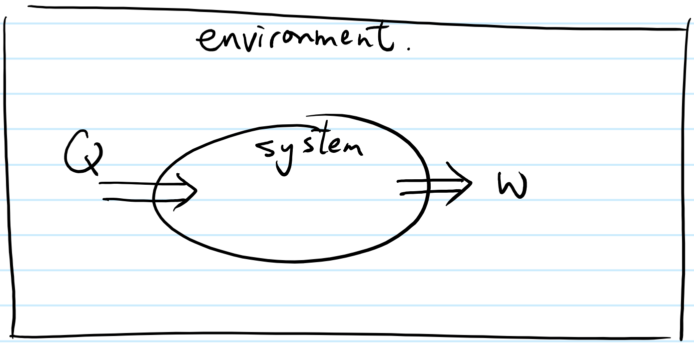
First Law of thermodynamics I

- Thermodynamic system: potential to exchange energy with its surroundings in form of heat (Q) and work (W)

Schematic picture.



$Q > 0$ if heat flow into system

$Q < 0$ heat flow away from sys.

$W > 0$ if work done by system

$W < 0$ work done on system

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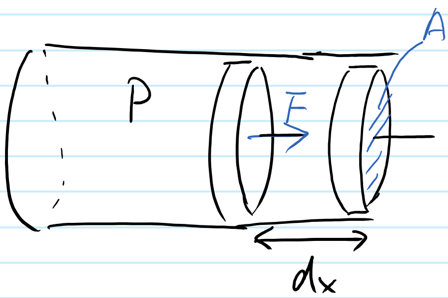
workdone by system against external pressure.

$$dW = \vec{F}\cdot d\vec{x} = F\,dx = p\underbrace{A\,dx}_{dV}$$ change in Volume



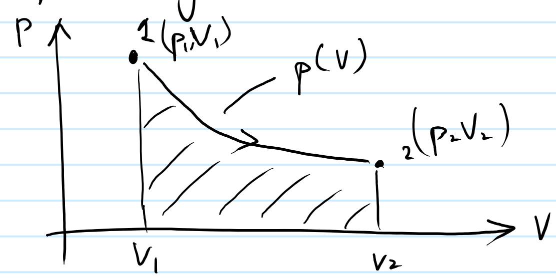
$$\Rightarrow \quad dW = p\,dV$$

$$W = \int_{V_1}^{V_2} p\,dV$$

V_2 ← final

V_1 ← initial

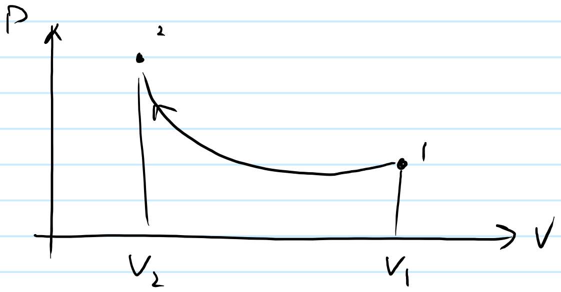
On p-V diagram,



$$W = \int_{V_1}^{V_2} p(V)\, dV = \text{Area under curve}$$

$W > 0$ as $V_2 > V_1$, expansion.

Work done by the gas



$$W = \int_{V_1}^{V_2} p(V)\, dV = (-\text{Area}) < 0$$

$\because V_2 < V_1$, compression

Work is done on the gas

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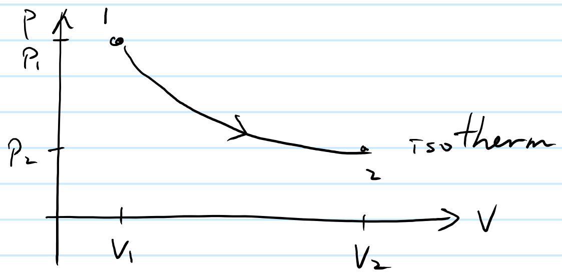
e.g. for ideal gas. $pV = nRT$

work done at constant T. $\Rightarrow p = \dfrac{nRT}{V}$

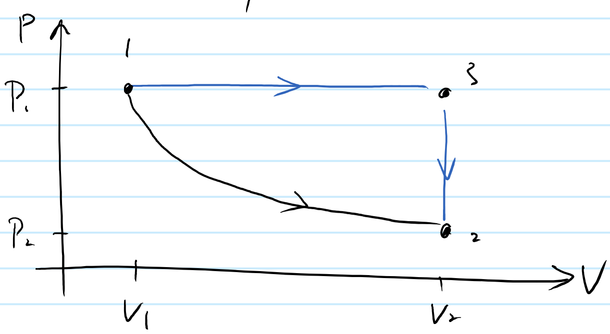


$$W = \int_{V_1}^{V_2} p\, dV = \int_{V_1}^{V_2} \frac{nRT}{V}\, dV$$

$$= nRT \ln V \Big|_{V_1}^{V_2}$$

$$= nRT \ln\left(\frac{V_2}{V_1}\right)$$

Consider a path $1 \to 3 \to 2$



$$W_{132} = W_{13} + W_{32}$$

$$W_{13} = \int_{V_1}^{V_2} p\, dV = p_1(V_2 - V_1)$$

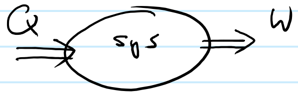
$$W_{32} = 0$$

$$\Rightarrow W_{132} = p_1(V_2 - V_1) \neq W_{12} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

$\Rightarrow$ Work done from one state to another is

<u>Path dependent.</u>!

Internal Energy



what if $Q > W$?

where does the energy go?

U : Kinetic energy + Potential energy of the system.

interaction among constituent particles
(Not external interactions e.g. gravity)

- $\Delta U = U_f - U_i$, If $\Delta U > 0$ internal E increases.
- for ideal gas : $U = K$ only (inert gas)

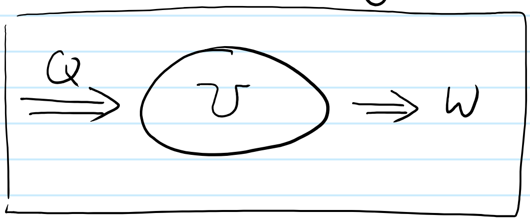
$$U = \frac{f}{2} nRT \quad \propto \text{ Temperature.}$$

- U depends only on the state, i.e. (p, V, T).

$\Rightarrow$ U is a state function.

$\Rightarrow$ ΔU is path independent. e.g. $\Delta U = \frac{f}{2} nR\,\Delta T$

First Law of thermodynamics



$Q = \Delta U + W$

or $\Delta U = Q - W$.

Conservation of energy

$$Q = \underbrace{\Delta U}_{\text{path independent}} + \underbrace{W}_{\text{path dependent}}$$

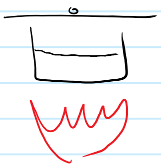
$\Rightarrow$ Q is path dependent.

- Joule's waterfall experiment.
- conversion of work into heat

Example of Q being path dependent.

Boiling Water

(A) with lid



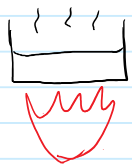
Volume is fixed

Pressure increases

$\Rightarrow$ gas won't expands

$\Rightarrow$ $W = 0$

(B) without lid.



Pressure is fixed at 1 atm.

Gas could expands

$\Rightarrow$ $W > 0$

By first law:

(A) $Q = \Delta U + W = \Delta U$ All heat converts into internal energy of the water directly.

(B) $Q = \Delta U + W > \Delta U$ Part of the heat converts into work done for expansion of the water vapour.

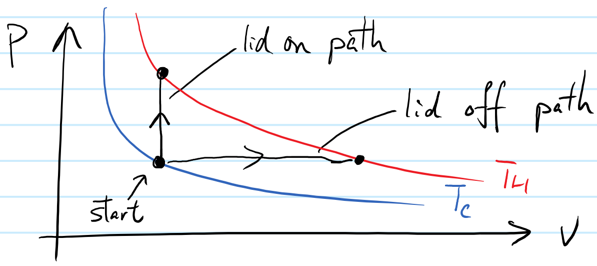
$\because W > 0$

$\Rightarrow$ Less increase in ΔU for the same amount of Q.

Boiling water with the lid on is more efficient!

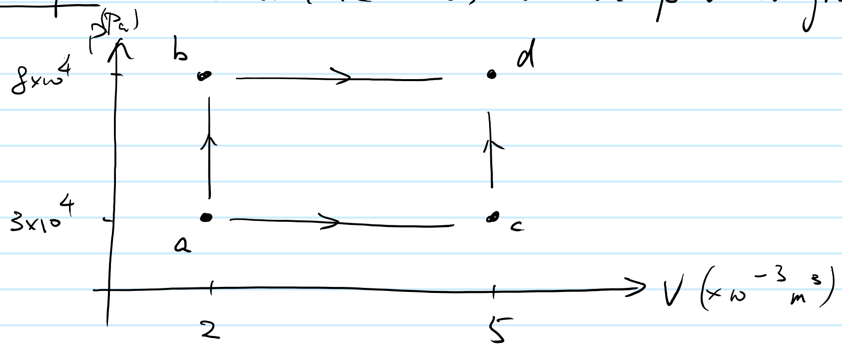
(as everyone knows)

$\Rightarrow$ Amount of heat is different when the processes are different.



$\begin{cases} \text{same } \Delta U \\ \text{diff. } W \end{cases}$

Example Calculate Q, W on p-V diagram.



given $\Delta U = U_d - U_a = 510\ J$.

Find Q_{abd} & Q_{acd}.

$$Q_{abd} = \underbrace{\Delta U_{abd}}_{510} + W_{abd}$$

$$W_{abd} = W_{ab} + W_{bd}$$
$$= 0 + P_b \cdot \Delta V$$
$$= P_b \cdot (V_d - V_b) = 8\times10^4 \times (3\times10^{-3}) = 240\ J$$

$$Q_{abd} = (510 + 240)\ J = 750\ J.$$

$$Q_{acd} = \underbrace{\Delta U_{acd}}_{510} + W_{acd}$$

$$W_{acd} = W_{ac} + \underbrace{W_{cd}}_{0}$$
$$= P_a\,\Delta V = 90\ J.$$

$$\Rightarrow Q_{acd} = 510 + 90 = 600\ J.$$

Key: Find W from p-V diagram.
ΔU from ΔT.
then Q using first law. $Q = \Delta U + W$.

Example

Boiling 1 gram of water to steam. @ 1 atm. @ 100°C

The water will expand when boiling

from $V_i = 1\ cm^3 = 10^{-6}\ m^3$ (water)

to $V_f = 1671 \times 10^{-6}\ m^3$ (steam)

Work by H_2O $= W = P \cdot \Delta V = 1.013 \times 10^5 \cdot 1670 \times 10^{-6}$

$= 169\ J$

heat absorbed as latent heat $= Q = m L_v = 10^{-3} \cdot 2.256 \times 10^6$

$= 2256\ J.$

$\boxed{L_v \text{ @ } 1\ atm = 2.256 \times 10^6}$

⇒ Increase in internal energy of water.

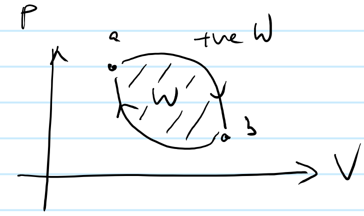
$\Delta U = Q - W$

$= 2087\ J.$

Terminologies:

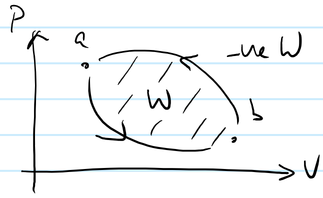
- Isolated system : $W = 0$, $Q = 0$ ⇒ $\Delta U = 0$
- cyclic process : $\Delta U = 0$ return to initial state after one cycle.

e.g.

① 

$a \to b \to a$

$\Delta U = 0$ but $W > 0$ (clockwise) $Q > 0$

② 

$W < 0$ (counter-clockwise). $Q < 0$