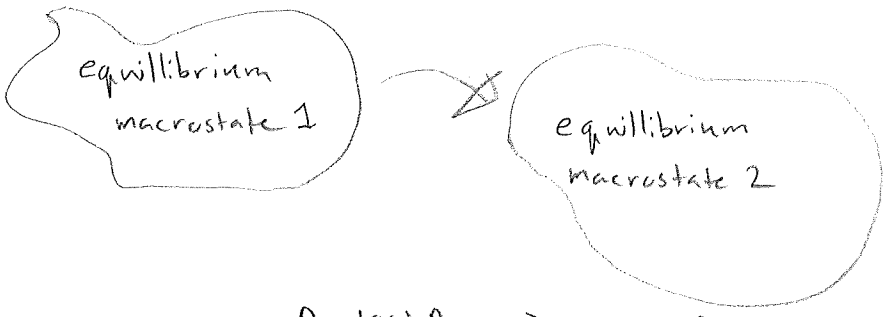
Thermodynamic Processes



ex: $P = 100\,kPa \rightarrow 250\,kPa$

notes:

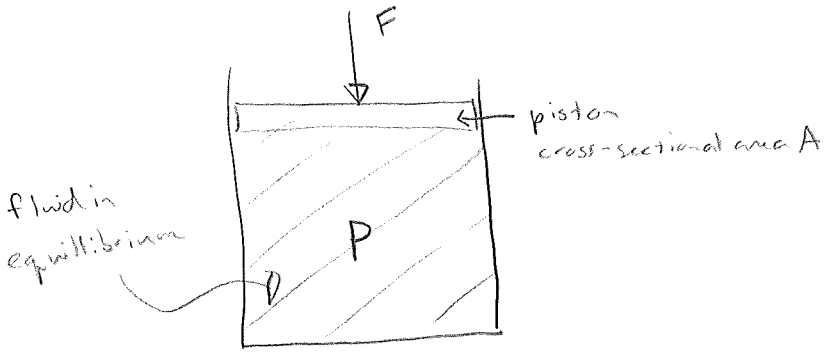
- no dynamics / time doesn't matter
- to use thermo, must be in equilliborium
  to change states, can't be in equilliborium (!)
  → assume change happens through
  succession of equilibrium macrostates
  quasistatic
  → idealized, but often good assumption
  for example, want to be slow relative
  to timescales of system

- processes can be reversible or irreversible
  ↑ can restore to original condition

• mixing cream in coffee
  irreversible

• pumping piston to compress gas
  reversible

Work



- during a process, surroundings can do work on the system, or system can do work on surroundings

- force exerted on piston by fluid (also force exerted on fluid by piston)

$$P = \text{force}/\text{area} \Rightarrow F = PA$$

$$\text{work} = \text{force} \cdot \text{distance}$$

$$dw = -F\,dx = -(PA)\,dx = -P\,dV$$

(dV = $A\,dx$)

negative $\Rightarrow$ fluid volume decreased, work done <u>on</u> fluid <u>by</u> piston is positive

- assume process is <u>quasistatic</u>, change fluid volume $V_1 \to V_2$

$$W_{1\to 2} = -\int_{V_1}^{V_2} P(T,V)\,dV$$

$P = f(T,V)$ as N fixed

- if fluid is <u>ideal gas</u> & <u>isothermal</u> process (T constant)

$$P = \frac{NkT}{V}$$

$$W_{1\to 2} = -NkT \int_{V_1}^{V_2} \frac{dV}{V} = -NkT \log(V_2/V_1)$$

- what did we mean by quasistatic?

sufficiently slow ....

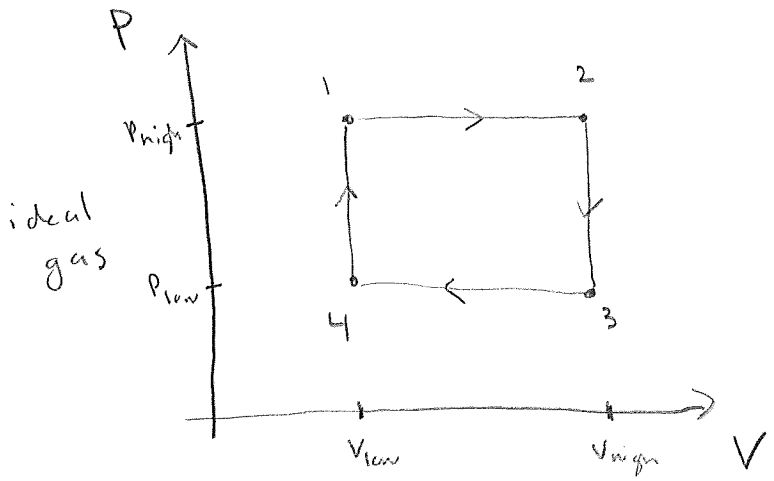
microscopic picture:

- move piston, molecules rearrange
need time to re-equilibrate

$v_p \ll \bar{v}$ ← mean molecule speed

~ sound speed 300 m/s

<u>Note</u>: work depends on <u>path</u>



- cyclic process

$1 \to 2 \to 3 \to 4 \to 1$

How much work is done?

First, consider $1 \to 2$, $3 \to 4$, constant pressure

(watch the signs!)

$$W_{12} = -\int_{V_1}^{V_2} P\,dV = -P_{high}(V_{high} - V_{low})$$

$$W_{34} = -\int_{V_3}^{V_4} P\,dV = -P_{low}(V_{low} - V_{high})$$

Now, let's calculate work on constant volume paths

$$W_{23} = -\int_{V_2}^{V_3} P\,dV = 0 \qquad \text{no change in volume!}$$

$$W_{23} = W_{41} = 0$$

What is the net work done?

$$W_{net} = W_{1\to2} + W_{2\to3} + W_{3\to4} + W_{4\to1}$$

$$= -P_{high}(V_{high} - V_{low}) + 0 + [-P_{low}(V_{low} - V_{high})] + 0$$

$$\boxed{W_{net} = -(P_{high} - P_{low})(V_{high} - V_{low})}$$

What if we went in the reverse order?

$$W_{net,reverse} = -W_{net}$$

(signs all flip since integrals reverse limits)

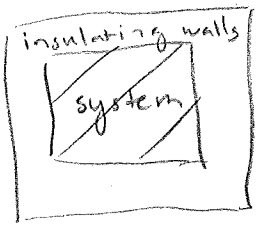
Note: We returned to original state, why is $W_{net} \neq 0$?

more work done at P_{high}!

$W_{1\to2} = -P_{high}(V_{high} - V_{low})$ $\quad P_{high} > P_{low}$

$W_{3\to4} = +P_{low}(V_{high} - V_{low})$ $\quad W_{1\to2} > W_{3\to4}$

First law of thermodynamics



← thermally isolated system

Consider changing macrostate of the system by an

adiabatic process

↖ macrostate changed only by work
no energy transfer by temperature difference

Here, $W_{1\to2} = E_2 - E_1 = \Delta E$ ↖ note this is how we are defining energy (internal energy)

$\Delta E \to$ path independent, emperical fact

E is a state function: characterizes state and is independent of path

Now, consider changing macrostate by any means (not necessarily adibiatic)

→ we can change E by doing work or heating via temperature difference (Q)

$$\boxed{\Delta E = W + Q} \leftarrow \text{1st law}$$

- E is path independent even though W is not (both W & Q are path dependent, but sum is not)
- this is a statement of conservation of energy
- units note: change in energy by adding heat is measured in calories (often)

calorie ≡ energy needed to raise temperature of water by 1°C

1 calorie = 4.186 J

NB: nutrition calories are kilocalories