

First law       $dE = \oint q + \oint \omega$

(signs in      ↑  
                ↑  
       on )

Work       $\omega = - \int_{r_0}^{r_i} F dr$       ( $d\omega = - F dr$ )

$$\omega = - P dV \quad \text{for constant pressure}$$

Heat capacity       $dq = C dT$

Heat capacity can depend on  
thermodynamic conditions

2 heat capacities

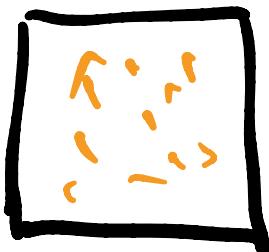
constant volume / constant P

$$C_V = (\partial Q / \partial T)_V \quad C_P = (\partial Q / \partial T)_P$$

is one bigger or smaller or same

$C_V > C_p$     $C_p > C_V$     $C_p = C_V$    depends  
1                  2                  3                  4

const volume



const pressure



how much energy does it take to increase T  
by  $1^\circ$

$$\Delta E = q + \omega$$

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

a) constant volume

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

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

b)

b) Constant pressure

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

[ $\epsilon$ ]

$$\epsilon = C_v \Delta T$$

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

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

$$H = E + PV$$

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

$$= dE + d(PV)$$

$$= dE + PdV + VdP$$

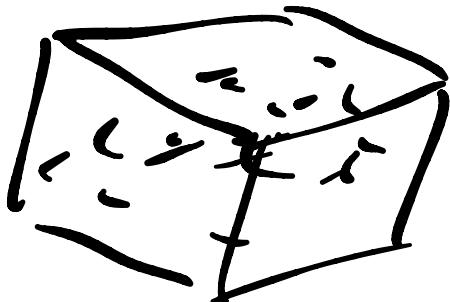
If constant pressure

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

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

Consider ideal gas

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



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

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

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

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

$$\approx 0.08206 \frac{\text{Latm}}{\text{K mol}}$$

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

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

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = \frac{MIG}{\partial T} \left( \frac{5}{2} n R T \right)_V$$

$$= \frac{3}{2} n R$$

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

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

$$c_{v, \text{water}} = 4.184 \text{ J/g°C} \cdot 18 \text{ g/mol}$$

$$\begin{aligned}
 C_P &= \frac{\partial}{\partial T} (H)_P \\
 &= \frac{\partial}{\partial T} (E + PV) \\
 &= \frac{\partial}{\partial T} \left( \frac{3}{2} nRT + nRT \right) \quad \downarrow \\
 &= \frac{5}{2} nR \quad (\text{monatomic})
 \end{aligned}$$

$$\begin{aligned}
 C_P > C_V &\quad \text{for ideal gas} \\
 C_P - C_V &= nR
 \end{aligned}$$

## Changing Conditions

What is work gas goes from

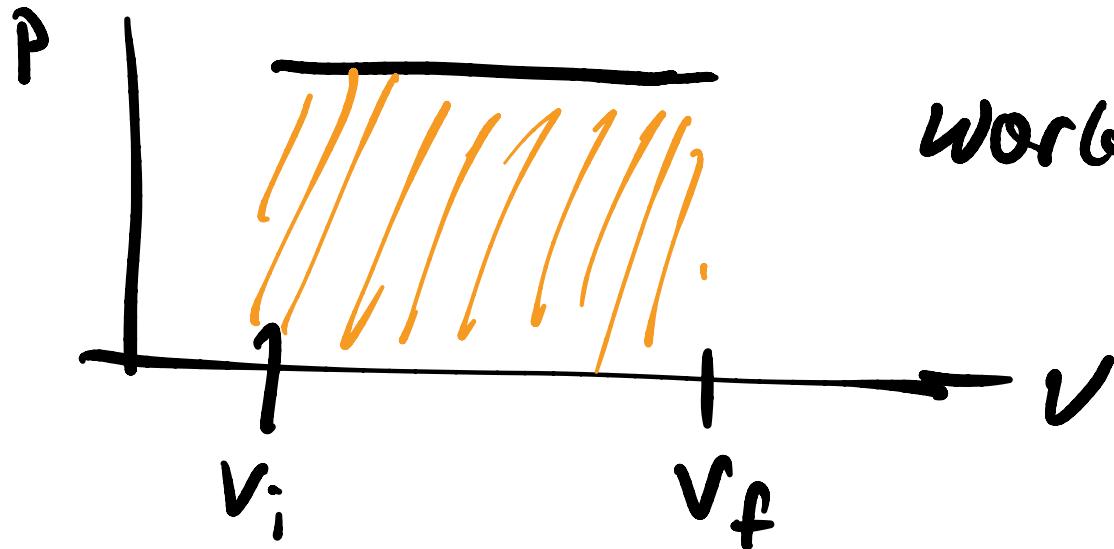
$$V_i \rightarrow V_f$$

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

area under  
a curve  
in  $P$  vs  $V$

# Scenario 1

constant pressure



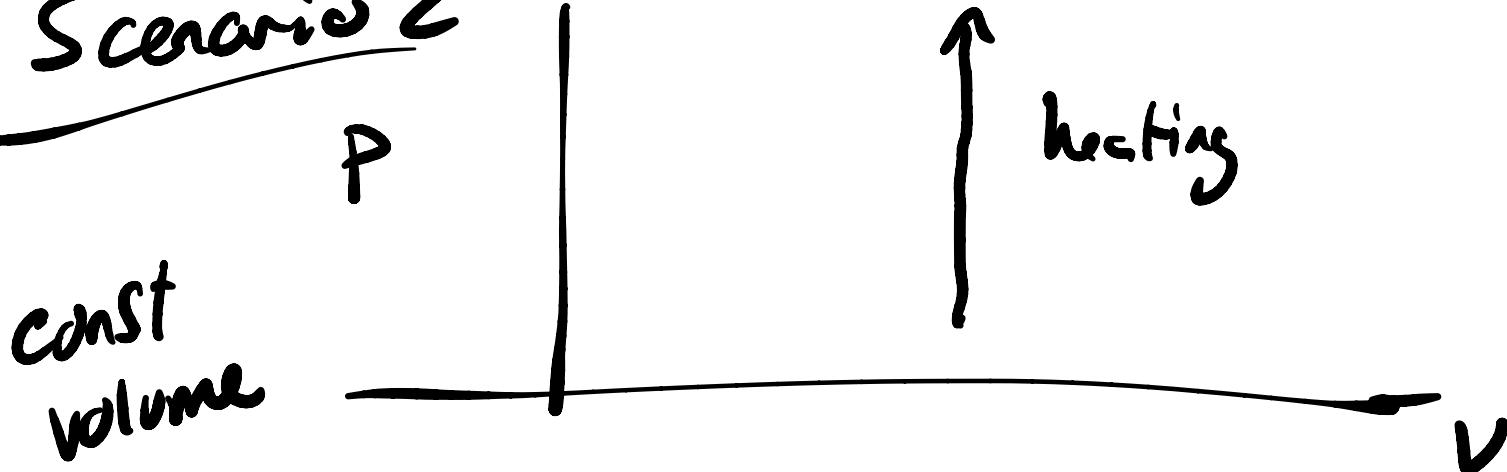
$$\underline{\Delta E} = \underline{C_p \Delta T} - \underline{P \Delta V}$$

check

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

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

Scenario 2



const  
volume

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

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

Scenario 3 Constant temp

isothermal expansion  
(reversible)



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

$$\Delta E = q + \omega$$

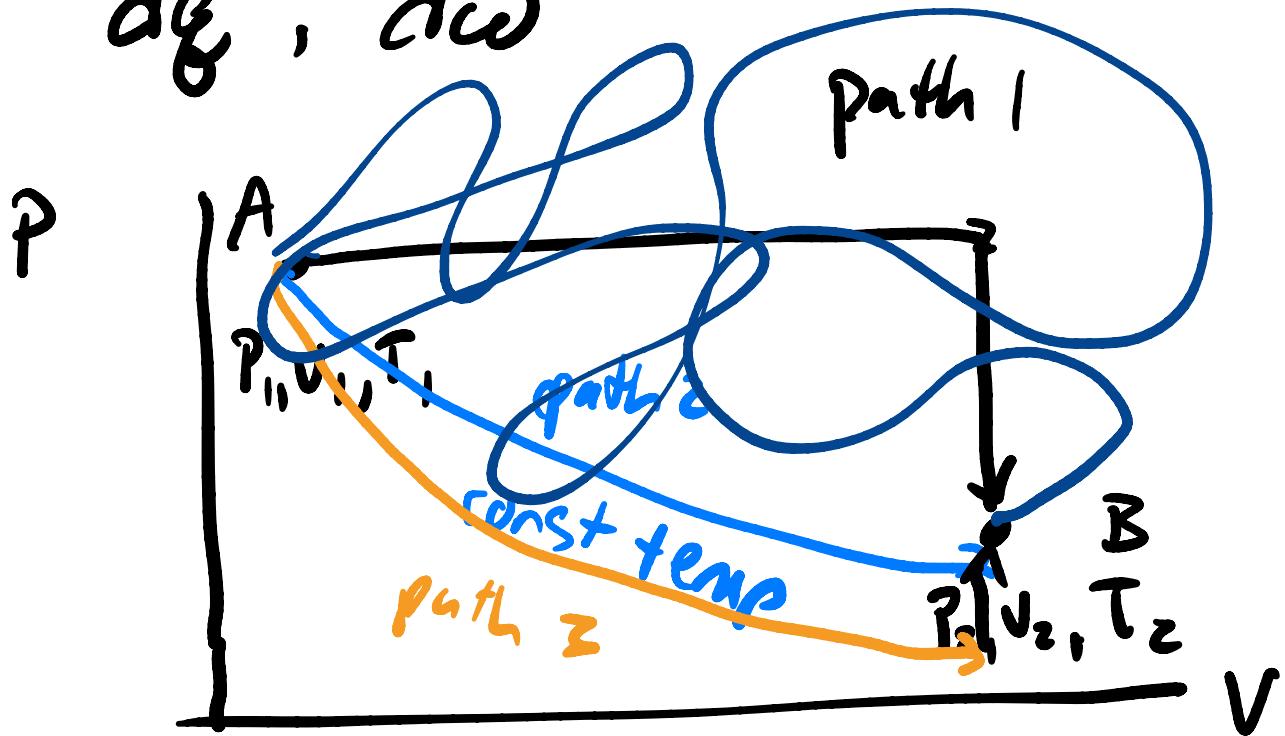
for ideal gas  $E = \frac{1}{2} nRT$

@ const temp,  $\Delta E = 0$

$$0 = q + \omega$$

$$q = -\omega = nRT \ln\left(\frac{V_f}{V_i}\right)$$

$\delta Q$ ,  $\delta W$



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  $\leftarrow E = \frac{3}{2}nRT$

