II. The First Law of Thermodynamics

- About Energy[†]

Add energy (different forms: "Heat", Work, Matter)

System responds: $U \rightarrow U + \Delta U$

(recall: It is often the CHANGE in energy that matters)

U = Internal energy (a state function)

Response $\Delta U \Rightarrow$ changes in State Variables due to some PROCESS[‡]

i.e. initial (equilibrium) state $\longrightarrow$ final (equilibrium) state

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[†] It is often said that Thermodynamics is about energy (1st Law) and entropy (2nd Law).

[‡] Processes is a big business in thermodynamics.

Let's not worry about exchanging Matter [not considering open systems]

$$\Delta U = W + Q \qquad (1) \quad (1^{st} \text{ law})$$

ΔU: Increase in the Internal Energy of the system

W: Work done ON system by surrounding
[if positive, ON the system]
[if negative, -ve work ON system means work done by system against the surrounding]

Q: Heat (a form of energy that is not accounted for by work done)+ into system

$Q > 0$ (into system)
$Q < 0$ (taken out from system)

+ This is the definition of Q, if one takes the logical development seriously, i.e. $Q = \Delta U - W$.

"U": What is it practically?

- Total kinetic energy plus potential energy (particles' interactions)
  [but not including the system's translational and rotational motions]
  - translational → CM of system
  - rotational → whole system rotating

  This is a microscopic viewpoint!

  → Used in Kinetic Theory of Gases AND Statistical Mechanics

- It is a State Function, e.g. $U = U(S,V)$, $U = U(T,V)$, ...

  ΔU in Eq.(1) depends only on the initial state and final state

  but NOT how the system goes from initial to final states

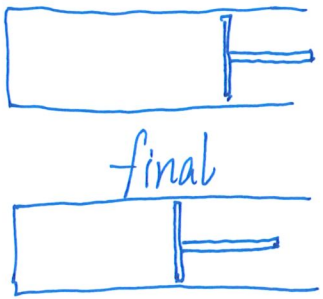
- To say something more on W and Q, we need some ideas on Processes

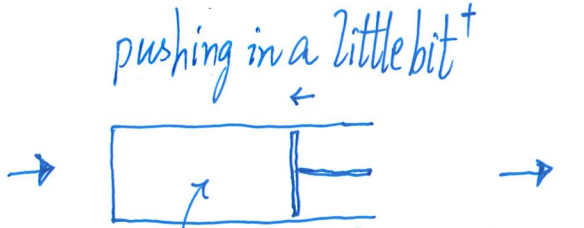
A. Reversible Processes

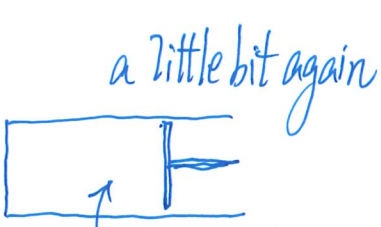
- Go very very slowly (quasistatic process)

go through a sucession of equilibrium states in between

e.g



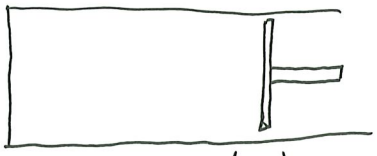




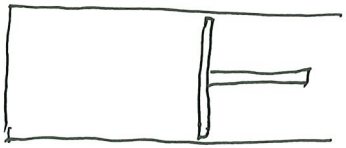
and again and again ... to final state

†See work is done on system by some external agent

- No friction [generally, no dissipation]

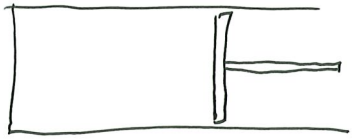


initial



pushed in a bit

Work done on system by surrounding



pushed out a bit back to initial

Same work done by system on surrounding

↑ Reversible!

but only if there is no friction!

[With friction, pushed in (dissipation)
pushed out (dissipation)]

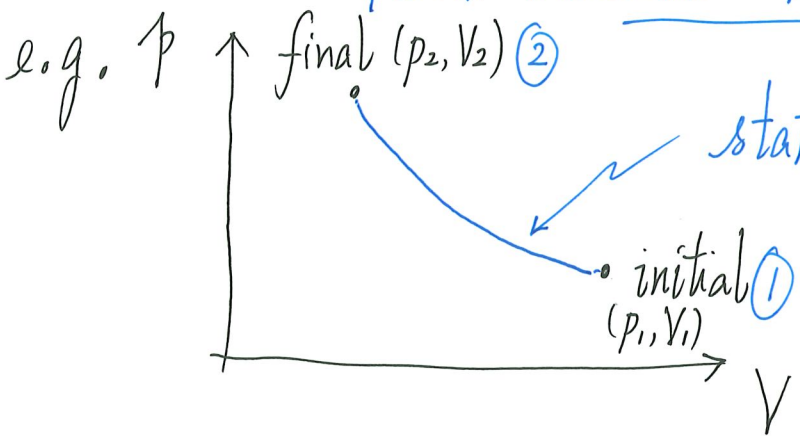
system AND surrounding can't get back!

Same argument ∴ No hysteresis [can get back to same state]

∴ Reversible processes : Quasistatic processes + No friction

Every stage is an equilibrium state [between end points → initial, → final]

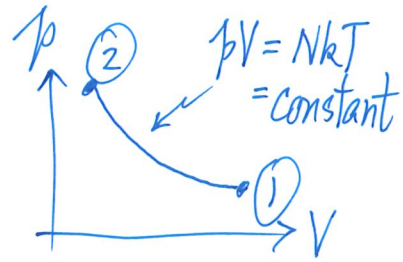
Can indicate reversible processes on indicator diagram

e.g. 

states in between can be shown on diagram

BUT, the path still needed to be specified†

e.g. isothermal compression

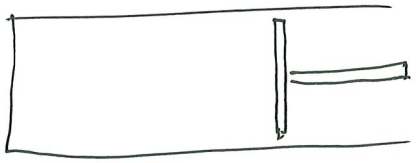


But if it is adiabatic compression, the curve is different!

Behind the scene, it says W is path-dependent

† so that the work done $W = -\int_1^2 p\,dV$ can be calculated in a finite process for the specified path

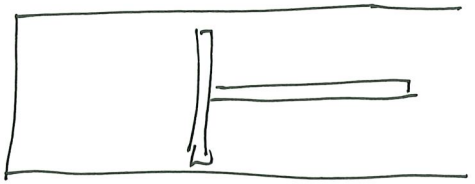
Contrast with irreversible processes



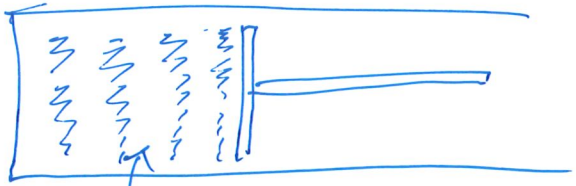
initial

suddenly push piston in

final



Can't put process on indicator diagram†



sound wave, turbulence, ...

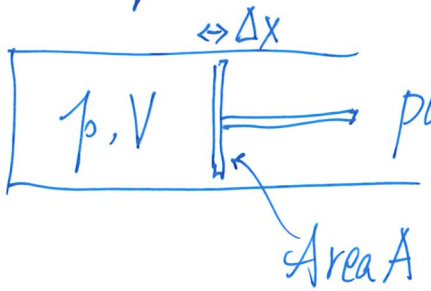
move back

Can't get back to initial situation for system and surrounding

†And work done W cannot be expressed in terms of state variables such as p, V of system

B. Why bother with Reversible Processes (so idealized!)

(a) Can express W in terms of System's state variables



$W = F_{ext} \cdot \Delta x$ in principle

not system's properties

(from Mechanics)

For Work Done on Gas-in-Piston system

Very slow, every stage at equilibrium

$$\frac{F_{ext}}{A} = p$$

[F_{ext} infinitesimally bigger than pA to push in]

$$W = p A \Delta x$$

p: system's pressure

$A \cdot \Delta x$ = Change in System's Volume $(-\Delta V)$

↑ system's V

$\therefore$ $\boxed{W = -p\Delta V}$ (reversible) (2)

Now expressed in system's variables

Sign Convention: Compressing system ($W>0$, work done ON system)

↳ $\Delta V < 0 \Rightarrow W > 0$ (OK)

System Expands (Work done by system, $W<0$)

↳ $\Delta V > 0$, $W = -p\Delta V < 0$ (OK)

For an infinitesimal dx, write as

$$đW = -pdV \quad \text{(reversible, infinitesimal)} \qquad (3)$$

- Expressed in system's variables
- But for a finite reversible change, $W = -\int_{\text{path}} pdV$ still needs a specified path (path dependent in general)

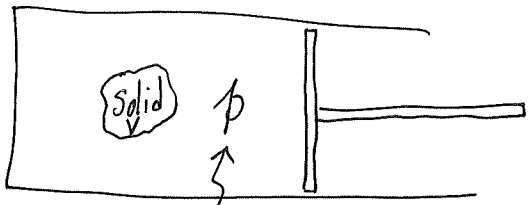
($đW$ stresses this point.)

but at least we have an expression for calculations.

1st law : $\boxed{dU = đQ - p\,dV}$ (4) (for $-p\,dV$ type work done)

reversible process (infinitesimal)

- Also work for Hydrostatic pressure on a solid



incompressible fluid (no change in volume when piston is pushed in)

$đW = -p\,dV$

work done by piston is transmitted to solid

$\boxed{dU = đQ - p\,dV}$ (4a) for hydrostatic pressure (reversible, infinitesimal)

(b) Can evaluate W when a path is specified (equivalent to specifying some constraint, e.g. keep temperature constant)
(not possible for irreversible processes)

(c) Idealized processes also give "idealized results" that are useful
e.g. reversible cycles (engines) are the most efficient†!
as good as one can get!

- Even Q for reversible processes is important
defining ΔS (change in entropy)

† This is related to the 2nd Law of thermodynamics

C. Historically, Heat was heat, Work was work

* Mechanics: Work Done [c.f. work-energy theorem]

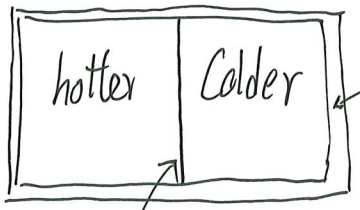
Work Done = Change in KE

if conservative force, PE

⇒ Mechanical Energy (KE + PE)

∴ Know that Work Done is an energy (starting from Newton's time)

* Heat:



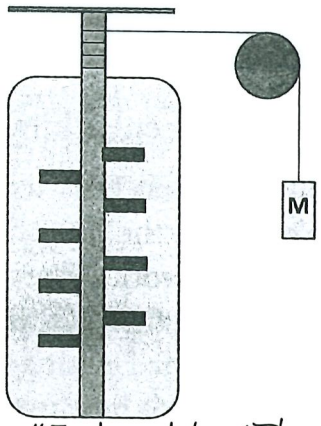
Heat exchange ["Heat Gained" = "Heat Lost"] and approach equilibrium

Caloric Theory

* Some Calorie flows from one body to another [and change the state of a body]

- By 1840, two accounts → an account for mechanical energy [Units: erg, J]
  → an account for heat [unit: Calorie]

Joule's experiment



(Taken from Shankar, "Fundamentals of Physics I"

Joule's experiment to find the mechanical equivalent of heat, 4.2*kJ*/*kcal*. As the weight descends, the fins turn and heat up the water. The missing mechanical energy in the weight becomes heat energy. (It is assumed that the rest of the apparatus does not absorb any appreciable part of the generated heat.)

Mechanical energy (Work done)
has heat equivalent

Found Conversion $4.2\,J \leftrightarrow 1$ calorie
[4.2 kJ to raise 1 kg of water by 1°C]

$$\Delta U = W + Q \quad (1)$$ (any process)

is an energy conservation statement including heat

Joule varied ways to do work [different weights M and different rounds of drop], found some amount W was needed in his adiabatic apparatus.

$W_{adiabatic} = \Delta U$ (simpler!)

$W_{adiabatic}$ = Work done by system for adiabatic process

↑ particularly simple! (as Joule observed)

1st law $\Delta U = W + Q$ (any process) [Benefit of hindsight]

Adiabatic $\Rightarrow Q = 0$ (any adiabatic process, not necessarily reversible)

$\therefore \Delta U = W_{adiabatic}$ (any adiabatic process)

- But ΔU depends only on end points (a certain value given end pts.)

$\Rightarrow$ **$W_{adiabatic} = \Delta U =$ a certain value no matter how the adiabatic process is carried out**

This is an exceptional case!

For non-adiabatic processes, W takes on values that are path-dependent (details of the process)

Aside: Formal & Traditional Approach

For Non-adiabatic processes, $\Delta U = W + Q$ (1)

same change in U can be realized by a combination of W and Q

- many combinations
- W and Q can take on many values depending on path taken from initial to final states

W is familiar (mechanics) and more easier to control, therefore

$Q = \Delta U - W$ was used to define Q (see p. II-2 footnote)

$$\Delta U = W + Q$$

W: known to be energy (Newton's time onwards)

Q: ← something else (caloric) (any process)

- First law recognized Q as an energy
- 1st law extends energy conservation to include Q in the balance sheet
- U is a state function ($U_{\text{initial pt}}$, $U_{\text{final pt.}}$)
  - but W and Q are only there <u>in the process</u> leading to ΔU

(<u>Can't</u> say some W/some Q in a state)

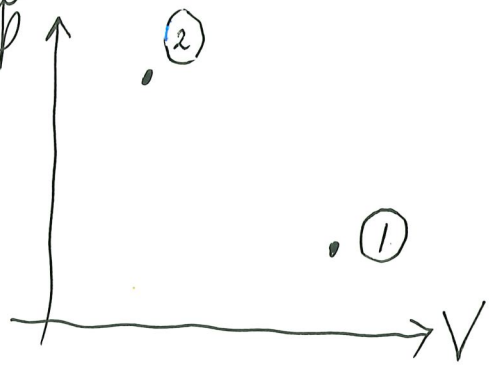
$$dU = \text{đ}W + \text{đ}Q = -p\,dV + \text{đ}Q \quad \text{(reversible, infinitesimal)}$$

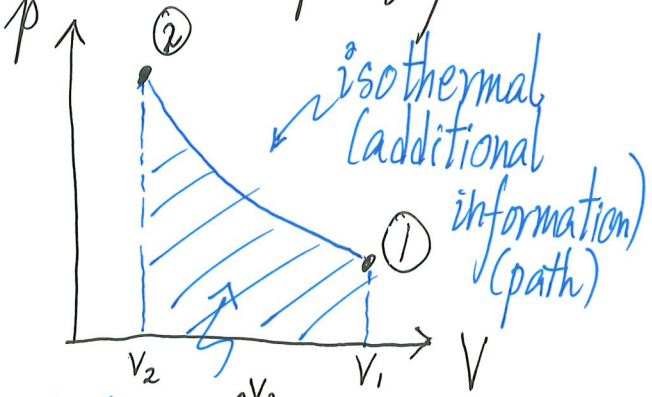
sets the stage that $W = \int_{\text{initial}}^{\text{final}} -p\,dV$ can be evaluated for a given path

D. More on Work

$$dW = -p\,dV \quad \text{(reversible)} \qquad (3)$$

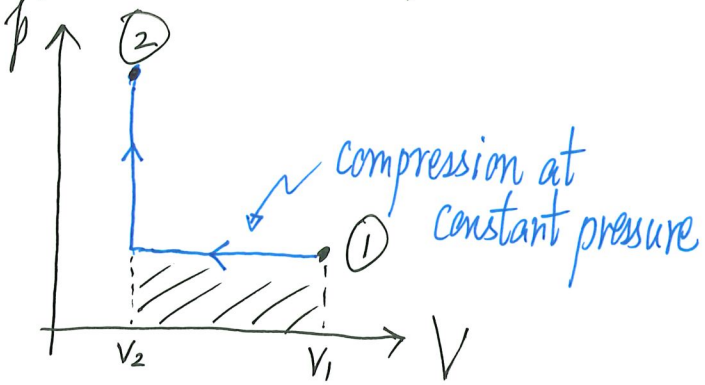
Finite change: It is NOT ENOUGH to specify the end points (initial/final states)





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

~Area under curve



$W = P_1(V_1 - V_2)$ ~Area

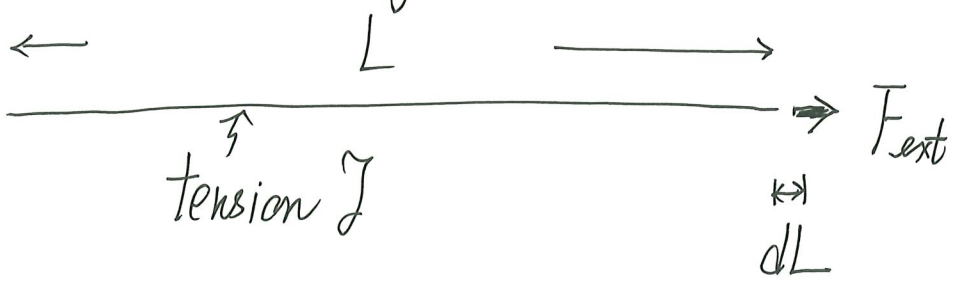
↖ depends on path (even reversible)
[non-adiabatic]

Other common forms of work done on a system in reversible infinitesimal changes

Gas / Fluid	$-p\,dV$	
Wire under Tension	$J\,dL$	(an infinitesimal extension dL under tension J)
Polarizing a dielectric	$E\,d\mathcal{P}$	(E: electric field, $\mathcal{P}$: total electric dipole moment; an infinitesimal $d\mathcal{P}$ under electric field E)
Magnetizing a paramagnetic material	$B_0\,d\mathcal{M}$	(B_0: Magnetic induction, $\mathcal{M}$: total magnetic dipole moment; an infinitesimal $d\mathcal{M}$ under B_0)

[Useful in copying results from $-p\,dV$ system to other systems]

E.g. "Copying" Arguments [wire of length L under tension $\mathcal{J}$]



Further extend from L to $L+dL$, $đW = F_{ext}\,dL$

now $dL>0$, $đW>0$

Reversible Process: $F_{ext} = \mathcal{J}$ (infinitesimally bigger to pull)

$đW = \mathcal{J}\,dL$ (now in terms of the system's variables)

1st law: $\boxed{dU = đQ + \mathcal{J}\,dL}$ (wire in tension) (4b) (reversible)

$(\mathcal{J}, L, T)$ play the role of state variables (c.f. (P, V, T))

(thus, all the formulas on partial derivatives follow)

"Copy" formulas $\left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial V}{\partial p}\right)_T \left(\frac{\partial p}{\partial T}\right)_V = -1$ (MSI-(32), Eq.(16))

$(p, V, T) \leftrightarrow (\mathcal{J}, L, T)$

$\therefore \underbrace{\left(\frac{\partial T}{\partial L}\right)_{\mathcal{J}}}_{\frac{1}{\left(\frac{\partial L}{\partial T}\right)_{\mathcal{J}}}} \underbrace{\left(\frac{\partial L}{\partial \mathcal{J}}\right)_T}_{\sim \frac{\text{strain}}{\text{stress}}} \underbrace{\left(\frac{\partial \mathcal{J}}{\partial T}\right)_L}_{\text{expressible into material's property}} = -1$ (Done!)

"What for?"

$\sim \frac{1}{\text{linear expansion coefficient}}$ (material's property, measureable)

$\sim \frac{1}{\text{Young's modulus}}$ (material's property, measureable)

- Fixing L [cable on bridge]

temperature changes (summer → winter)

How does tension vary?

[a meaningful question]

E. Heat Capacity

Q into a system, System will change from one equilibrium state to another with a temperature different ΔT

Heat capacity $C = \lim_{\Delta T \to 0} \frac{Q}{\Delta T} = \frac{dQ}{dT}$ ← that's the "dQ" in 1st law (so still need to satisfy condition)

↑ heat capacity, depends on material in system AND amount of material

For fair comparisons among different materials:

"Specific heat"† $c = \frac{1}{m} \frac{dQ}{dT}$ OR molar heat capacity

heat capacity per unit mass ← mass

per mole

† It is NOT heat, it is "specific heat capacity."

Recall: Q comes in through some process

(a) C_V – Heat Capacity at constant volume

$$dQ = dU + pdV$$

constant volume

$$\therefore dQ_V = dU$$

emphasize condition

[Remark: Isochoric reversible processes give particularly simple dQ_V

(c.f. just as adiabatic work done (i.e. $Q=0$) is particularly simple $dW_{adiabatic} = dU$)]

$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad (5)}$$ †

† So, we are thinking in general term that $U(T,V)$.

(b) C_p - Heat Capacity at Constant Pressure

∴ Need $\frac{dQ_p}{dT}$ ← specify constant P condition

dQ_p : Isobaric and reversible process that leads to dT

[dU has $-pdV$ term, it is not the right condition here]

Introduce another energy (called "potential") function (a state function)

$$\boxed{H = U + pV} \quad (6)$$ [technically, a Legendre Transform]

$$dH = dU + d(pV) = dU + pdV + Vdp$$

[see total differential, Eq.(6) in MSI]

$$= (dQ - pdV) + pdV + Vdp = dQ + Vdp$$

1st law

$$dH = đQ + Vdp \quad (7) \qquad [\text{c.f. } dU = đQ - pdV]$$

Now has a term referring to dP

"Meaning": A funny energy called Enthalpy H, which is $U + pV$ and so a state function, that can be changed in a reversible infinitesimal process by dH in two ways: Heat $đQ$ and a form of energy Vdp. Thus, $H = H(p, \text{some other state variables})$[+]. In contrast, $U(V, \text{other variables})$.

$$đQ = dH - Vdp \qquad \text{(reversible, infinitesimal)}$$

$$\therefore đQ_p = dH \quad (8) \qquad \text{for } dP = 0 \text{ process}$$

(p emphasizes condition of constant p)

[+] dH has a term $\left(\frac{\partial H}{\partial p}\right)_{V,\ldots} dp$ in its total differential, and this term echoes the Vdp term in dH.

$$\therefore \quad \boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \qquad (9)$$

where $H = U + pV$ (state function)

enthalpy (焓) is a state function

U, p, V: state variables

(c) C_V vs C_p: Which one is bigger?

Physical Thought: Constant $V \Rightarrow$ system doesn't do any work

So, Q into system all uses to increase temperature

Constant $p \Rightarrow$ system does work (expands to maintain p)

So, Q into system partially uses to increase temperature

$\Rightarrow$ Need more Q to achieve ΔT

$\therefore C_p > C_V$

Generally, $C_p = C_V - T\left(\frac{\partial p}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)^2 = C_V + \underbrace{TVK\beta^2}_{\text{positive}}$

Module: K; Expansivity: β

F. From $U(V, \text{something})$ to $H(p, \text{something})$: Legendre Transform

$dU = -p\,dV + (\text{other terms})$, $U(V, \text{other variables})$

so $dU = \left(\frac{\partial U}{\partial V}\right)_{\text{other}} dV$ corresponds to $-p\,dV$

$dH = V\,dp + (\text{other terms})$, $H(p, \text{other variables})$

so $dH = \left(\frac{\partial H}{\partial p}\right)_{\text{other}} dp$ corresponds to $V\,dp$ term

$H(p) = \underbrace{U(V)}_{U(V, \text{other variables})} + pV$ takes $U(V)$ to $H(p)$

↑ focus on V here

What is the physical behind this transformation?

$$H(p) = U(V) + \underbrace{pV}_{\text{unit of energy}}$$

p ↑ intensive, V ↖ extensive (scale with system's size)

- a pair (c.f. $\mathcal{F}$ ↑ tension, L ↖ length of wire)
- a conjugate pair of variables

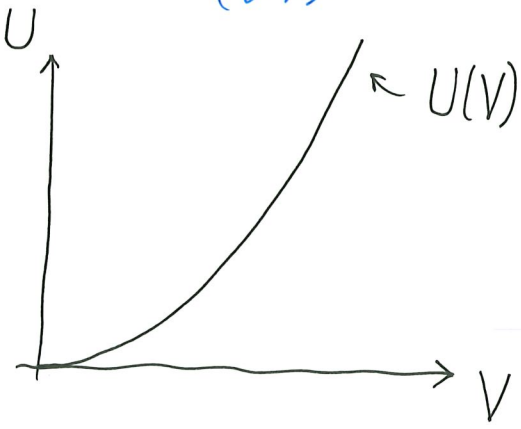
As $dU = \left(\frac{\partial U}{\partial V}\right)_{\substack{\text{others} \\ \text{kept fixed}}} dV$

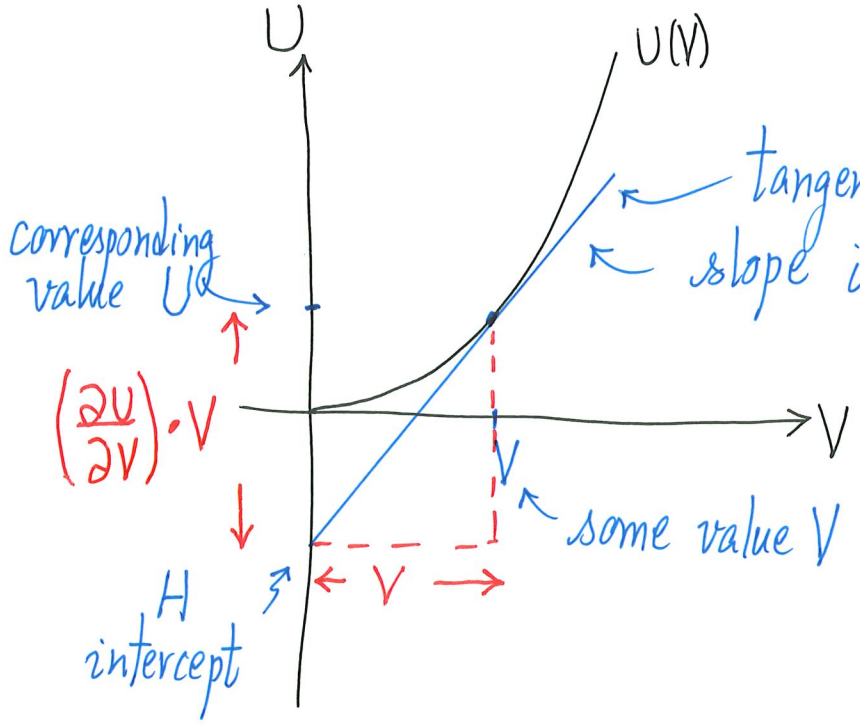
$dU = -p\,dV + \text{other terms}$ (1st law)

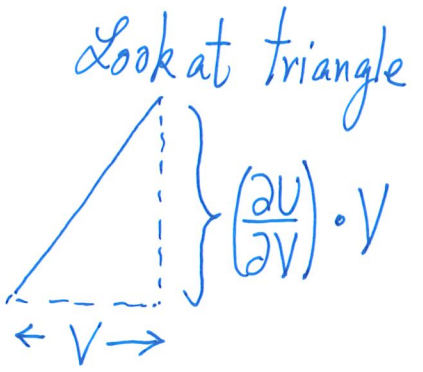
$$\boxed{p = -\left(\frac{\partial U}{\partial V}\right)_{\text{others fixed}}}$$

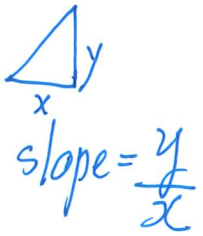
← On a graph of U as a function of V (others fixed) $\left(\frac{\partial U}{\partial V}\right)$ is the slope of tangent

Let's say $U(V)$





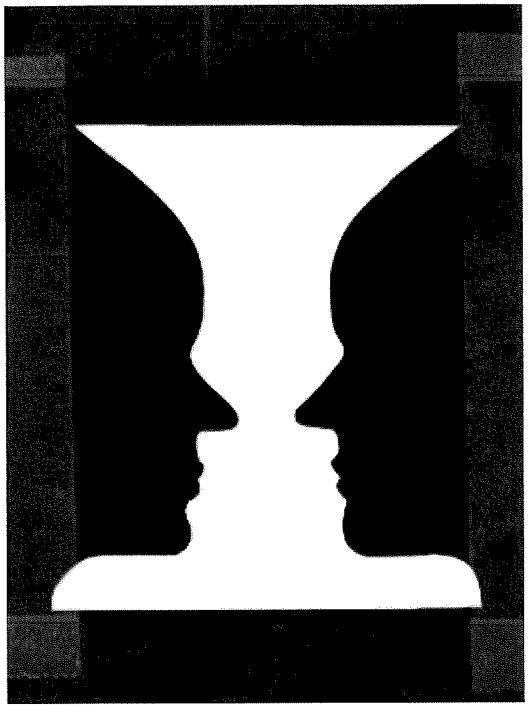




look at the y-axis (U-axis): $U - \left(\frac{\partial U}{\partial V}\right)\cdot V = U + pV = \underbrace{H}_{\text{the intercept}}$

So, if we look at U(V) differently, by giving the slopes ($\sim p$) AND the intercepts instead of U(V), then we are using H(p). They are different ways of viewing one thing.

- Analogous to



- Many other similar transformations in thermodynamics

$$U(S) \rightarrow F = U - TS \quad \text{and} \quad F(T)$$

S: entropy (2nd law)

F: Helmholtz free energy

Refs

- C. J. Adkins, Equilibrium Thermodynamics
- C. B. P. Finn, Thermal Physics
- A. B. Pippard, The Elements of Classical Thermodynamics