Ideal Gases

Experimental results on gases:

Boyle's Law
PV = constant (fixed amount of gas, constant T)

Charles' Law
V/T = constant (fixed amount of gas, constant P)
(T is in Kelvins)

Combining these two laws:

THE IDEAL GAS LAW

$$PV = nRT$$

where n is the number of moles of gas
and R is the gas constant,
$R = 8.31\ \mathrm{J/(mol \cdot K)}$

Alternate form:

$$PV = NkT$$

where N is the number of molecules in the gas
and k is the Boltzmann's constant,

$$k = 1.38 \times 10^{-23}\ J/K$$

(Comparing the two forms gives $R = N_A k$.)

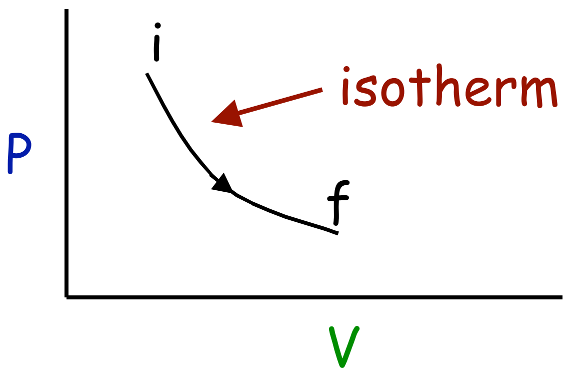
All real gases approach the "ideal gas" in the limit of very low density.

Work done at constant T

(ideal gas)

Isothermal expansion:

$PV = nRT = \text{constant}$



$P = nRT/V$

- Isotherm: a curve along which T is constant.

Work done by gas: $\Delta W = \int_i^f P\,dV$

$\Delta W = \int_i^f (nRT/V)\,dV = nRT \ln(V_f/V_i)$

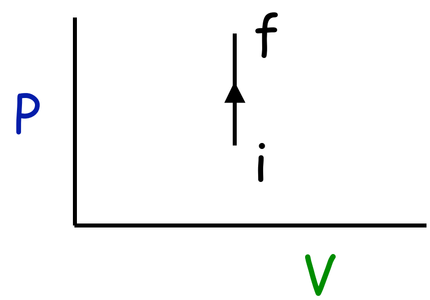
Note: if $V_f > V_i$ (expansion), then ΔW is +
if $V_f < V_i$ (compression), then ΔW is -

Work done in other processes

$$□W = \int_i^f P\, dV$$

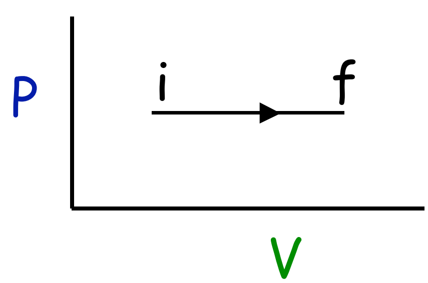
Constant Volume:

$$□W = 0$$



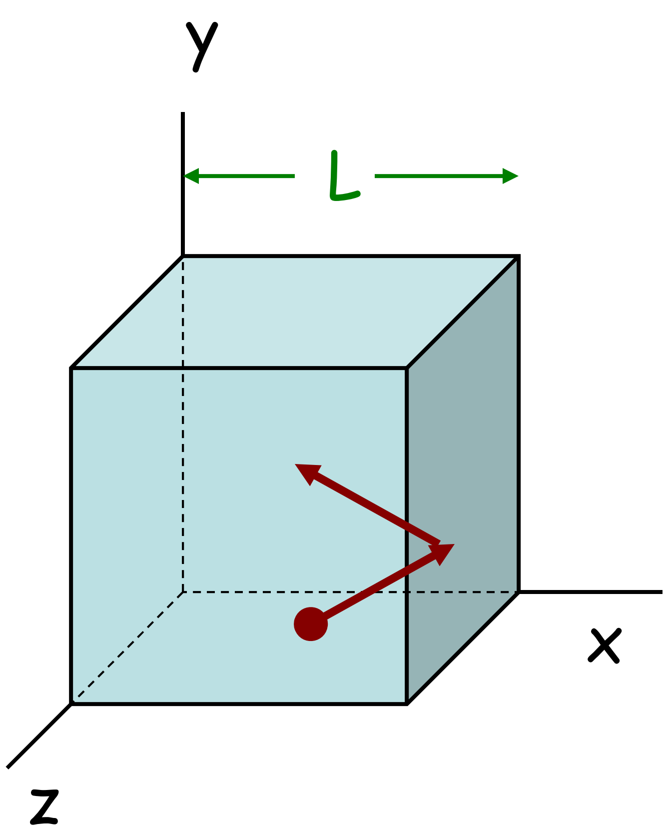
Constant Pressure:

$$□W = P\,(V_f - V_i)$$



Kinetic Theory of Gases

Consider N molecules (n moles with $n = N/N_A$) in a cubical box of side L, i.e. Volume = L^3.



Change in momentum at the x=L wall is
$\Delta p_x = 2\ m\ v_x$

Time between collisions with the x=L wall is
$\Delta t = 2\ L\ /\ v_x$

Average rate of change of momentum in x-direction:

$$\Delta p_x/\Delta t = (2mv_x)/(2L/v_x) = m\,v_x^2/\,L$$

This is force exerted by the molecule.

$$\text{Total Force} = \sum_{i=1}^{N} (m\,v_x^2)_i\,/\,L$$

$$\text{Pressure } P = \text{Force/Area} = F/L^2$$
$$= (m/L^3) \sum (v_x^2)_i$$

$$\Rightarrow \quad P = (m/L^3)\,N \left\langle v_x^2 \right\rangle$$

average

mN = nM is the total mass.

where n = # of moles
M = molar mass

$$\Rightarrow \quad P = (nM/V) \left\langle v_x^2 \right\rangle$$

For any molecule: $v^2 = v_x^2 + v_y^2 + v_z^2$

$\Rightarrow \quad \langle v_x^2 \rangle = (1/3) \langle v^2 \rangle$

$\Rightarrow \quad P = (nM/3V) \langle v^2 \rangle$

Define root-mean-square speed v_{rms}:

$$v_{rms} = \sqrt{\langle v^2 \rangle}$$

$\Rightarrow \quad PV = (nM/3) v^2_{rms}$

From <u>ideal gas law</u>: $PV = nRT$

$\Rightarrow \quad (nM/3) v^2_{rms} = nRT$

$$\Rightarrow \quad \boxed{v_{rms} = \sqrt{3RT/M}}$$

microscopic $v_{rms} \Leftrightarrow$ macroscopic T

Kinetic Energy

Average (translational) kinetic energy per molecule

$$= (1/2)\, m \langle v^2 \rangle = (1/2)\, m\, (3RT/M)$$

Using $M/m = N_A$,

$$\langle K \rangle = 3RT/(2N_A) = (3/2)\, k\, T$$

□ $$\boxed{\langle K \rangle = (3/2)\, k\, T}$$

A measurement of the Temperature of a gas is equivalent to a measure of the average kinetic energy of its molecules.

Molecular Speeds at Room Temp

(T=300 K)

Gas	molar mass(g)	v_{rms}(m/s)
Hydrogen, H_2	2	1920
Helium, He	4	1370
Water vapor, H_2O	18	645
Nitrogen, N_2	28	517
Oxygen, O_2	32	483
Carbon Dioxide, CO_2	44	412
Sulfer Dioxide, SO_2	64	342

Table 20.1

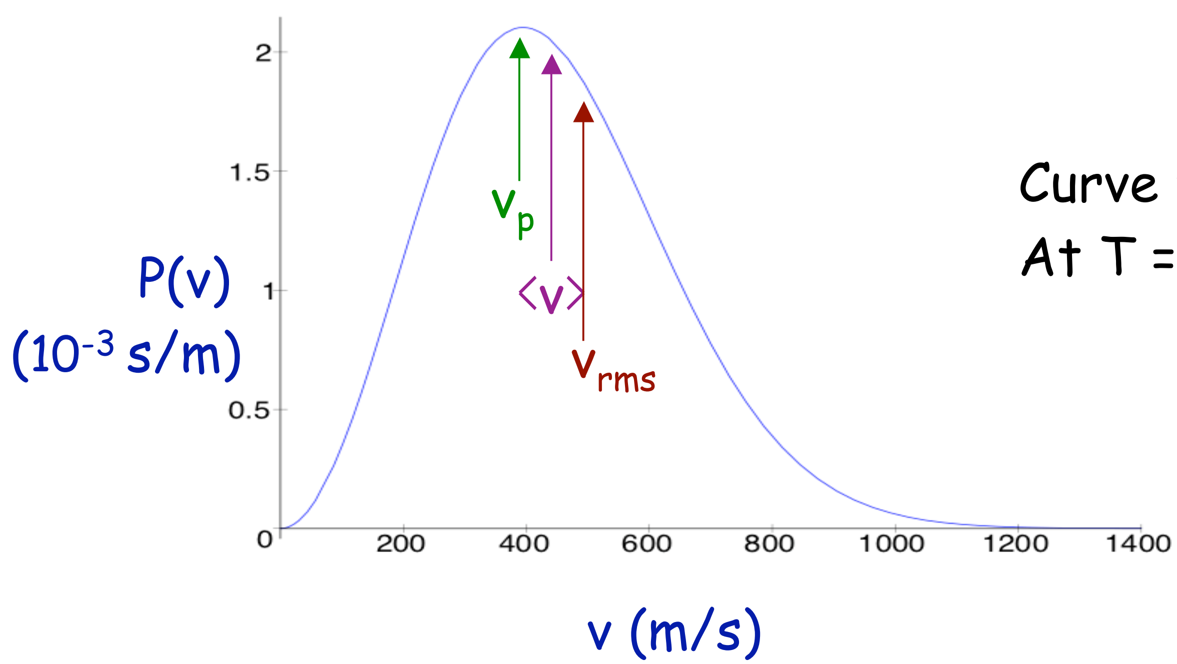
Maxwell's Speed Distribution

The distribution of molecular speeds was first written down by Maxwell (1852):

$$P(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-\frac{Mv^2}{2RT}}$$

$P(v)\,dv$ is the probability that a molecule has speed between v and $v + dv$.

It is normalized to 1. $\int_0 P(v)\,dv = 1$.



Curve for O_2
At T = 300 K

Average speed:

$$\langle v \rangle = \int_0 v\, P(v)\, dv = \sqrt{8RT/(\pi M)}$$

Root-mean-square speed:

$$\langle v^2 \rangle = v^2_{rms} = \int_0 v^2\, P(v)\, dv = 3RT/M$$

Most probable speed (maximum of distribution curve):

$$v_p = \sqrt{2RT/M}$$

Internal Energy

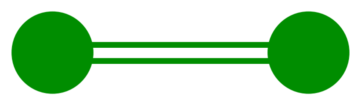
(due only to kinetic energy of atoms)

- Monatomic gas - Single atoms:

$U = N\,(3/2)\,kT = (3/2)\,nN_A kT = (3/2)\,nRT$

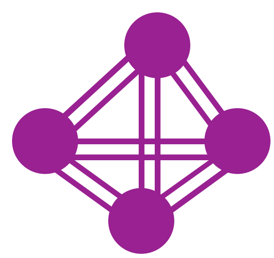
Each atom has 3 Degrees of Freedom.
(K. E. in x, y, or z directions).

- Diatomic molecule:



Rotates (in two planes)
□ 5 degrees of freedom.

$U = (5/2)\,nRT$



- Polyatomic molecule:

Rotates in all 3 planes
□ 6 degrees of freedom.
(3 translational + 3 rotational).

$U = (6/2)\,nRT = 3\,nRT$

"Equipartion of Energy"

Molar Specific Heats

(of ideal gas)

Recall: Specific heat tells how T changes as Q is added.

This depends on the conditions:
Constant V or Constant P.

Constant Volume: $\Delta Q = n\, C_V \Delta T$
where C_V is specific heat at constant V.

1st Law of TD: $\Delta Q = \Delta U + \Delta W$

At constant V, $\Delta W = 0$.

□ $\Delta Q = \Delta U = (3/2)\, nR\Delta T$ (monatomic gas)

Comparing with definition of C_V gives:

$$C_V = (3/2)\, R = 12.5\ \mathrm{J/(mol \cdot K)}$$

Constant Pressure: $\Delta Q = n\, C_P \Delta T$

where C_P is specific heat at constant P.

1st Law of TD: $\Delta Q = \Delta U + \Delta W$

At constant P, $\Delta W = P\, \Delta V$.

Ideal gas law: $P\, \Delta V = nR\, \Delta T$

$\Rightarrow \quad \Delta Q = (3/2)\, nR\, \Delta T + nR\, \Delta T = (5/2)\, nR\, \Delta T$

$\Rightarrow \quad C_P = (5/2)\, R$ (again, for monatomic gas)

In General:

$$\boxed{C_P = C_V + R}$$

Quantum Mechanics and Equipartition of Energy

Quantum Theory predicts:

rotational energies are quantized (only have certain discrete values).

- Rotational degrees of freedom only "turn on" above some minimum temperature (roughly when kT is larger than the lowest rotational energy level of the molecule).

(Fig. 19-11 of Fishbane)

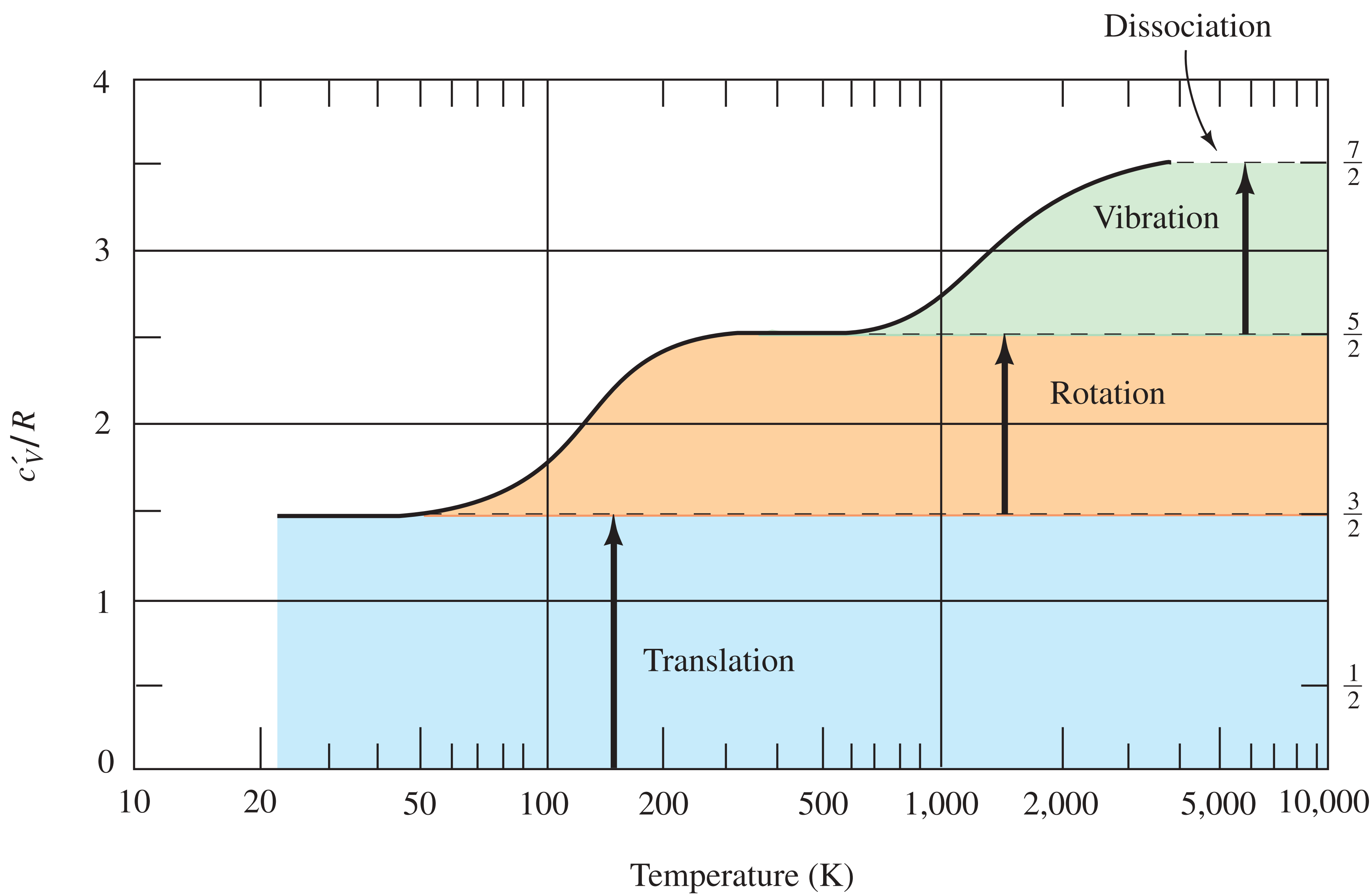


Figure Number: 19 11
Fishbane/Gasiorowicz/Thornton
Physics for Scientists and Engineers, with
Modern Physics 3E

Adiabatic Expansion ($\Delta Q = 0$)

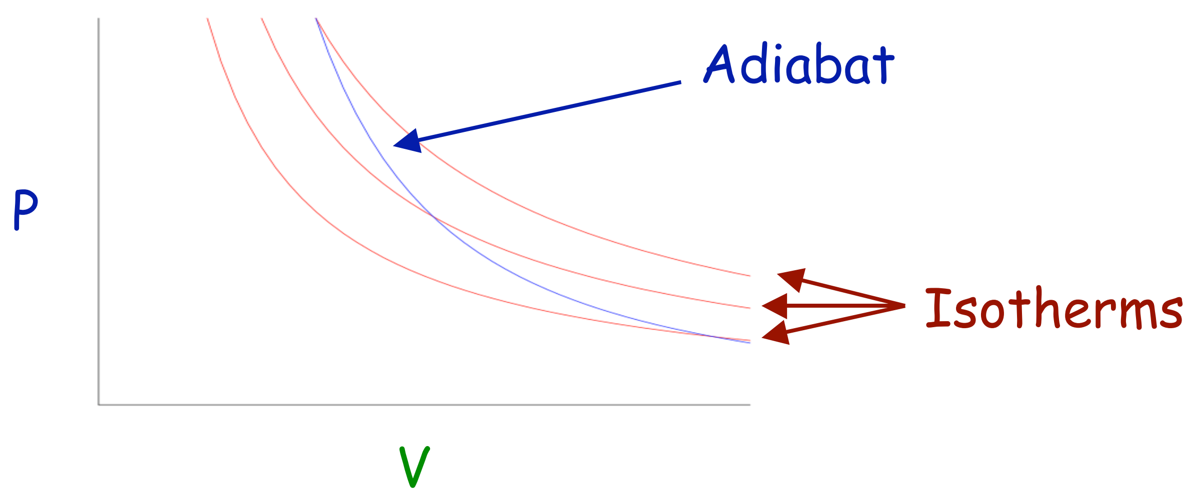
Occurs if:

- change is made sufficiently quickly
- and/or with good thermal isolation.

Governing formula:

$$PV^{\gamma} = \text{constant}$$

where $\gamma = C_P / C_V$



Because PV/T is constant (ideal gas):

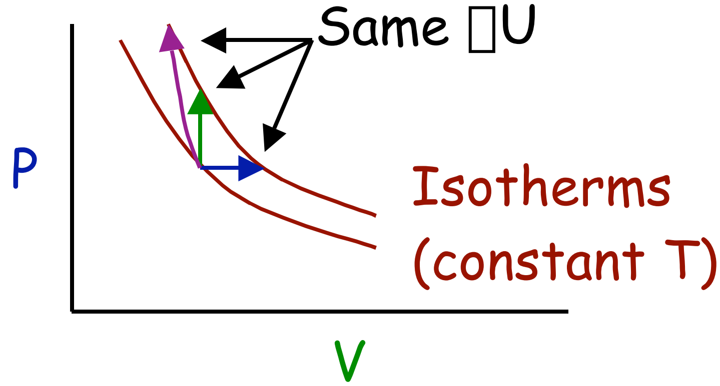
$$V^{\gamma-1}T = \text{constant} \qquad \text{(for adiabatic)}$$

Proof of PV^{γ}=constant

(for adiabatic process)

1) Adiabatic: $dQ = 0 = dU + dW$
$= dU + PdV$

2) U only depends on T:



$dU = n\,C_V\,dT$ (derived for constant volume, but true in general)

3) Ideal gas: $T = PV/(nR)$
$dT = [(dP)V + P(dV)]/(nR)$

Plug into 2): $dU = (C_V/R)[VdP + PdV]$

Plug into 1): $0 = (C_V/R)[VdP + PdV] + PdV$

Rearrange:

$$(dP/P) = -(C_V+R)/C_V\,(dV/V)$$
$$= -\gamma(dV/V)$$

where $\gamma = (C_V+R)/C_V = C_P/C_V$

Integrate both sides:

$$\ln(P) = -\gamma\ln(V) + \text{constant}$$

or

$$\ln(PV^{\gamma}) = \text{constant}$$

or

$$PV^{\gamma} = \text{constant}$$

QED

Irreversible Processes

Examples:

- Block sliding on table comes to rest due to friction: KE converted to heat.

- Heat flows from hot object to cold object.

- Air flows into an evacuated chamber.

Reverse process allowed by energy conservation, yet it does not occur.

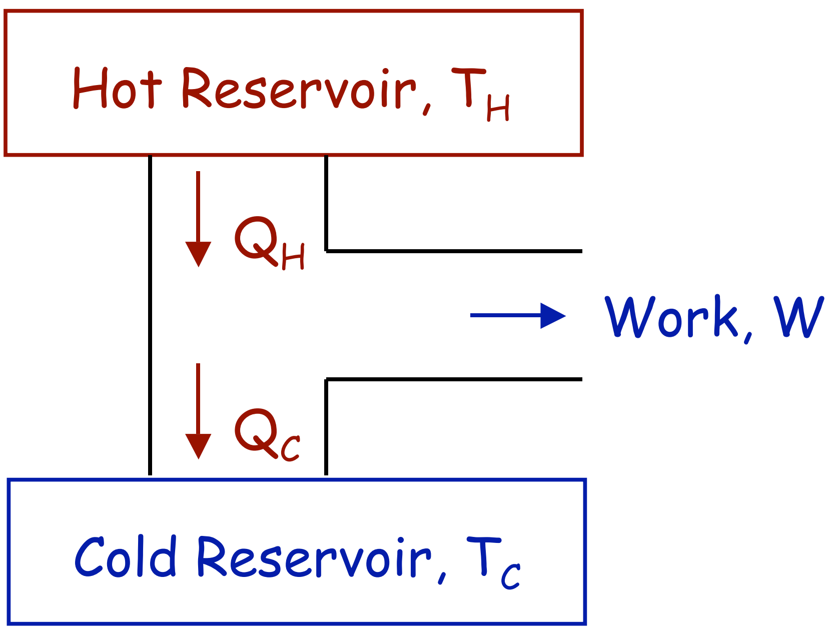
→ arrow of time

Why?

2nd Law of Thermodynamics (entropy)

Heat Engines

Heat engine: a cyclic device designed to convert heat into work.



2nd Law of TD (Kelvin form):

It is impossible for a cyclic process to remove thermal energy from a system at a single temperature and convert it to mechanical work without changing the system or surroundings in some other way.