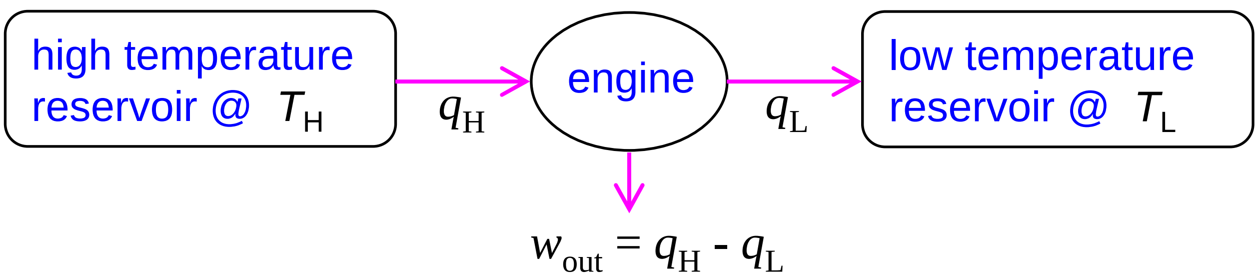
Heat Engines

A heat engine is a system capable of transforming heat into __________ by some cyclic process.

We will see that an __________ cyclic process can not produce net work. (2nd Law of Thermodynamics)

The __________ of a heat engine is defined as the ratio of the work produced to the heat __________ :

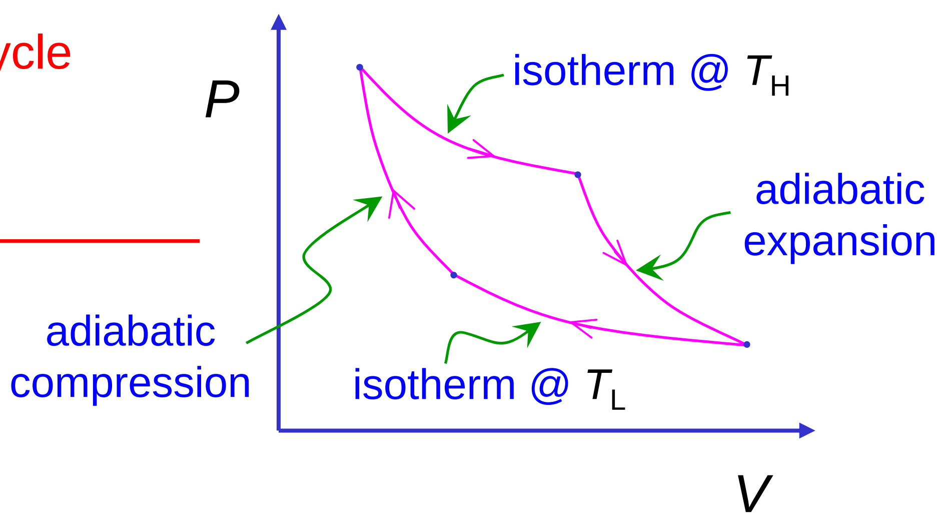
$$\varepsilon = \frac{w}{q_{\mathrm{H}}} = \frac{q_{\mathrm{H}} - q_{\mathrm{L}}}{q_{\mathrm{H}}} = \boxed{\quad}$$



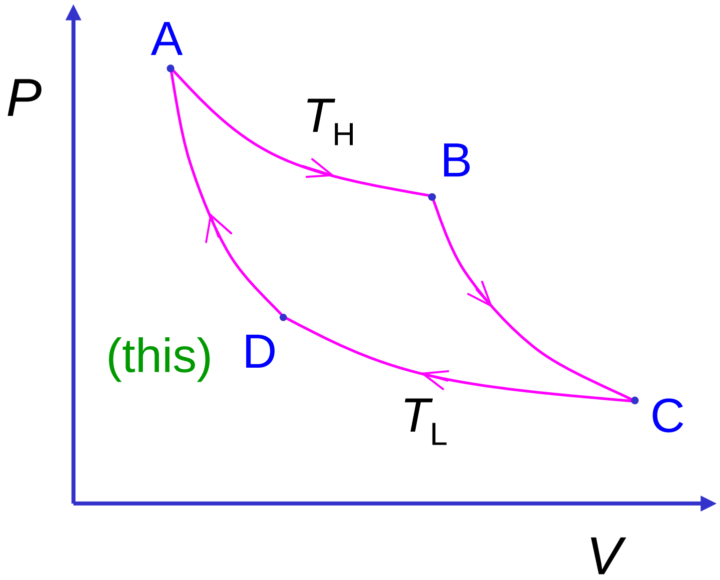
A heat __________ is a heat engine in reverse. Work is needed to transfer heat from a lower to a higher temperature reservoir.

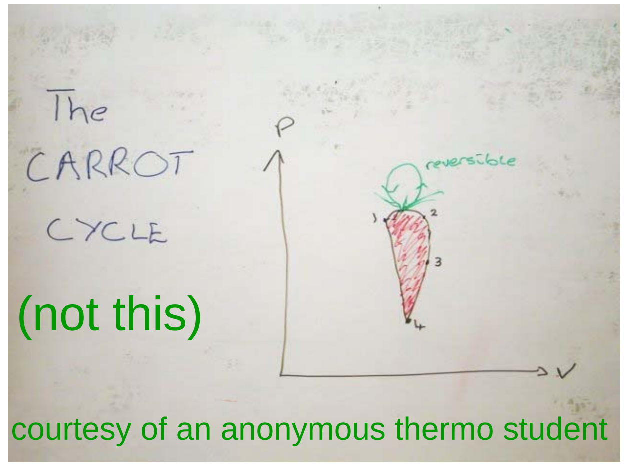
__________ Cycle

- ideal gas
- all steps __________



The Carnot Cycle





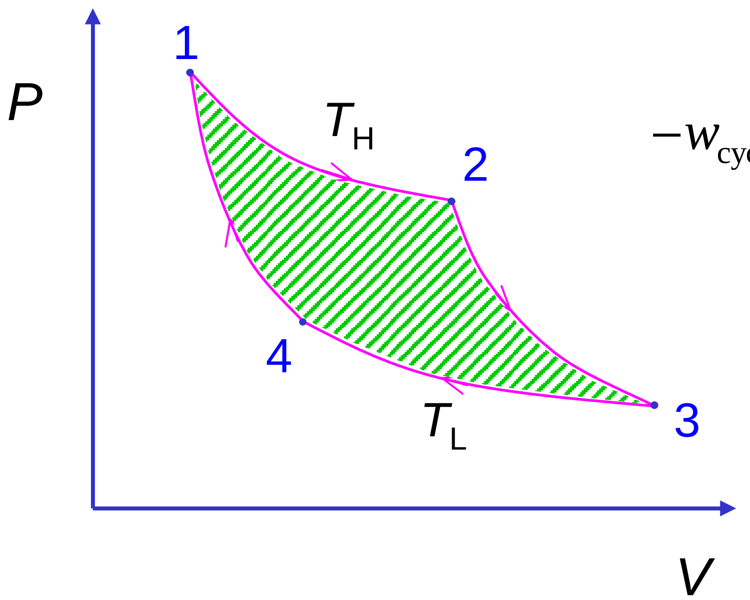
step	w	q	ΔU
A → B	$-nRT_H \ln(\underline{\hspace{2cm}})$	$-w_{AB}$	0
B → C	ΔU_{BC}	0	$-C_V(T_H - T_L)$
C → D	$-nRT_L \ln(\underline{\hspace{2cm}})$	$-w_{CD}$	0
D → A	ΔU_{DA}	0	$C_V(T_H - T_L)$
Total	$nR(T_H - T_L)\ln(\underline{\hspace{2cm}})$	$-w_{cyc}$	0

$$\varepsilon = \frac{\underline{\hspace{1cm}}}{q_{in}} = \frac{nR(T_H - T_L)\ln(V_A / V_B)}{\underline{\hspace{6cm}}} = 1 - \frac{T_L}{T_H}$$

$$\varepsilon = \frac{(T_H - T_L)}{T_H}$$

for best efficiency,
______________ T_H
______________ T_L

________ Changes in the Carnot Cycle



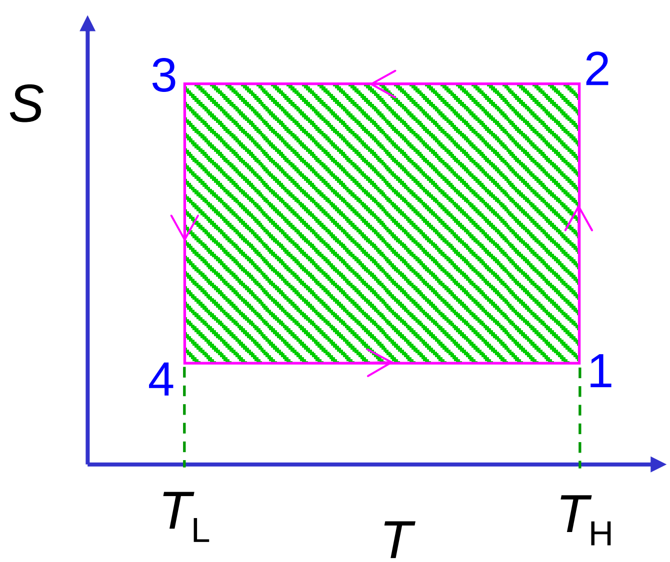
$$-w_{\text{cycle}} = \oint P dV$$
$$= \text{________ of } PV \text{ plot}$$
$$= q_{\text{cycle}}$$

________ expansion (1 → 2):

$$\Delta U = 0 \Rightarrow -w = q > 0 \quad \textit{Define Entropy } \Delta S = \frac{q}{T} \therefore \Delta S > 0$$

________ compression (4 ← 3): $\Delta S < 0$

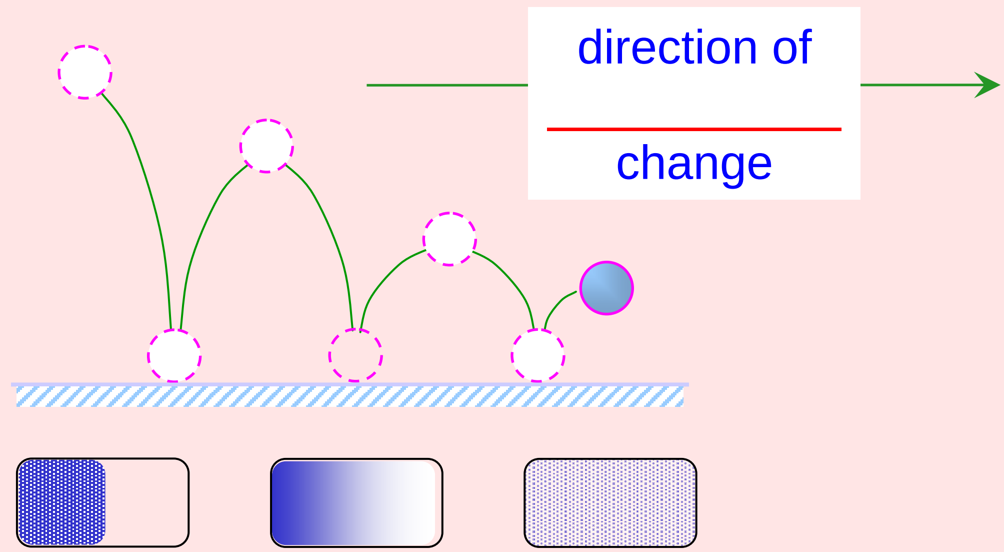
________ steps (2 → 3 and 1 ← 4): $q = 0 \Rightarrow \Delta S = 0$



$$q_{\text{tot}} = T_H (S_2 - S_1)$$
$$+ T_L (S_4 - S_3)$$
$$= (T_H - T_L)(S_2 - S_1)$$
$$= \text{________ of } ST \text{ plot}$$
$$= -w_{\text{cycle}}$$

Spontaneous Change

(So, why do we need entropy, anyway?)



The direction of spontaneous change is that which

- leads to ________ dispersal of the total energy
- moves from a state of low intrinsic probability towards one of ________ probability.

Work is needed to reverse a spontaneous process.

We need a quantity – ________ – to describe energy dispersal, i.e. the probability of a state.

Spontaneous processes are ________ .

They "________ " entropy

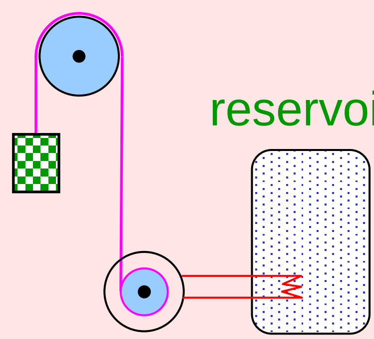
Reversible processes do not generate entropy – but they may ________ it from one part of the universe to another.

 Modified by Jed Macosko 9/20/2006

Entropy 1

- Entropy is a ________ variable (property) which determines if a state is accessible from another by a ________ change.
- Entropy is a measure of chaotic dispersal of energy.
- The natural tendency of spontaneous change is towards states of higher entropy.
- There are both thermodynamic (how much ________ is produced?) and statistical definitions (how ________ is a state?). They both become equivalent when statistics is applied to a ________ number of molecules.

Consider a falling weight which drives a generator and thus results in heat *q* being added to the reservoir (the surroundings).



Define a ________ variable *S*

$$dS(\text{surr}) = -\delta q / T$$

Then use stored energy to restore the weight to its original height. The reservoir gives up δq_{rev} to the system, and there is no overall change in the ________ .

this would only work for infinitesimal changes

$$dS(\text{sys}) = \underline{\quad\quad} dS(\text{surr}) = \frac{\delta q_{\text{rev}}}{T}$$

 Modified by Jed Macosko 9/20/2006

Entropy 2

In general, $dS(\text{sys}) + dS(\text{surr}) \geqslant 0$

$dS(\text{sys}) \geqslant -dS(\text{surr})$

Equality for reversible processes only

or, for the ________ , $dS \geqslant \frac{\delta q}{T}$ ________ inequality

For an ________ system, $q = 0$ hence $\Delta S \geqslant 0$

Isothermal Processes $\Delta S = q_{\text{rev}} / T$

e.g. $\Delta S(\text{fusion}) = \frac{\Delta H_{\text{fus}}}{T_{\text{m}}}$ $\Delta S(\text{vap}) = \frac{\Delta H_{\text{vap}}}{T_{\text{b}}}$

________ Rule: $\Delta S(\text{vap}) \approx$ ___ J K^{-1} mol^{-1}

Can be used to estimate ________ if T_{b} is known. Not good for ______________ liquids.

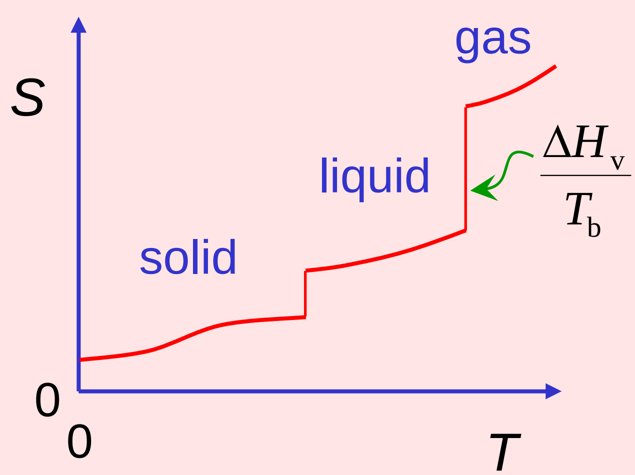
Temperature Variation $\delta q_{\text{rev}} =$ ___ dT

$$(\Delta S)_V = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

and $(\Delta S)_P = \int_{T_1}^{T_2} \frac{C_P}{T} dT$

________ Entropy

$$S(T) = S(0) + \int_0^T \frac{C_P}{T} dT$$



 Modified by Jed Macosko 9/20/2006

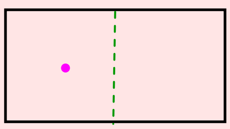
Entropy 3 (Statistical Mechanics)

Entropy depends on Probability.

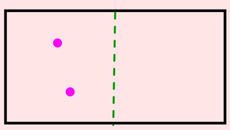
Consider the number of ways Ω of arranging *n* molecules between two sides (A and B) of a container.

The probability $\mathcal{P}_A$ that all molecules are on side A depends on the ________ of Ω___ to the total number of arrangements.

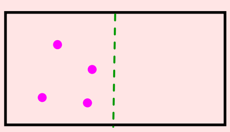
A B



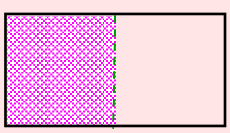
$\Omega_A = 1 \quad \Omega_{tot} = 2 \qquad \mathcal{P}_A = \frac{1}{2}$



$\Omega_A = 1 \quad \Omega_{tot} = 4 \qquad \mathcal{P}_A = \frac{1}{4}$



$\Omega_A = 1 \quad \Omega_{tot} = 16 \qquad \mathcal{P}_A = \frac{1}{16}$



$\Omega_A = 1 \quad \Omega_{tot} = \_\_\_ \qquad \mathcal{P}_A = \_\_\_$

State A becomes less and less probable as *n* increases. Conversely, the probability of the less ordered, roughly evenly distributed states, increases.

Since entropy is a measure of ________, it follows that *S* depends on Ω.

Boltzmann equation $S = k \_\_\_ \Omega$

Since $\mathcal{P}(\mathrm{x\ AND\ y}) = \mathcal{P}_x \_\_\_ \mathcal{P}_y$, $\ln \mathcal{P}_{x+y} = \ln \mathcal{P}_x + \ln \mathcal{P}_y$

 Modified by Jed Macosko 9/20/2006

The ________ Law of Thermodynamics

- "An ________________ cyclic process in which there is a net conversion of ________ into work is impossible."
- "No process is possible in which the sole result is the absorption of heat from a reservoir and its conversion into work." It is possible to convert ________ work into heat!
- "It is impossible for heat to be transformed from a body at a lower temperature to one at a higher temperature unless ________ is done."
- "The entropy of an isolated system ________ during any natural process." The universe is an isolated system.

  ΔS(sys) < 0 is allowed provided ΔS(sys) + ΔS(surr) > 0

- "All reversible ________ cycles operating between the same two temperatures have the same thermodynamic efficiency."
- "There is a state function called entropy S that can be calculated from __$S = \delta q_{rev}/T$. The change in entropy in any process is given by $dS \geq \delta q/T$, where the inequality refers to a spontaneous (irreversible) process."

The 1st Law uses U to identify ________ changes of state.

The 2nd Law uses S to identify ________ changes among the permissible ones.