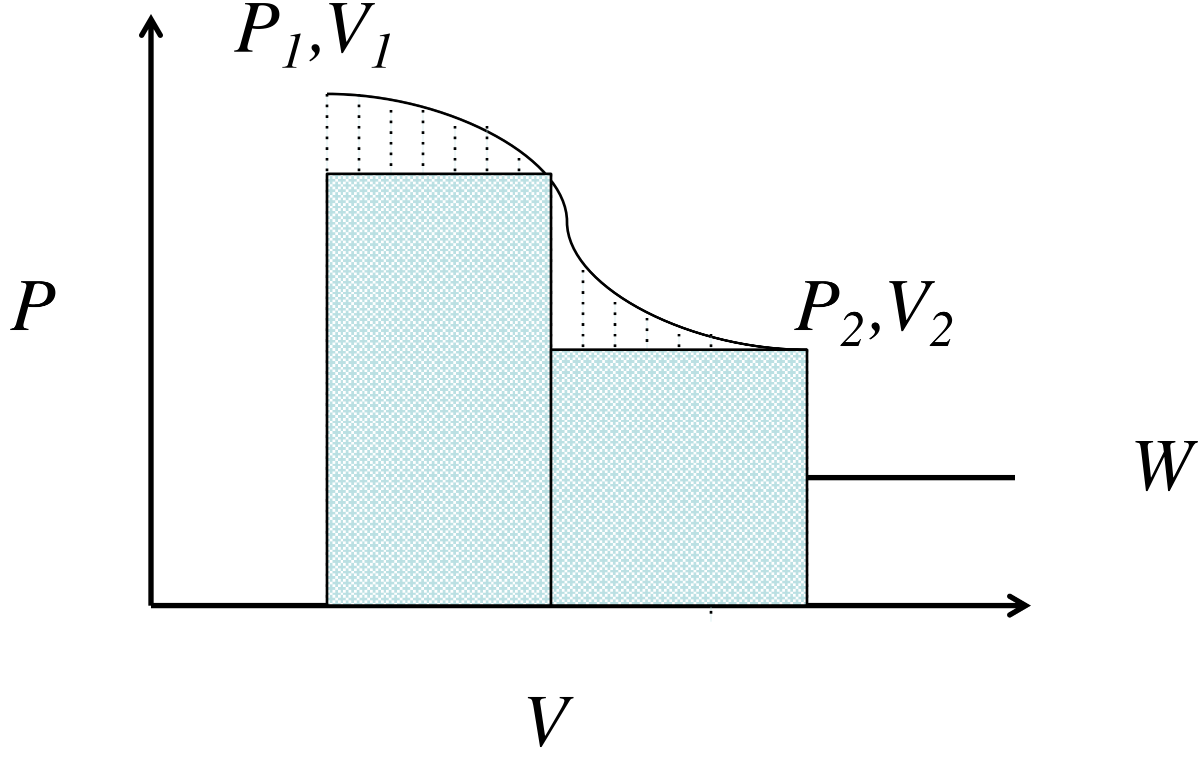
$$W^{rev} \leq W^{net}$$ more work need to be done by surrounding in irreversible compression

Net heat

$$Q^{net} = -W^{net} \leq -W^{rev} = Q^{rev}$$

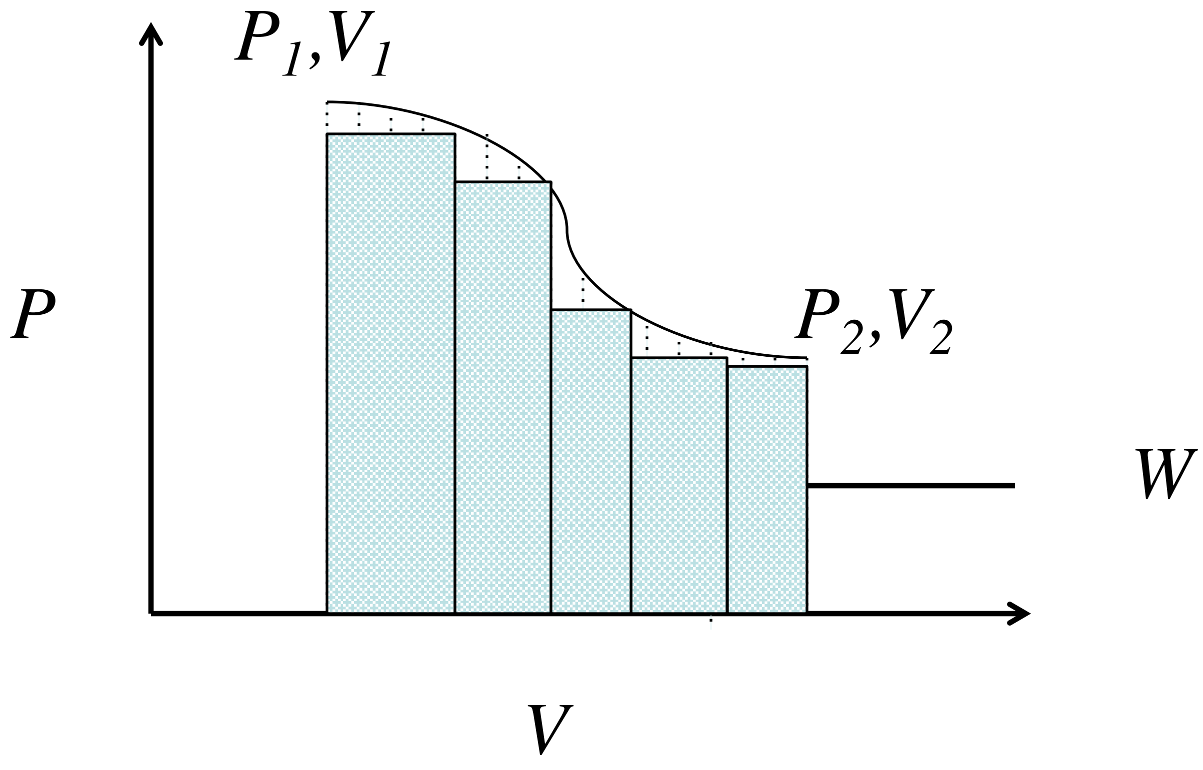
$$\frac{Q^{rev}}{T} \geq \frac{Q^{net}}{T}$$ special case of Clausius inequality

Two Step Process



Step-wise change
lost (dissipated) work decreases

Quasistatic Process



Quasistatic process as a limit of infinite number of steps

Quasistatic process is reversible – dissipation becomes vanishingly small

Questions to Think about

- Why the 1st law of thermodynamics is not "simply" energy conservation?
- What assumptions are essential in the analysis of the cylinder-piston example?
- How would the results change if the gas is not ideal?
- Consider the reverse process of increasing the pressure by adding weight on top of the piston