

First law

$$dE = dQ + dW$$

(signs \uparrow in \uparrow on)

Work

$$W = - \int_{r_0}^{r_1} F dr \quad (dW = -Fdr)$$

$$W = -PdV \quad \text{for constant pressure}$$

Heat capacity

$$dQ = C dT$$

Heat capacity can depend on
thermodynamic conditions

2 heat capacities

constant volume / constant P

$$C_v = \left(\frac{\partial q}{\partial T} \right)_v \quad C_p = \left(\frac{\partial q}{\partial T} \right)_p$$

is one bigger or smaller or same

$$C_v > C_p$$

1

$$C_p > C_v$$

2

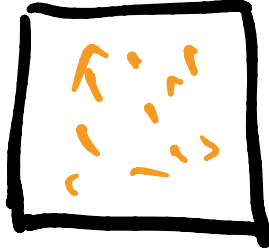
$$C_p = C_v$$

3

depends

4

const volume



const pressure



how much energy does it take to increase T by 1°

$$\Delta E = q + w$$

$$q = \int_{T_1}^{T_2} C dT = C \Delta T$$

a) constant volume

$$w = -P \Delta V = 0$$

$$\Delta E = C_V \Delta T$$

b)

b) constant pressure

$$\Delta E = C_p \Delta T - P \Delta V$$

$\left[\begin{array}{l} \text{a) } \\ \text{b) } \end{array} \right. \quad E = C_v \Delta T$

$$\rightarrow C_p = \frac{\Delta E + P \Delta V}{\Delta T} = \left(\frac{\partial (E + P \Delta V)}{\partial T} \right)_P$$

$$C_v = \Delta E / \Delta T \equiv \left(\frac{\partial E}{\partial T} \right)_V$$

$$H = E + PV$$

(enthalpy)

$$dH = d(E + PV)$$

$$= dE + d(PV)$$

$$= dE + PdV + VdP$$

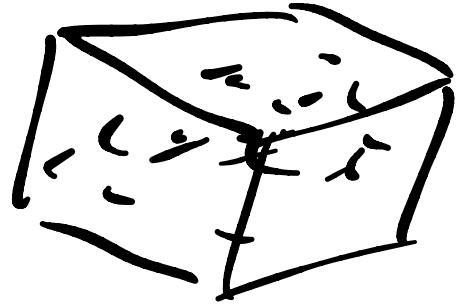
if constant pressure

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Consider ideal gas

$$\textcircled{1} \quad PV = nRT$$



$$\textcircled{2} \quad E = \frac{3}{2} nRT \quad (\text{monatomic})$$

$$= \frac{5}{2} nRT \quad (\text{diatomic})$$

$$= \frac{A}{2} nRT \quad A = 2n + 1$$

$$R = 8.314 \text{ J/k mol}$$

$$= 0.08206 \frac{\text{l atm}}{\text{k mol}}$$

$$l = [\text{length}^3] \quad \text{atm} = [P] \\ = [F] / [l]^2$$

$$\text{l atm} \sim [F][l]$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V \stackrel{\text{MIG}}{=} \frac{\partial}{\partial T} \left(\frac{3}{2} n RT \right)_V$$
$$= \frac{3}{2} n R$$

molar heat capacity $C_V/n \sim c_V = \frac{3}{2} R$

$$12 \text{ J/k mol}$$

$$C_{\text{water}} = 4.184 \text{ J/g}^\circ\text{C} \cdot 18 \text{ g/mol}$$

$$C_p = \frac{\partial}{\partial T} (H)_p$$

$$= \frac{\partial}{\partial T} (E + PV)$$

$$= \frac{\partial}{\partial T} \left(\frac{3}{2} nRT + nRT \right)$$

$$= \frac{5}{2} nR \quad (\text{monatomic})$$

$$C_p > C_v$$

for ideal gas

$$C_p - C_v = nR$$

Changing conditions

What is work

$$V_i \rightarrow V_f$$

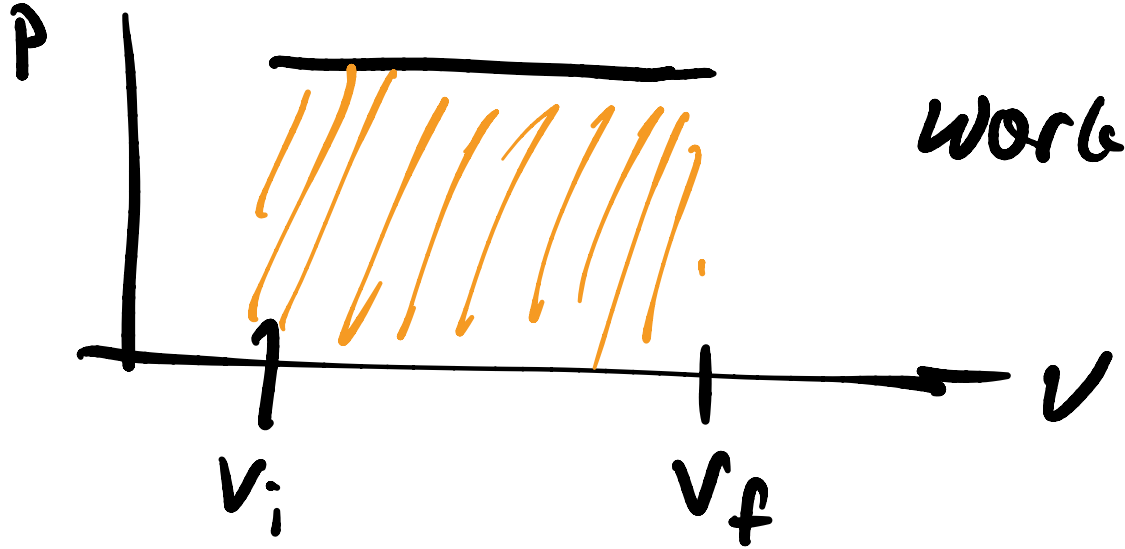
$$W = - \int_{V_i}^{V_f} P dV$$

gas goes from

area under
a curve
in P vs V

Scenario 1

constant pressure



$$\Delta E = C_p \Delta T - P \Delta V$$

$$T = \frac{PV}{nR}$$

check



$$\Delta T = T_2 - T_1 = \frac{P}{nR} (V_2 - V_1)$$

Scenario 2



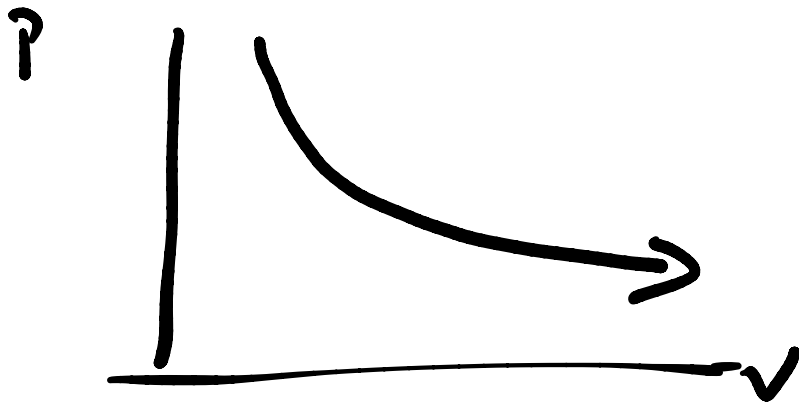
$$W = -P \Delta V = 0$$

$$\Delta E = C_V \Delta T$$

Scenario 3

Constant temp

isothermal expansion
(reversible)



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

$$\begin{aligned} W &= - \int_{V_i}^{V_f} P(V) dV = -nRT \ln V \Big|_{V_i}^{V_f} \\ &= -nRT \ln(V_f/V_i) \end{aligned}$$

$$\Delta E = q + w$$

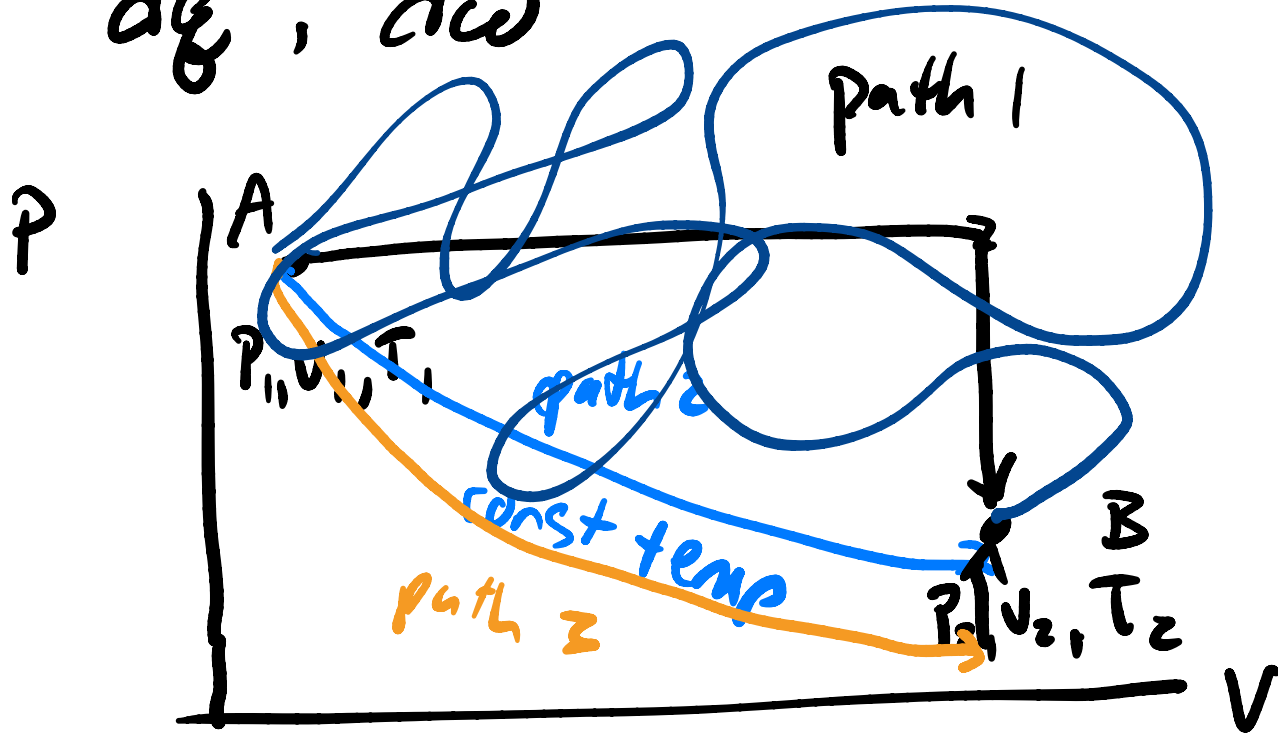
for ideal gas $E = \frac{f}{2} nRT$

@ const temp, $\Delta E = 0$

$$0 = q + w$$

$$q = -w = nRT \ln(V_f/V_i)$$

dq, dw



Energy is a state function

Adiabatic expansion

no heat flows in or out

$$dE = \cancel{dq} + dw$$

$$dE = -PdV = -\frac{nRT}{V} dV$$

ideal gas

depends on volume

Expansion $-PdV$ is negative

Energy goes down $\leftarrow E = \frac{3}{2}nRT$

