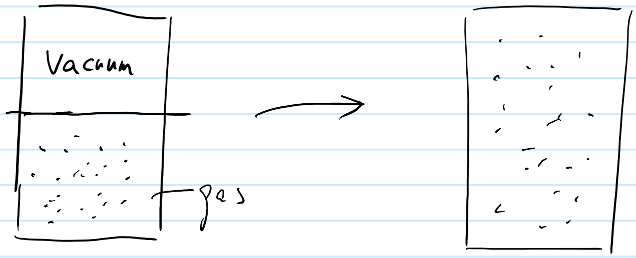
First Law of Thermodynamics II

Typical processes:

- Free Expansion:



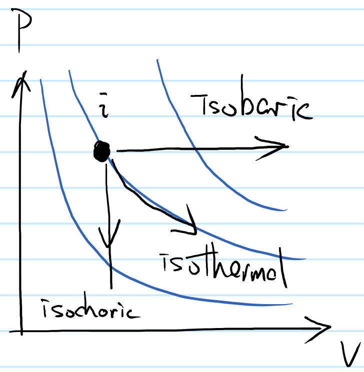
① free = no cost = no workdone by gas

$W = 0$

② speed distribution of gas molecules remains unchanged.

$\Rightarrow \Delta T = 0 \Rightarrow \Delta U = 0$

③ $Q = \Delta U + W = 0$



- Isochoric process (constant V, $dV=0$)
- Isobaric process (constant p, $dp=0$)
- Isothermal process (constant T, $dT=0$ $\Rightarrow Vdp + pdV = 0$)

Heat capacity on different processes (Ideal Gas)

Recall: Molar heat capacity $= C = \frac{1}{n}\frac{dQ}{dT}$.

dQ is process (path) dependent.

$\Rightarrow C$ is also process dependent.

Isochoric process: $dV = 0$

$$dU = dQ - dW$$

$$\Rightarrow \quad dQ = dU + \underbrace{dW}_{pdV = 0}$$

$$= dU \qquad\qquad U = \frac{f}{2}nRT \text{ for ideal gas}$$

$$= \frac{f}{2} nR\,dT$$

$$\Rightarrow \quad \boxed{C_V = \frac{1}{n}\frac{dQ}{dT} = \frac{f}{2}R}$$

seen in earlier lecture.

fixed V.

Isobaric Process: $dp = 0$

$$dQ = dU + pdV$$

$dU = \frac{f}{2}nR\,dT = \underbrace{nC_V\,dT}_{\text{always true}}$

even for process where $dV \neq 0$

$\because$ dU is independent of process.

using $pV = nRT$

$$\Rightarrow \quad d(pV) = nR\,dT$$

$$pdV + Vdp = nR\,dT$$

$$\Rightarrow \quad pdV = nR\,dT + Vdp$$

So, $dQ = \frac{f}{2}nR\,dT + nR\,dT + \cancel{Vdp}^{\,0}$

$$= \left(\frac{f}{2} + 1\right) nR\,dT$$

$$\Rightarrow \quad \boxed{C_p = \left(\frac{f}{2} + 1\right) R = C_V + R}$$

fixed p

$C_p > C_V$ more heat is needed to raise the same temperature under constant pressure, extra energy is needed to do work when expanding.

for monoatomic gas : $f = 3$, $C_V = \frac{3}{2}R$, $C_p = \frac{5}{2}R$

diatomic gas $60K \lesssim T \lesssim 600K$: $f = 5$, $C_V = \frac{5}{2}R$, $C_p = \frac{7}{2}R$

Define : ratio of heat capacity $= \gamma = \frac{C_p}{C_V} > 1$

$$\gamma_{monoatomic} = \frac{5}{3} = 1.667$$

$$\gamma_{diatomic} = \frac{7}{5} = 1.4$$

$$\gamma = \frac{C_V + R}{C_V} \Rightarrow C_V = \frac{R}{\gamma - 1}$$

<u>Adiabatic Process</u> : Process where no heat exchange.

$$dQ = 0 \Rightarrow W = -\Delta U$$

expansion : $W > 0 \Rightarrow \Delta U < 0$ cooling

compression : $W < 0 \Rightarrow \Delta U > 0$ heating.

Question : How does the path of adiabatic process on a p-V diagram look like?

Consider a state changes from (p, V, T) to $(p+dp, V+dV, T+dT)$ with dp, dV and dT satisfy a constraint that $dQ = 0$.

What dp, dV and dT will we have?

Answer:

$$dU = \cancel{dQ}^{\,\to 0} - p\,dV = -p\,dV = -\frac{nRT}{V}\,dV$$

$$\| \quad nC_v\,dT$$

$$\Rightarrow \quad \frac{dT}{T} + \frac{R}{C_v}\frac{dV}{V} = 0 \qquad\qquad \frac{R}{C_v} = \gamma - 1$$

$$\boxed{\frac{dT}{T} + (\gamma-1)\frac{dV}{V} = 0} \quad \leftarrow \text{define the adiabatic path / line.}$$

How should T & V relate along the adiabatic line?

Solve $\frac{dT}{T} + (\gamma-1)\frac{dV}{V} = 0$

integrate both sides $\int\frac{dT}{T} + (\gamma-1)\int\frac{dV}{V} = 0$

$$\Rightarrow \ln T + (\gamma-1)\ln V = \text{constant.}$$

$$\Rightarrow \ln(TV^{\gamma-1}) = \text{constant.}$$

$$\Rightarrow \boxed{TV^{\gamma-1} = \text{constant}}$$

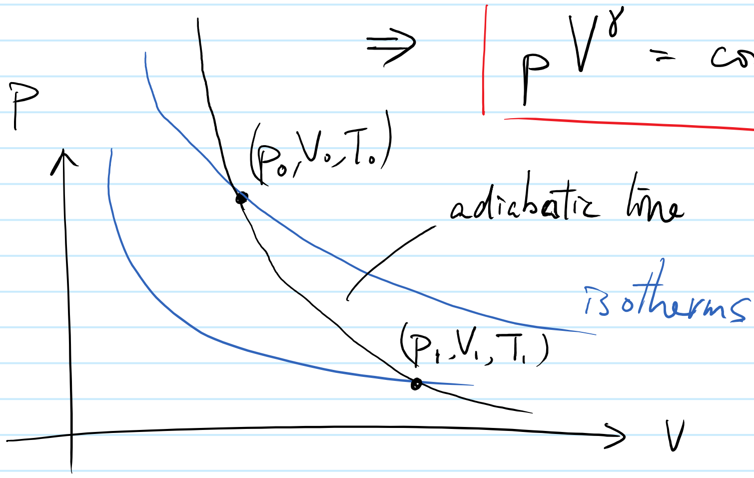
Different constant values

using $T = \frac{pV}{nR}$

$$TV^{\gamma-1} = \frac{pV^\gamma}{nR} = \text{constant.}$$

$$\Rightarrow \boxed{pV^\gamma = \text{constant}} = \underline{p_0 V_0^\gamma}$$

some ref. point on the line.



$$\begin{cases} p_1 V_1^\gamma = p_0 V_0^\gamma \\ T_1 V_1^{\gamma-1} = T_0 V_1^{\gamma-1} \end{cases}$$

Work done in adiabatic process.

$$W = -\Delta U = -n C_v \Delta T = -n C_v (T_f - T_i)$$

$$W = n C_v (T_i - T_f)$$

$$= n C_v \left(\frac{p_i V_i}{nR} - \frac{p_f V_f}{nR} \right)$$

$$= \frac{C_v}{R} (p_i V_i - p_f V_f)$$

$$\boxed{W = \frac{1}{\gamma - 1} (p_i V_i - p_f V_f)}$$

Summary: in adiabatic process, the state (p, V) satisfies

$$pV^\gamma = p_0 V_0^\gamma$$

as well as $pV = nRT$. (EOS is still valid)

- adiabatic line are steeper in p-V diagram.

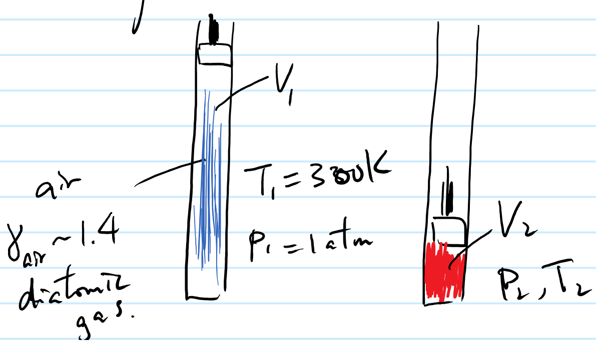
$$\because \quad p = \frac{\text{constant}}{V^\gamma}, \quad \gamma > 1$$

compared to isotherms where

$$p = \frac{nRT}{V} = \frac{\text{constant}}{V}$$

Adiabatic compression. (demo)

gas being compressed quickly does not have enough time to exchange heat with surroundings. $\Rightarrow Q = 0$



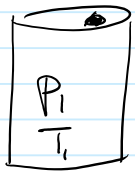
$T_2 = ?$ if $V_2 = \frac{V_1}{10}$

$$T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 746\,K \simeq 473\,°C$$

Video demo

Cloud appearing when opening a can of soft drink.

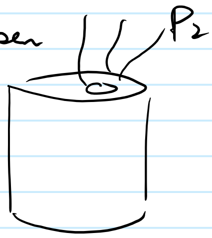


Pressure in a can $= P_1 \sim 1.2$ atm

Temperature of can taken out from fridge

$$T_1 = 4\,^\circ C = 277\,K.$$

when open



$P_2 = 1$ atm

$T_2 = ?$

γ of CO2 = 1.29

Assume the gas inside the can expands adiabatically (fast)

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$pV = nRT$$

$$V \propto \frac{T}{p}$$

$$\Rightarrow \frac{T_1^{\gamma}}{P_1^{\gamma-1}} = \frac{T_2^{\gamma}}{P_2^{\gamma-1}}$$

$$T_2 = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \cdot T_1 = 265.8\,K = -7\,^\circ C$$

cold enough to condense the water vapour in the air to form cloud.