

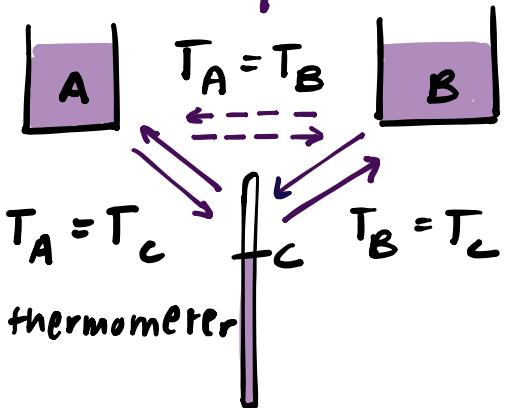
$T_1$  release heat } Net!  
 $T_2$  absorb heat } both release and absorb heat simultaneously



### Thermal Equilibrium

$$T_1 = T_2$$

### zeroth Law of Thermodynamics



### Phase transition at BC and DE

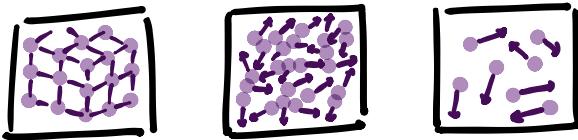
No temp change = No KE change

Heat transferred  $\Rightarrow$  Internal energy

Heat absorbed at BC < DE  
 to overcome intermolecular forces      to overcome atmospheric pressure

- \* Heat transfer from higher to lower temperature regions
- \* Thermal equilibrium and the zeroth Law of Thermodynamics
- \* Kinetic model explanations for melting and boiling without temperature change
- \* Specific latent heat:
  - Vaporization vs fusion
- \* Specific heat capacity:
  - Definition, application, and determination using electric methods
- \* Specific latent heat definition and application

### STATES OF MATTER



### Solid

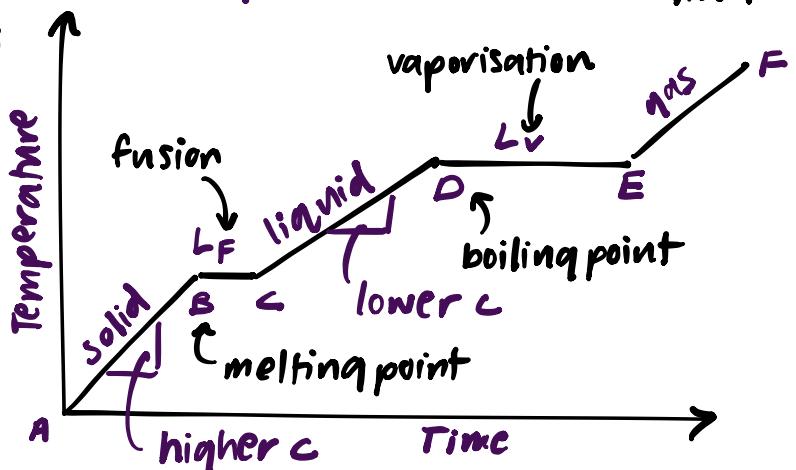
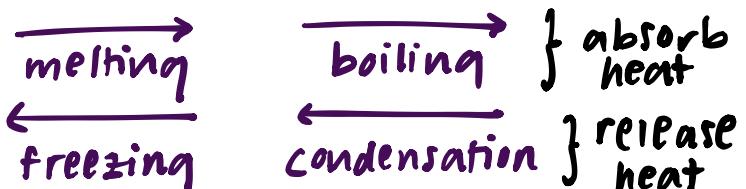
- closely packed
- high density
- fixed shape & volume
- vibrate about equilibrium
- strong inter-molecular force

### Liquid

- slightly farther apart
- lower density
- fixed volume, variable shape
- has random restricted motion
- weaker IM force

### Gas

- far apart
- lower density
- no fixed shape or volume
- move randomly at high speed
- negligible IM force



## Specific Heat Capacity, C

L heat required to increase 1 kg of substance by  $1^{\circ}\text{C}$

$$c_{\text{H}_2\text{O}} = 4.2 \times 10^3 \text{ J kg}^{-1} (\text{C}^{\circ})^{-1}$$

$$c = \frac{Q}{m\Delta T}$$

$\text{J kg}^{-1} (\text{C}^{\circ})^{-1}$

$$|T| = {}^{\circ}\text{C}$$
$$|\Delta T| = C^{\circ}$$

Heat Capacity, C

$$C = \frac{Q}{\Delta T}$$

$$\rightarrow Q = mc\Delta T$$
$$Q = C\Delta T$$

$$L_f = L_v = \frac{Q}{m} \quad \text{J kg}^{-1}$$

$$Q = mL$$

## Specific Latent Heat

of Fusion / of Vaporisation

heat required to change 1 kg of mass from solid to liquid / from liquid to gas without temperature change

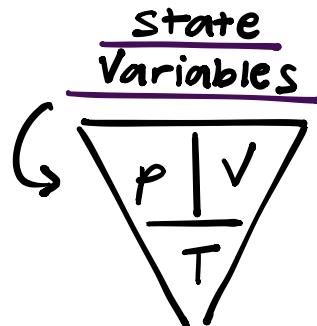
# APPLICATION OF IDEAL GAS LAWS IN PHYSICS

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A diagram illustrating the Ideal Gas Law  $PV = nRT$ . The equation is enclosed in a rectangular frame. Inside the frame, the following annotations are present:

- absolute pressure**: points to the  $P$  term.
- no of moles**: points to the  $n$  term.
- absolute temperature**: points to the  $T$  term.
- volume of container**: points to the  $V$  term.
- gas constant**: points to the  $R$  term.
- Kelvin!**: points to the  $T$  term with an arrow pointing upwards.

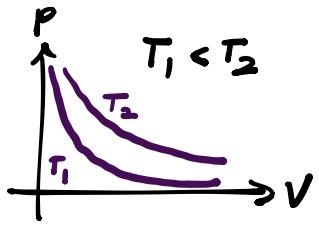
- \* Boyle's Law, Charles' Law, and Pressure Law
- \* Graphical representation of gas laws
- \* Relationship between gas laws and the equation of state
- \* Ideal gas equation:  $pV = nRT$  or  $pV = nkT$



① Boyle's Law

$$\Delta T = 0$$

$$P \propto \frac{1}{V}, P V = k$$



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

$$\textcircled{2} \quad k = \frac{nR}{P}$$

$$\textcircled{3} \quad k = \frac{nR}{V}$$

$$\frac{PV}{T} = \underline{\text{constant}}$$

does not exist  
as gas

$$= nR$$

$$\text{mass, m} / 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Molar Mass, M} \quad N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$= \left( \frac{N}{N_A} \right) R$$

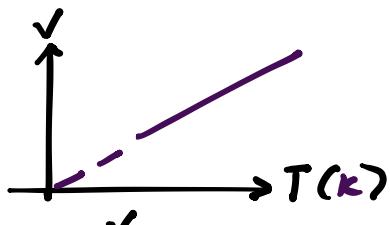
Boltzmann  
constant

$$\frac{PV}{T} = NK \quad k = \frac{R}{N_A} = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

② Charle's Law

$$\Delta P = 0$$

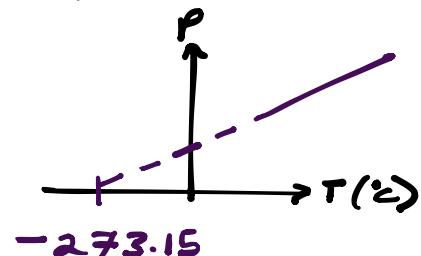
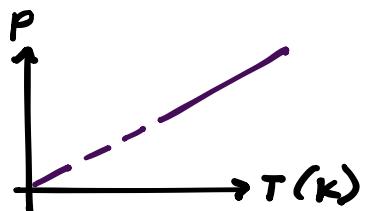
$$V \propto T, \frac{V}{T} = k$$



③ Pressure Law

$$\Delta V = 0$$

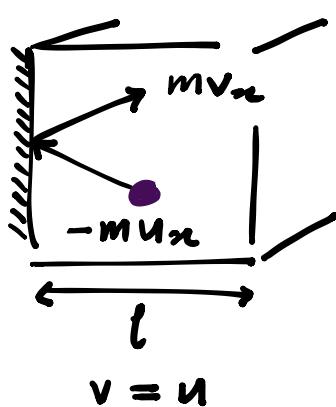
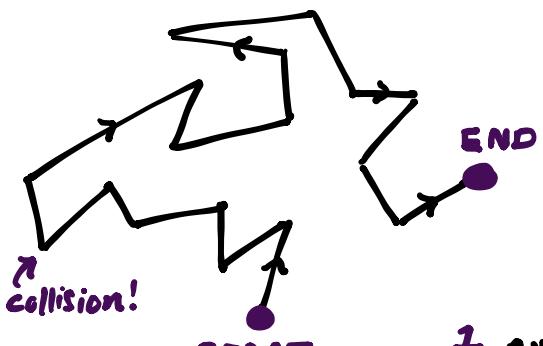
$$P \propto T, \frac{P}{T} = k$$



$$\boxed{PV = NkT}$$

## Brownian Motion

the random movement of particles in a fluid due to collisions with surrounding molecules



$$\Delta(mv_x) = mv_x - (-mv_x) \\ = 2mv_x$$

$$\Delta t = \frac{2l}{v_x} \text{ (time per collision)}$$

$$F = \frac{\Delta mv}{\Delta t} \text{ (force on the wall)}$$

$$F = \frac{mv_x^2}{l} \text{ (due to one molecule)}$$

$$\overline{v^2} = \frac{v_{x1}^2 + v_{x2}^2 + \dots + v_{xN}^2}{N}$$

↳ Mean Square Speed

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + \dots + v_N^2}{N} \implies v_{rms} = \sqrt{\overline{v^2}}$$

- \* Brownian motion and molecular movement
- \* Assumptions of the kinetic theory of gases
- \* Relationship between molecular movement and gas pressure:  $P = \frac{1}{3} \rho \overline{v^2}$
- \* Boltzmann constant:  $k = \frac{R}{N_A}$
- \* Comparison of  $\rho V = \frac{1}{3} N m v^2$  and  $\rho V = N k T$ , linking translational energy to  $T$
- \* Root mean square speed:  $v_{rms} = \sqrt{\frac{3kT}{m}}$
- \* Maxwell distribution of speeds and its dependence on temperature
- \* Most probable speed:  $v_p = \sqrt{\frac{2kT}{m}}$
- \* Average speed:  $\bar{v} = \sqrt{\frac{8kT}{\pi m}}$

## Ideal Gas Assumptions:

- 1 All gases are made up of atoms or molecules
  - ↳ move ↓
- 2 randomly & haphazardly
- 3 Volume of atoms & molecules <<< occupied by gas
- 4 negligible intermolecular forces (except during collision)
- 5 elastic!
- 6 time of collision << time between collision (straight) (constant  $v$ ) (constant  $k_E$ )

$$F = \frac{m}{l} N \overline{v_x^2} \text{ (due to } N \text{ molecules)}$$

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2} \\ \overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}, \overline{v^2} = 3 \overline{v_x^2}$$

$$F = \frac{m}{l} N \frac{\overline{v^2}}{3}$$

density

$$P = \frac{1}{3} \frac{Nm\overline{v^2}}{Al} = \frac{1}{3} P \overline{v^2}$$

## Root-Mean-Square Speed

## Average Translational Kinetic Energy of Molecules

Boltzmann constant:

$$k = \frac{K}{N_A}$$

$m$ , mass of 1 molecule  
 $M$ , molar mass  
 $N$ , number of molecules

$$\frac{1}{2} m \bar{v}^2 = \frac{3}{2} kT$$

Boltzmann constant

$$\frac{\bar{v}^2}{m} = \frac{3kT}{m}$$

$$V_{rms} = \sqrt{\frac{3kT}{m}}$$

$$\left(\frac{1}{2} m \bar{v}^2\right) N_A = \frac{3}{2} k N_A T$$

$$\frac{1}{2} M \bar{v}^2 = \frac{3}{2} kT$$

$$\bar{v}^2 = \frac{3kT}{M}$$

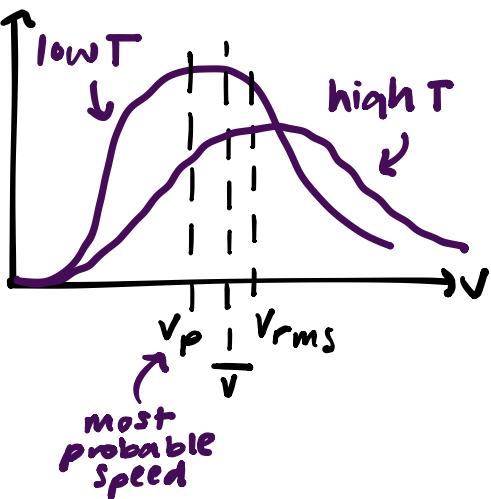
$$\left(\frac{1}{2} m \bar{v}^2\right) N = \frac{3}{2} N kT$$

$$k_{Total} = \frac{3}{2} N kT$$

$$\rho = \frac{1}{3} \rho \bar{v}^2$$

$$V_{rms} = \sqrt{\frac{3\rho}{\rho}}$$

no of molecules



$$V_p = \sqrt{2 \frac{kT}{m}}$$

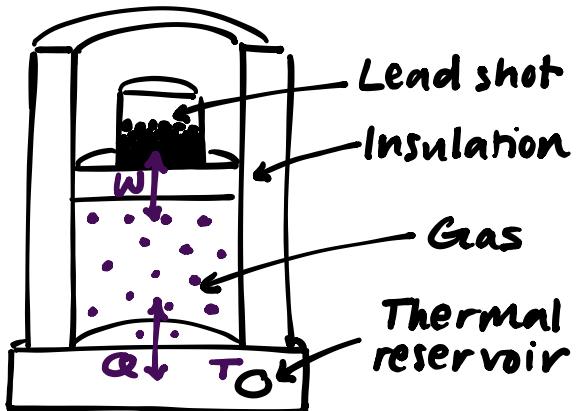
$$\bar{v} = \sqrt{\frac{8}{\pi} \frac{kT}{m}}$$

$$V_{rms} = \sqrt{3 \frac{kT}{m}}$$

For large number of molecules

# FIRST LAW OF THERMODYNAMICS

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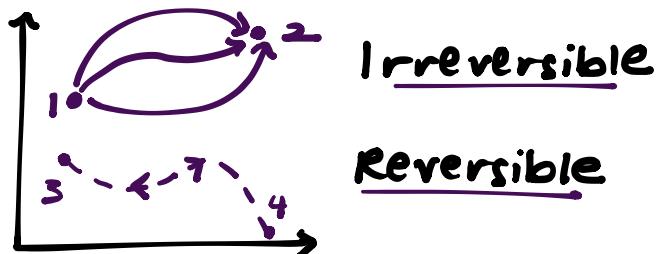
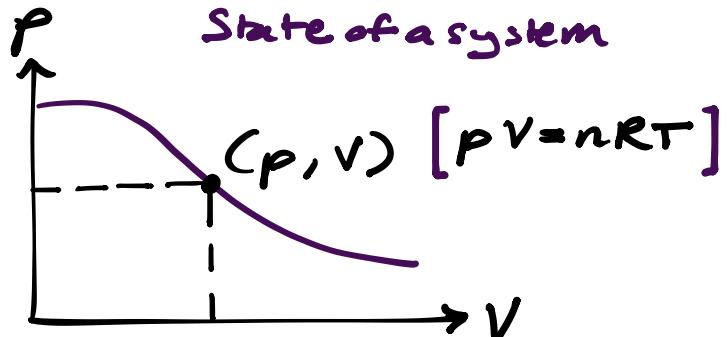


$$Q = \Delta E_{th} + W$$

- \* Represent gas states in a  $pV$ -diagram
- \* Differentiate between reversible and irreversible processes
- \* Relate internal energy to temperature
- \* Derive  $W = p\Delta V$  and interpret work from a  $pV$ -diagram
- \* Recognise path dependence of work and path independence of internal energy change
- \* Deduce  $c_p = c_v + \kappa$  and explain why  $c_p > c_v$
- \* Determine  $c_v, c_p$  and  $\gamma = \frac{c_p}{c_v}$  for different gas types

$$\text{Heat supplied} = \begin{matrix} \text{Internal energy} \\ + \end{matrix} \quad \begin{matrix} \text{External work} \\ \text{done} \end{matrix}$$

$Q$	absorb	release
$\Delta E_{th}$	increase	decrease
$W$	by system	on system
$\Delta V$	increase	decrease



## Monoatomic Gas

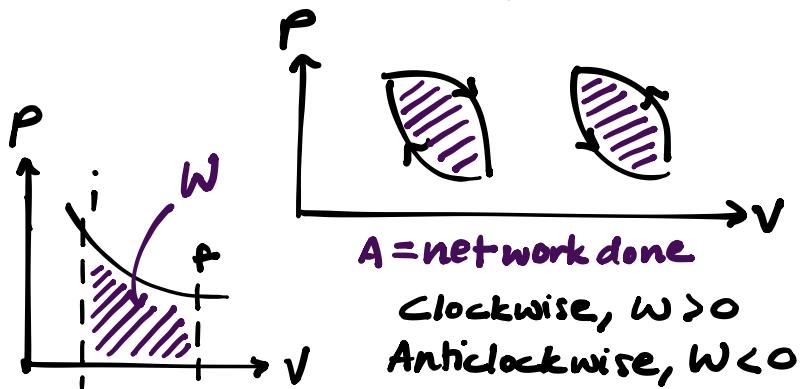
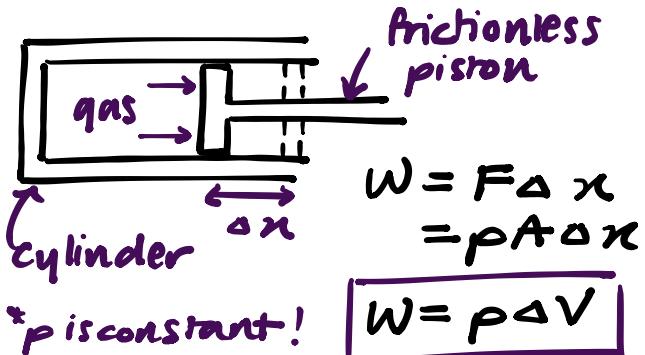
$$\Delta E_{th} = K_E \text{ (translational)}$$

## Diatomic & Polyatomic Gas

$$\Delta E_{th} = K_E \text{ (translational + rotational)}$$

$$\begin{aligned} E_{th} &\propto T \\ \Delta E_{th} &\propto \Delta T \end{aligned}$$

$E_{th}$  is a function of state (independent of path)



## Molar specific heat

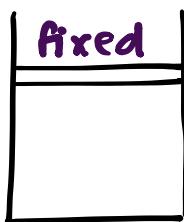
Heat required to raise the temperature of 1 mol of gas

At constant pressure,  $c_p$  At constant volume,  $c_v$

$$c = \frac{Q}{n\Delta T}$$

unit:  
 $\text{J mol}^{-1}\text{K}^{-1}$

$c_p > c_v$  ← energy  
energy provided → heat + work      provided → heat



$$Q = \Delta E_{th} + W$$

$$\Delta V = 0$$

$$Q = \Delta E_{th}$$

$$Q = nC_V\Delta T$$

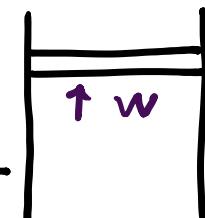
$$\Delta E_{th} = nC_V\Delta T$$



$$Q = \Delta E_{th} + W$$

$$Q = nC_p\Delta T$$

$$\Delta E_{th} + W = nC_p\Delta T$$



$$\bar{E}_k = \frac{3}{2} kT$$

$$E_k = N\bar{E}_k$$

$$= \frac{3}{2} NkT$$

$$= \frac{3}{2} N \left( \frac{R}{N_A} \right) T$$

$$E_k = \frac{3}{2} nRT$$

$$E_{th} = E_k$$

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

$$\Delta E_{th} = \frac{3}{2} nR\Delta T$$

$$\Delta E_{th} = nC_V\Delta T$$

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

$$C_p = C_V + R$$

$$C_p$$

$$C_p = C_V + R$$

$$C_p = C_V + R$$

$$\text{Mono } \frac{3}{2} R \quad \frac{5}{2} R \quad \frac{5}{3}$$

$$\text{Di } \frac{5}{2} R \quad \frac{7}{2} R \quad \frac{7}{5}$$

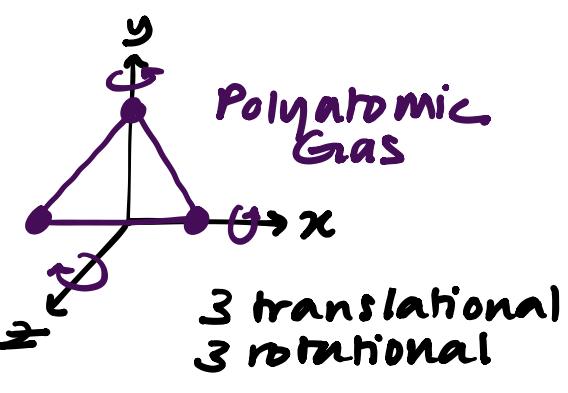
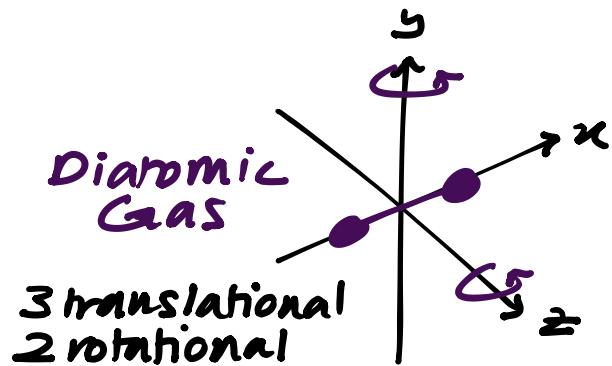
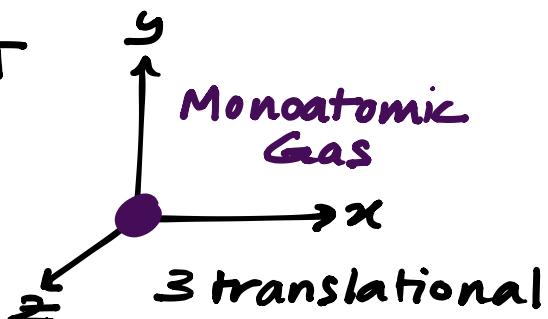
$$\text{Poly } 3R \quad 4R \quad \frac{4}{3}$$

$$nC_V\Delta T + W = nC_p\Delta T$$

$$nC_V\Delta T + p\Delta V = nC_p\Delta T$$

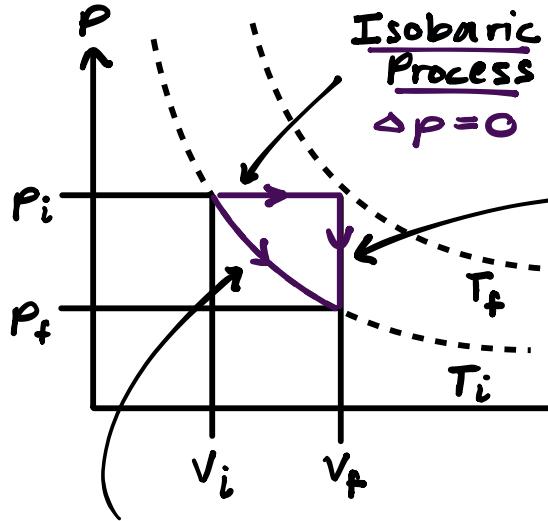
$$nC_V\Delta T + nR\Delta T = nC_p\Delta T$$

$$C_V + R = C_p$$



## Principle of Equipartition of Energy

energy is shared equally among all degrees of freedom



$$Q = \Delta E_{th} + W = nC_p \Delta T$$

$$Q = nC_v \Delta T$$

$$\Delta E_{th} = -W$$

### Isothermal Process

$$W = nRT \ln \frac{V_f}{V_i}$$

$$\rho V^\gamma = \text{const}$$

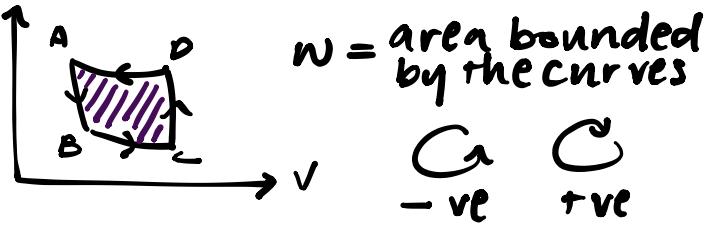
$$TV^{\gamma-1} = \text{const}$$

$$T^\gamma P^{1-\gamma} = \text{const}$$

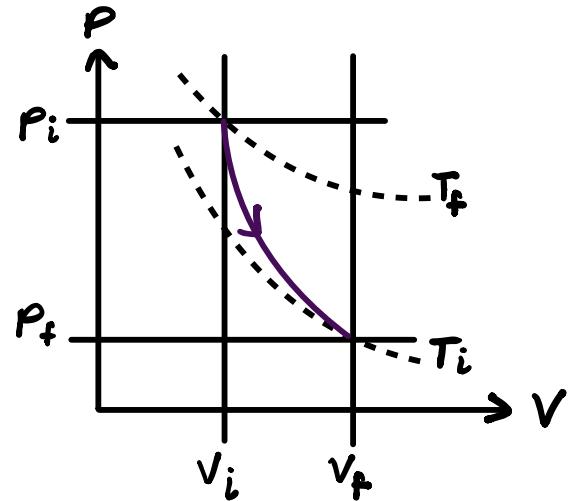
$$W = \frac{P_i V_i - P_f V_f}{\gamma-1}$$

### Cyclic Process

$$\Delta E_{th} = 0$$

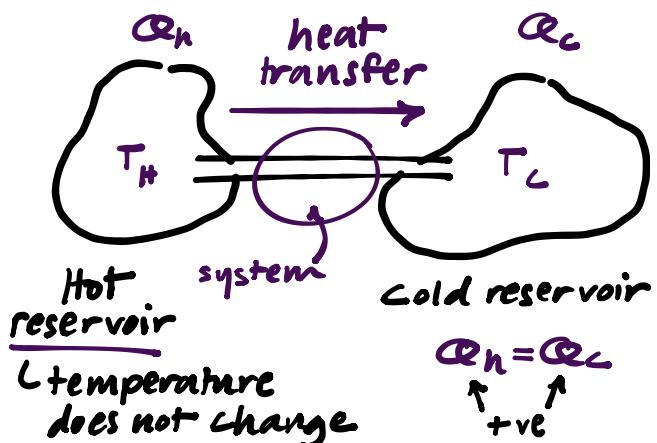


$$W_{out} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$



## SECOND LAW OF THERMODYNAMICS

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- \* Clausius statement of the second law of thermodynamics
- \* Kelvin-Planck statement of the second law of thermodynamics
- \* Energy-transfer diagram of a heat engine
- \* Analysis of heat engines and the Carnot cycle
- \* Entropy change in a simple system
- \* General statement of the second law in terms of entropy

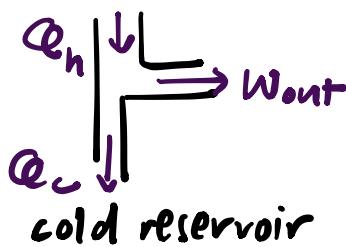
### Clausius:

- [ Heat can flow spontaneously from a hot object to a cold object ]
- [ Heat will not flow spontaneously from a cold object to a hot object ]

### "Heat engine"

- closed-cycle device

hot reservoir



heat energy  $\rightarrow$  work

$$\Delta E_{th} = 0$$

$$W_{out} = Q_{net}$$

$$W_{out} = Q_H - Q_C$$

### Thermal efficiency

$$\eta = \frac{W_{out}}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

heat source & heat sink

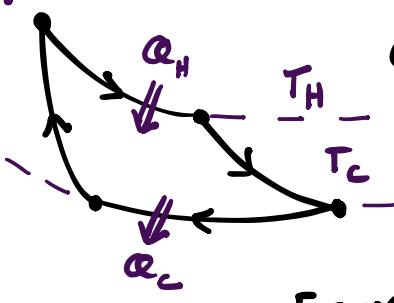
i.e. fuel i.e. cooling water

### Kelvin-Planck:

[ There are no perfect heat engines,  $\eta = 1$  ]

### "Carnot Engine"

- ideal gas cycle
- two adiabatic and two isothermal
- perfectly reversible



### Carnot Thermal efficiency

$$\eta_{\text{Carnot}} = 1 - \frac{T_C}{T_H}$$

From  $\eta$  and  $\eta_{\text{Carnot}}$ ,

$$\frac{T_C}{T_H} = \frac{Q_C}{Q_H}$$

### entropy, S

constant temperature

$$\Delta S = \frac{Q}{T}$$

varying temperature

$$\Delta S = \int_a^b \frac{dQ}{T}$$

$$dQ = m_C dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{m_C dT}{T}$$

$$\Delta S = m_C \ln \frac{T_f}{T_i}$$

(total)

General Statement:

[ the entropy of an isolated system never decreases ]

$$\Delta S_{\text{Syst}} + \Delta S_{\text{Env}} > 0$$