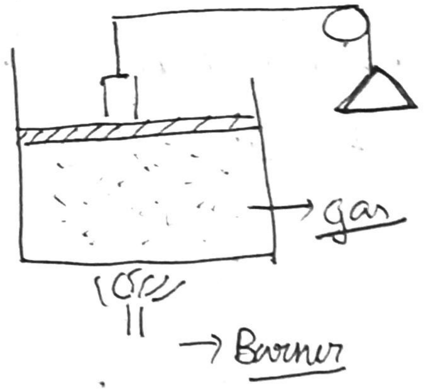
16th January 2024



The piston can work on gas, and vice-versa.

$$\Delta U = \Delta Q + \Delta W$$

ΔU → Change in internal energy

ΔQ → Heat supplied to system

ΔW → Work done on/by system

→ $\Delta Q \equiv +ve$ when added to the system

→ $\Delta W \equiv +ve$ when work is done <u>on</u> the system by surroundings

This is the <u>1st Law</u> of <u>thermodynamics</u>.

(*) This has no physics other than energy conservation.

NOW,

$$\Delta Q = \Delta U + (-\Delta W)$$

→ Some heat energy increases internal energy of system

→ Some heat energy does work by raising piston, etc.

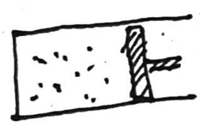
→ The same amount ΔU can be done by <u>different combinations</u> of ΔQ and ΔW.

Like, Money = Cash + Cheque

This tells you that U is a <u>state function</u> (Example of exact differential)

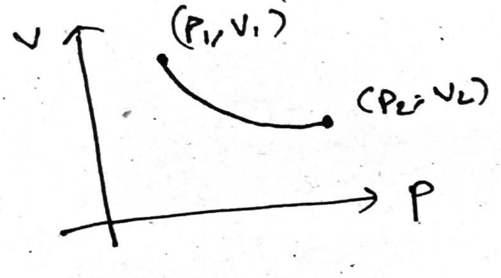
⇒ It does not matter how you reached a state (path independent)

On the other hand, ΔW is path dependant.



$$\Delta W = P\Delta V \qquad (\text{from } F \cdot ds = dW)$$

In this system,

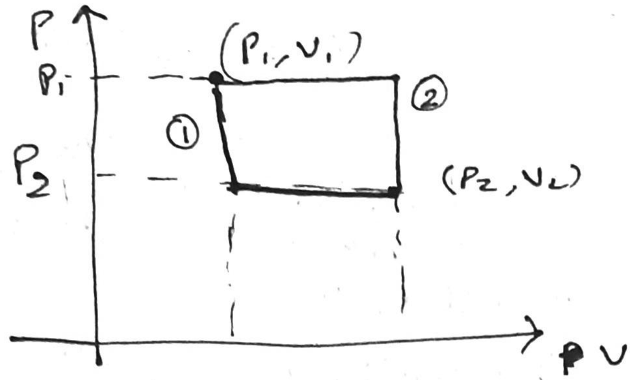


There are many paths from (P_1, V_1) to (P_2, V_2)

We imagine path where <u>the points are in equilibrium</u> (as P and V need to be well defined)

This way of moving from (P_1, V_1) to (P_2, V_2) is a quasistatic process — every intermediate point is well defined thermodynamic equilibrium states.

(*) Note that this always has an attached timescale.



ΔW for this case,

$\Delta W_1 = P_2(V_2 - V_1)$

$\Delta W_2 = P_1(V_2 - V_1)$

So, $\Delta W_1 \neq \Delta W_2$

$\rightarrow$ ΔW is path dependent.

ΔQ will also change, but it will change such that ΔU remains the same.

First law $\rightarrow$ $dU = dQ + dW$

$$\Rightarrow dU = dQ - pdV$$

$$\Rightarrow dQ = dU + pdV$$

Internal energy,

$$U = U(T, V)$$

$$\therefore dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

This allows us to write,

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) dV$$

(*) Isochoric process — V remains constant.

We define some quantity

$$C_V \equiv \left(\frac{dQ}{dT}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V$$

Response function: To see how system responds when we do something.
(Easy to measure in lab)

Heat capacity at constant volume.

In a similar way,

$$C_P \equiv \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial u}{\partial T}\right)_V + \left\{P + \left(\frac{\partial u}{\partial V}\right)_T\right\}\left(\frac{\partial V}{\partial T}\right)_P$$

Heat capacity at constant pressure

Note these are not related ~~to~~ to ideal gas systems.

$$\therefore C_P = C_V + \left[P + \left(\frac{\partial u}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\Rightarrow C_P - C_V = \left[P + \left(\frac{\partial u}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$ → True in general

Now we consider the case of ideal gas → (Diff for diff system)

$$PV = RT$$

$$\Rightarrow \boxed{P\left(\frac{\partial V}{\partial T}\right)_P = R}$$

Also,

$$\left(\frac{\partial u}{\partial V}\right)_T = 0 \quad \text{(Ideal gas)}$$

Why? Since there are no interactions b/w particles of ideal gas. If we bring them closer (dV), no PE changes occur. If $dT = 0$, KE is const $\Rightarrow du$ is not changing.

Note that this depends on the molecular picture.

$\Rightarrow$ for the first law itself, $\left(\frac{\partial u}{\partial V}\right)_T = 0$ is not trivial, until we commit to the microscopic picture.

So, for ideal gas,

$$\boxed{C_p - C_v = R}$$

Mayer's Relation

☐ How do you compute this for Van der Waals gas?
(Home reading)

Tutorial Begins

$$dQ = du + pdV$$

$$= \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV + pdV$$

Now let us look at what happens for ideal gas.

$$dQ = C_v dT + pdV$$

$$\left(\text{As } \left(\frac{\partial u}{\partial V}\right)_T = 0\right)$$

○ Adiabatic transformation of ideal gas →

$$pV = RT$$

$$\Rightarrow pdV + Vdp = RdT \quad (R \to C_p - C_v)$$

$$\Rightarrow pdV + Vdp = (C_p - C_v)dT$$

LHS $\Rightarrow C_v dT + pdV = C_p dT - Vdp$

As process is adiabatic; $dQ = 0$

$$\Rightarrow C_v dT + pdV = 0$$

$$\therefore C_p dT - Vdp = 0$$

$$\Rightarrow \boxed{Vdp = C_p dT}$$

and $\boxed{pdV = -C_v dT}$

Combining,

$$\frac{dp}{p} = -\frac{C_p}{C_V}\frac{dv}{V}$$

$\Rightarrow$ Integrate it $\Rightarrow$ $\ln p = -\gamma \ln V + \ln C$ (const)

Where $\gamma \equiv \frac{C_p}{C_V}$

$\Rightarrow \boxed{pV^{\gamma} = \text{constant}}$ for ideal adiabatic change

<u>Quasistic processes for ideal gas</u> $\rightarrow$ (Generalization)

∘ $\boxed{pV^{n} = \text{constant}}$

<u>Case I</u> : $n = 0$, $p = \text{constant}$ (isobaric)

<u>Case II</u> : $n = 1$, $pV = \text{constant}$ (isothermal)

<u>Case III</u> : $n = \gamma$, $\gamma = \frac{C_p}{C_V}$, $pV^{\gamma} = \text{const}$ (adiabatic)

for <u>diff value of n, diff processes</u>.

<u>Case IV</u> : $n \to \infty$, effect of p is negligible (isochoric)

for an ideal gas,

$$dQ = C_V dT + p dv$$

So, ~~d~~ $\Delta Q = \int_1^2 C_V dT + \int_i^f p dv$

How does p change with v? we use $pV^n = c$

$$\Rightarrow \Delta Q = C_V (T_f - T_i) + \int_i^f \frac{A}{V^n} dv$$

Taken as temp independent, but that may not be right

for Ideal Gas, $C_V = \text{constant}$? ☐ Think

Normally, we take response functions to be <u>constant</u>.

We do it for $n=1$ (Special case) (most common)

$$\Delta Q = C_v(T_f - T_i) + \int_i^f \frac{A}{V^n}\, dV$$

$$= C_v(T_f - T_i) + RT_i \ln\left(\frac{V_f}{V_i}\right)$$

$= 0$ (isotherm) Substituting A

for $n \neq 1$, we get

$$\Delta Q = C_v(T_f - T_i) + R\left(\frac{T_i - T_f}{n-1}\right)$$

- ☐ Try integrating.
- ☐ Take limits of $n = 0$, $n \to \infty$, $n = \gamma$ for the expression of ΔQ given later.

We do Adiabatic,

$$\Delta Q = C_v(T_f - T_i) + R\left(\frac{T_i - T_f}{\gamma - 1}\right)$$

$$= C_v(T_f - T_i) + \frac{(C_p - C_v)(T_i - T_f)}{\frac{C_p - C_v}{C_V}}$$

$$= 0$$

⊛ General formulae for moving from one state to another quasistatically.

☐ Now calculate ΔW and ΔQ for diff paths, and check that ΔU is a state function.