General Points

- **Finish required material today**
- **<u>End of this and the next</u> lecture will be expanded discussion of section 21-7 (on entropy) … <u>not on final</u>**
- **By next Monday (Dec 8), will post sample final exam and solutions.**
- **Will have regular office hours on Monday afternoon next week. Special office hours next Friday … to be scheduled – check website.**
- **Review session next week, to go over sample exam; schedule today with Mr. Bansal.**
- **Real final on Monday, December 15, 1 PM here**
  - **Must be taken**
  - **You may bring your own <u>double-sided</u> handwritten formula sheet (8½ X 11 inch).**

Thermodynamics and Gases

Last Time

- Specific Heats more generally
- Adiabatic Expansion
- Reversible and Irreversible Processes
- Entropy
- 2nd Law of Thermodynamics

Today

- More entropy
- Uses in engines, heat pumps, refrigerators
  - End of material for final exam
- Lead to more insightful view of "entropy"
  - not on the final exam
  - Probability distributions

review

2^{nd} Law of Thermodynamics: gases

- **Net entropy change of any process of a closed system is either zero (reversible) or greater than zero (irreversible)**
  - discussion section 21-2
- **Entropy is a state function; depends only on parameters of the system: calculate general change for gas**

$$\Delta S \geq 0$$

$$dQ = dE_{int} + dW$$

$$dQ = nC_V dT + p dV$$

$$\Delta S_{i \to f} = S_f - S_i$$

$$= \int_i^f \frac{dQ}{T}$$

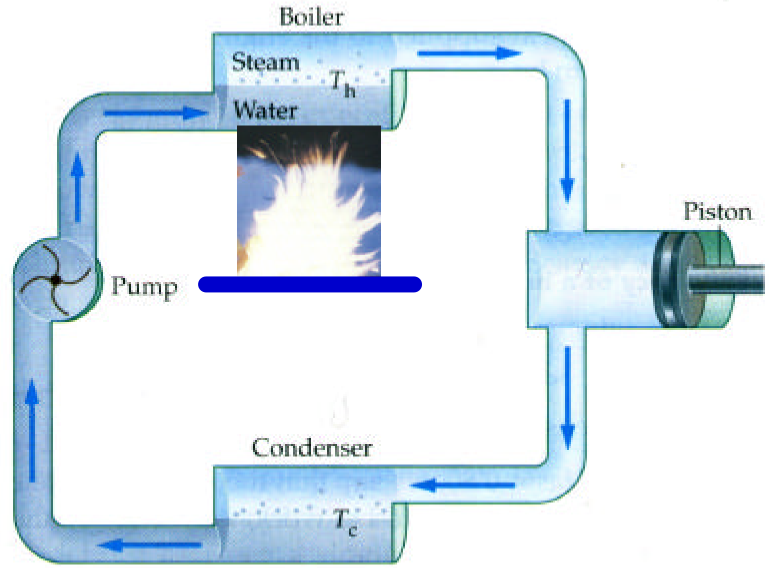
$$\Delta S_{rev} = \Delta S_{irrev}$$

entropy change for ideal gas

$$\Delta S = \int_i^f \frac{dQ}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V}$$

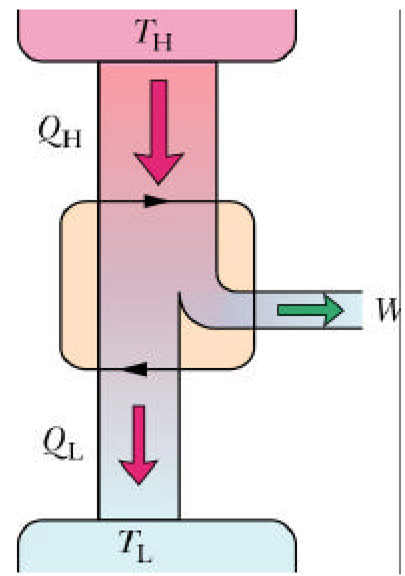
$$\Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Steam Engines (also nuclear power, etc)



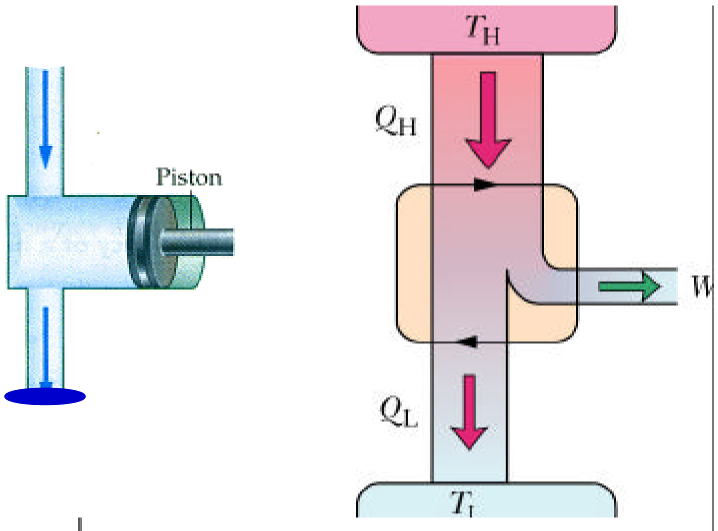
- **All use the same principles**
  - furnace putting heat into water (boiler) and converting to hot steam
  - heat energy does work by pushing on a piston
  - some heat energy carried away, either to condenser (to be reused via pump) or vented to air --- water is condensed to recycle
  - essential to return the gas in front of piston <u>in the same state as at the beginning of the cycle</u>

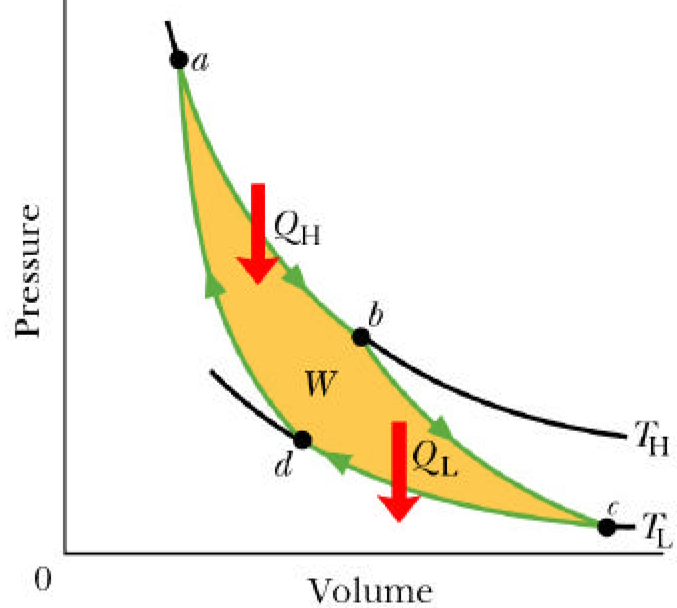
$\Delta S=0$



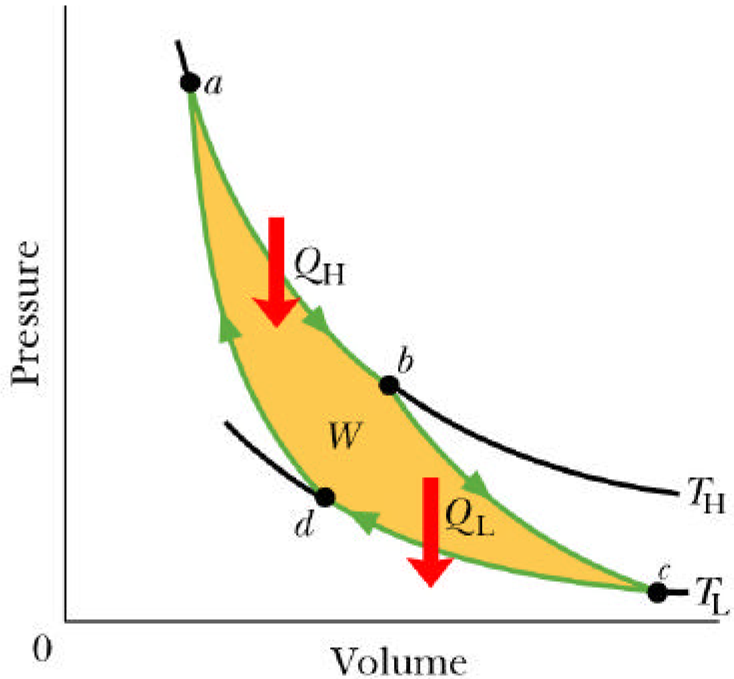
Carnot Cycle has highest efficiency attainable for engine

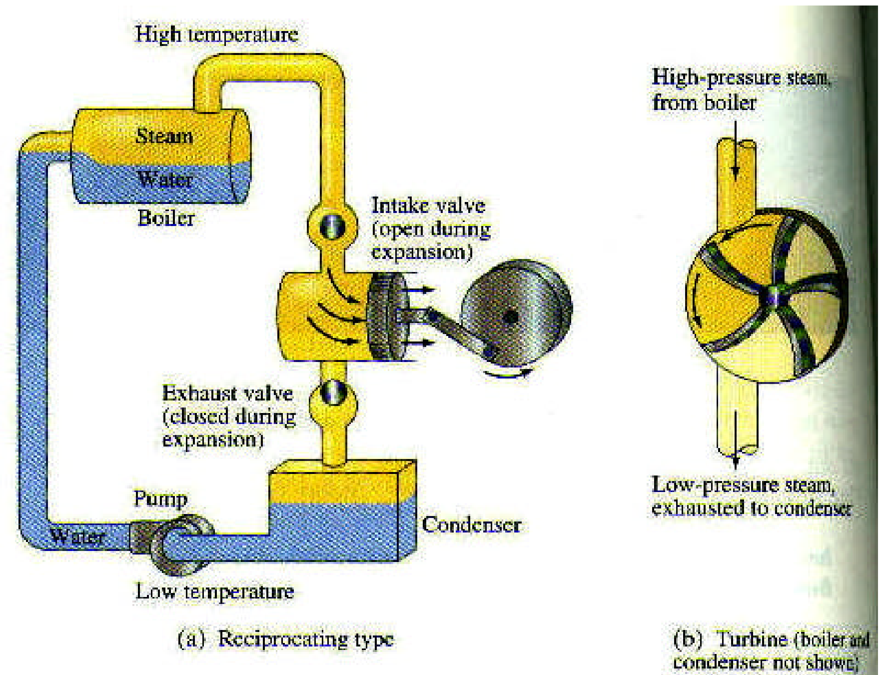
- **a-b: <u>isothermal</u> expansion of gas from hot reservoir (at $T=T_h$) as piston is pushed out**
- **b-c: further <u>adiabatic</u> expansion as piston moves to furthest extent**
- **c-d: <u>isothermal</u> compression of piston at temperature of cool reservoir ($T=T_l$)**
- **d-a: further <u>adiabatic</u> compression back to original state**
- **Back at *a* completes one cycle … gas is in its initial state and the next cycle can begin**





Carnot Cycle





Completely reversible gas cycle: $DS=0$

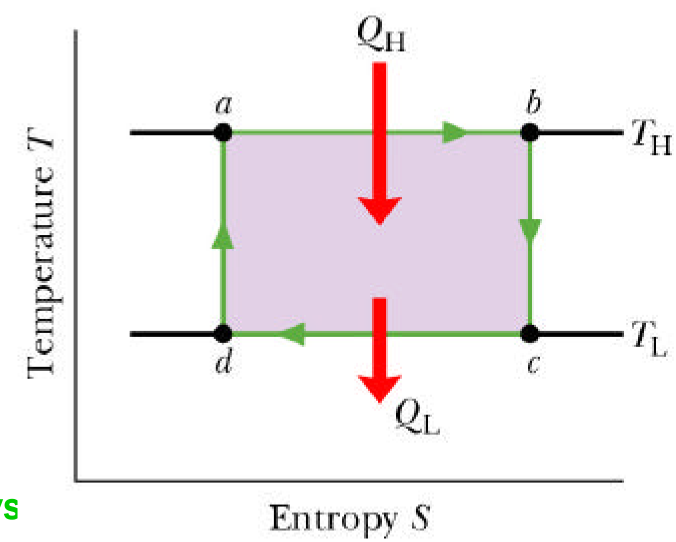
Take Q_H , Q_L **to be +ve**

$$W = Q_H - Q_L$$

$$DS = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

Carnot cycle has the highest <u>ideal</u> efficiency of any thermodynamic cycle

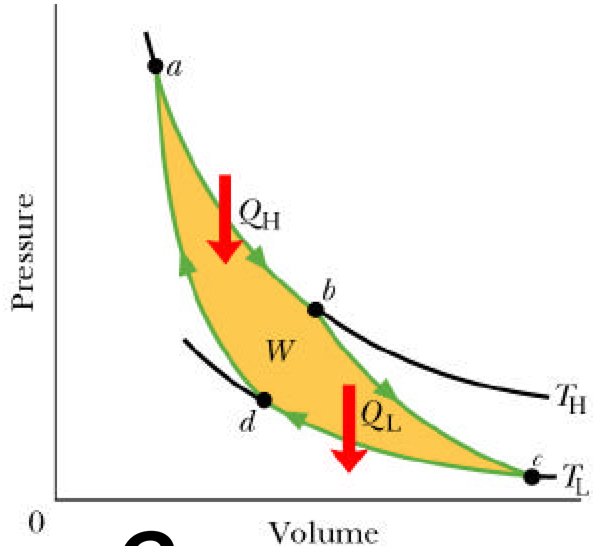
$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$



Efficiency of "Ideal" Steam Engine

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

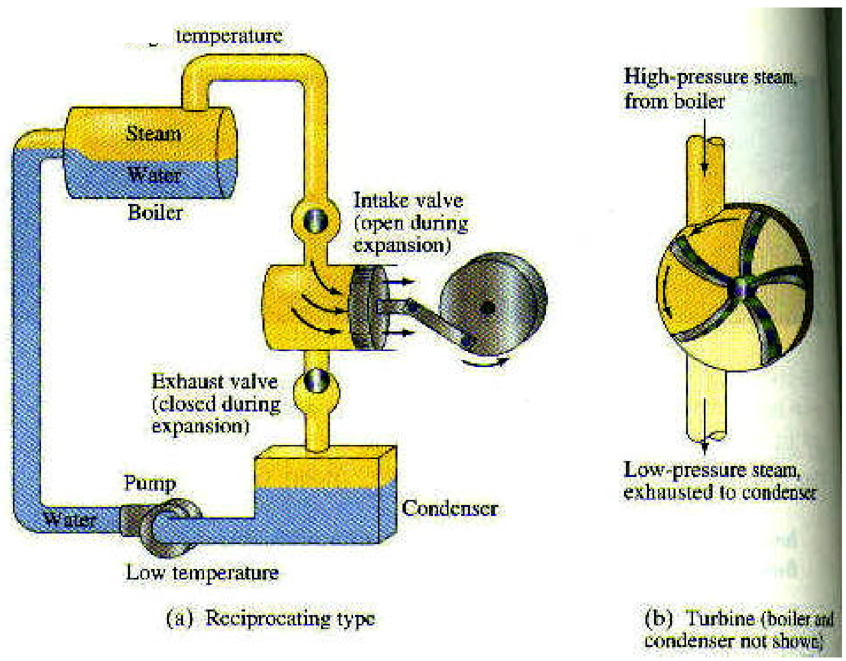


- **How much work get out for energy put in?**
- **Cost is to heat the boiler: Q_H**
- **Useful output W**
- **Lost energy: Q_L**

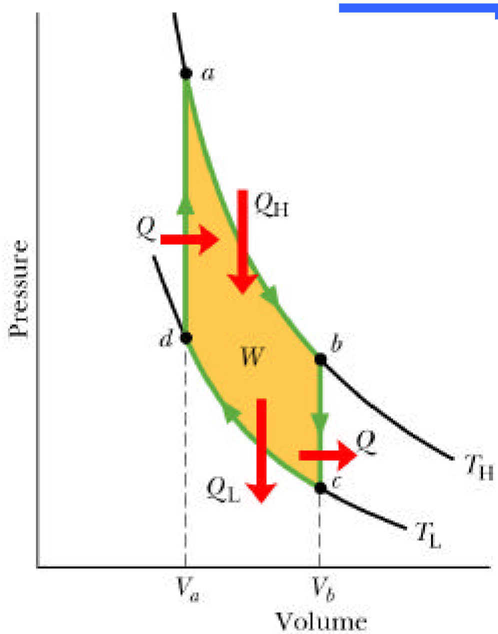
$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H}$$

$$e = 1 - \frac{T_L}{T_H}$$

$$e_{\text{real world}} \le 1 - \frac{T_L}{T_H}$$



Other engines

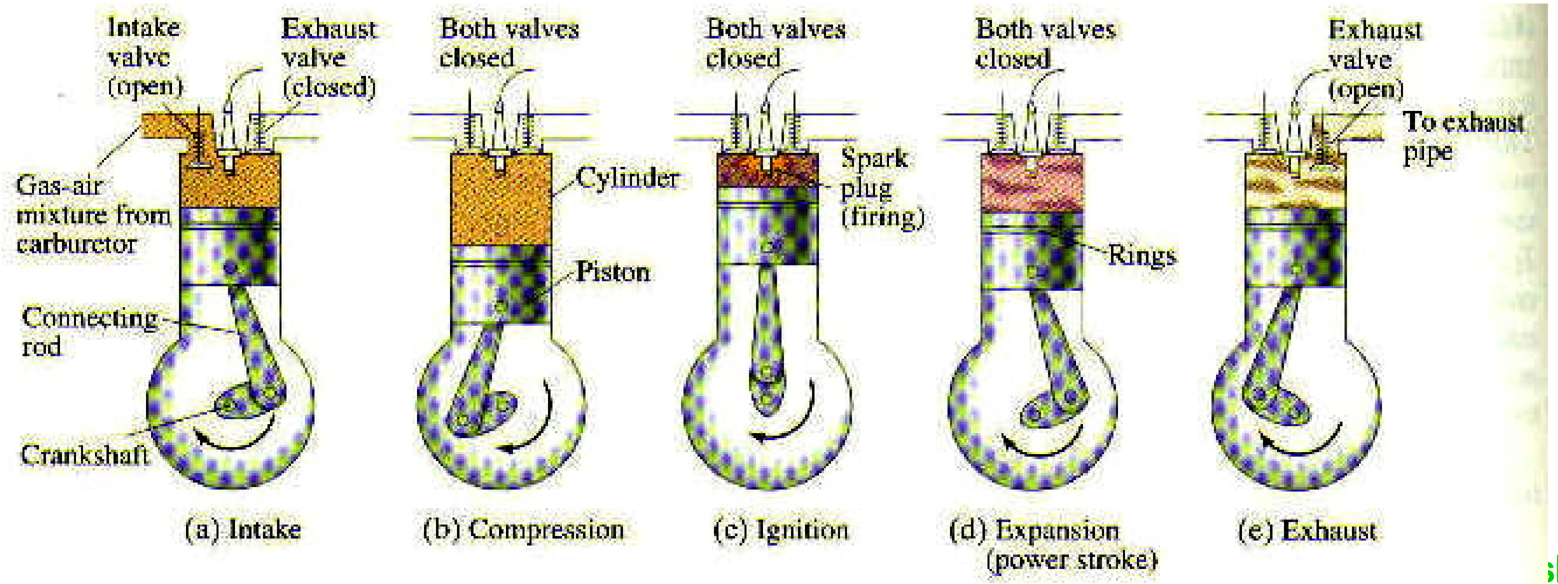


Stirling Engine (left)

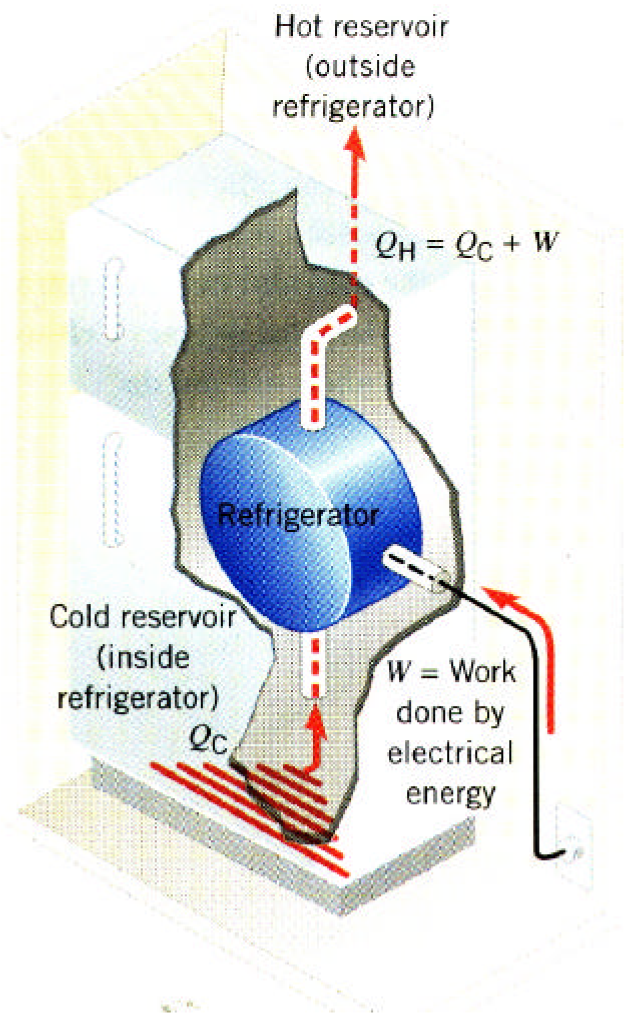
- Isochoric rather than adiabatic legs of cycle
- Text incorrect: same ideal efficiency as Carnot cycle

Internal Combustion engine (below)

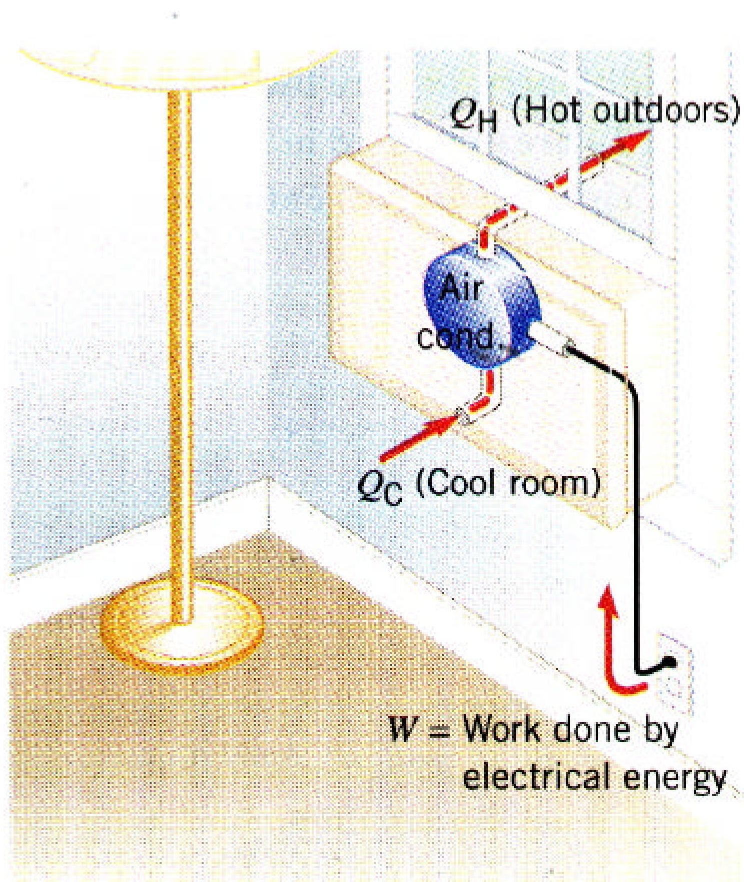
- Otto cycle: similar to Stirling but adiabatic compression … efficiency different (lower)



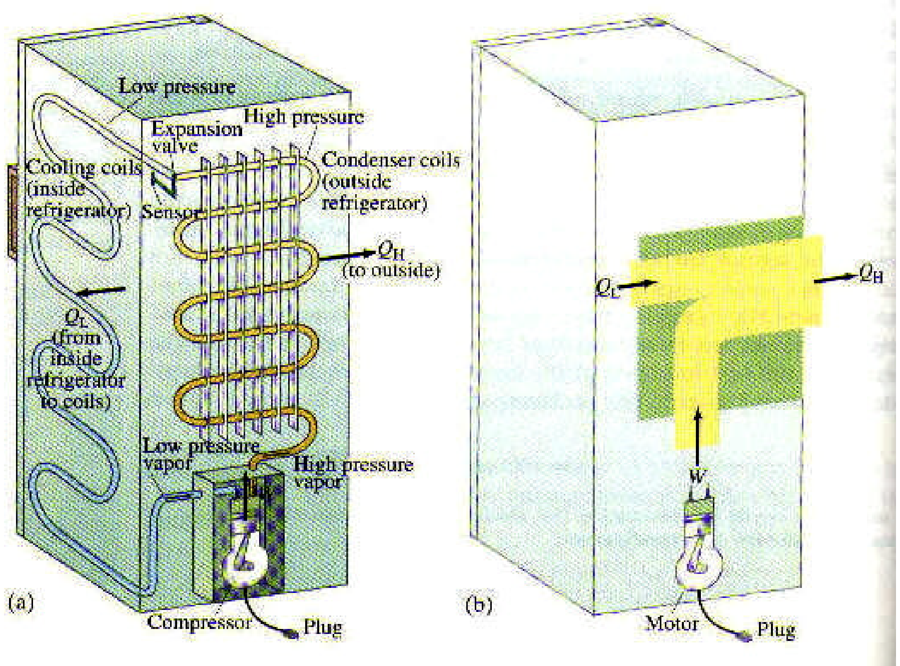
Refrigerators and Air Conditioners

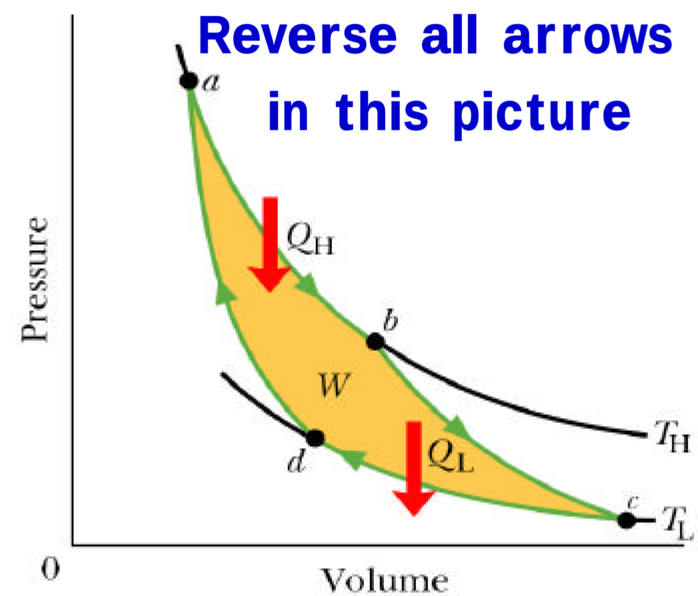


- Common system in refrigerators, air conditioners, (heat pumps)
- Do work and remove heat from cold environment
- deliver heat to warm environment



Refrigerators





- How much work to put in for heat energy taken out
- Cost is work: W
- Useful output: Q_L
- Vented energy: Q_H
- Define "coefficient of performance" (cop)

$$Q_H = W + Q_L$$

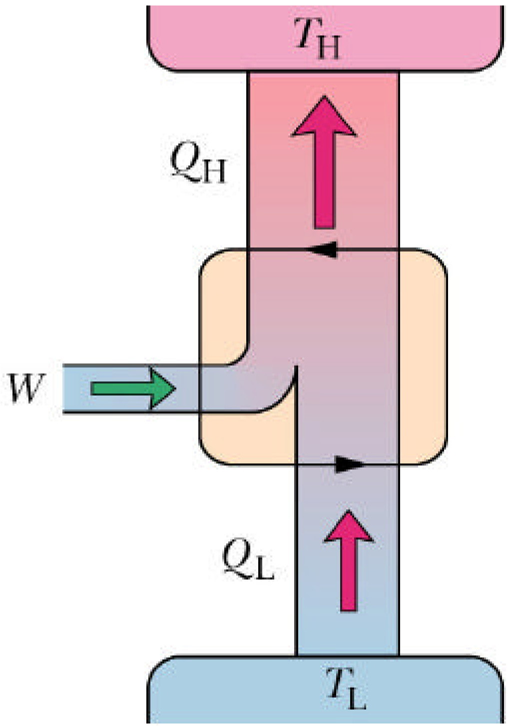
$$cop \equiv \frac{Q_L}{W} = \frac{Q_L}{Q_H - Q_L}$$

$$cop = \frac{T_L}{T_H - T_L}$$

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

Heat Pump



$$DS = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0$$

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H}$$

$$Q_H = W + Q_L$$

$$cop \; ^{o} \; \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L}$$

$$cop = \frac{T_H}{T_H - T_L}$$

- Similar to refrigerator, only in reverse
- Note cop>1
- So Q_H>W
  - Contrast electric heater

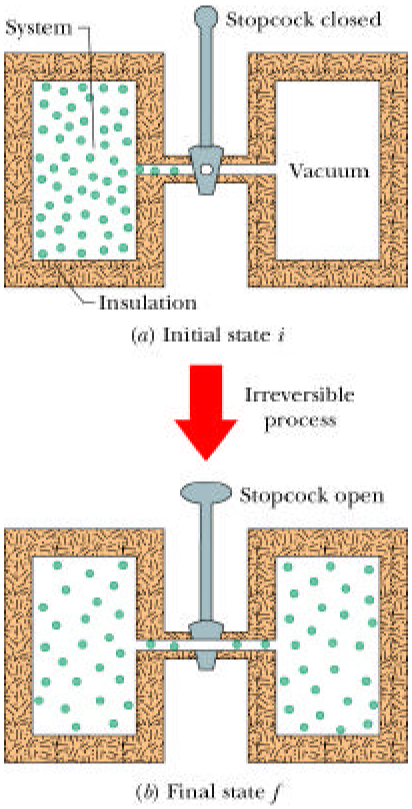
culture

Origin of Entropy

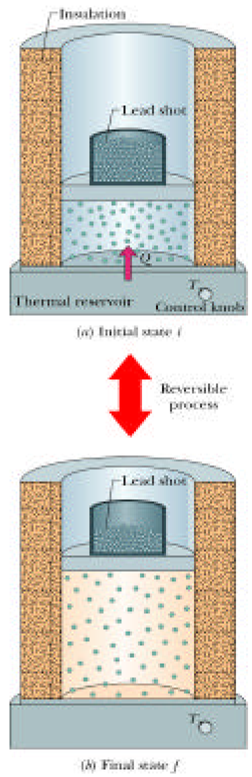
- **Short description in text (21-7)**
  - **Remainder today and Monday, we will try to provide more elaborate answer than given section 21-7**
  - **This and following will <u>not</u> be on the final exam**
- **Short answers:**
  - **Entropy is a measure of the disorder of the system**
  - **Entropy is a measure of probability of finding state in a given configuration**

review

Entropy increase of free expansion of gas



irreversible in a closed system



reversible isothermal equivalent

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{nRT}{T} \ln\frac{V_f}{V_i}$$

$$\Delta S = nR \ln\frac{V_f}{V_i}$$

- **This is the entropy change of the gas for <u>both processes</u>**
- **more general**

entropy change for ideal gas

$$\Delta S = \int_i^f \frac{dQ}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = nC_V \ln\frac{T_f}{T_i} + nR \ln\frac{V_f}{V_i}$$

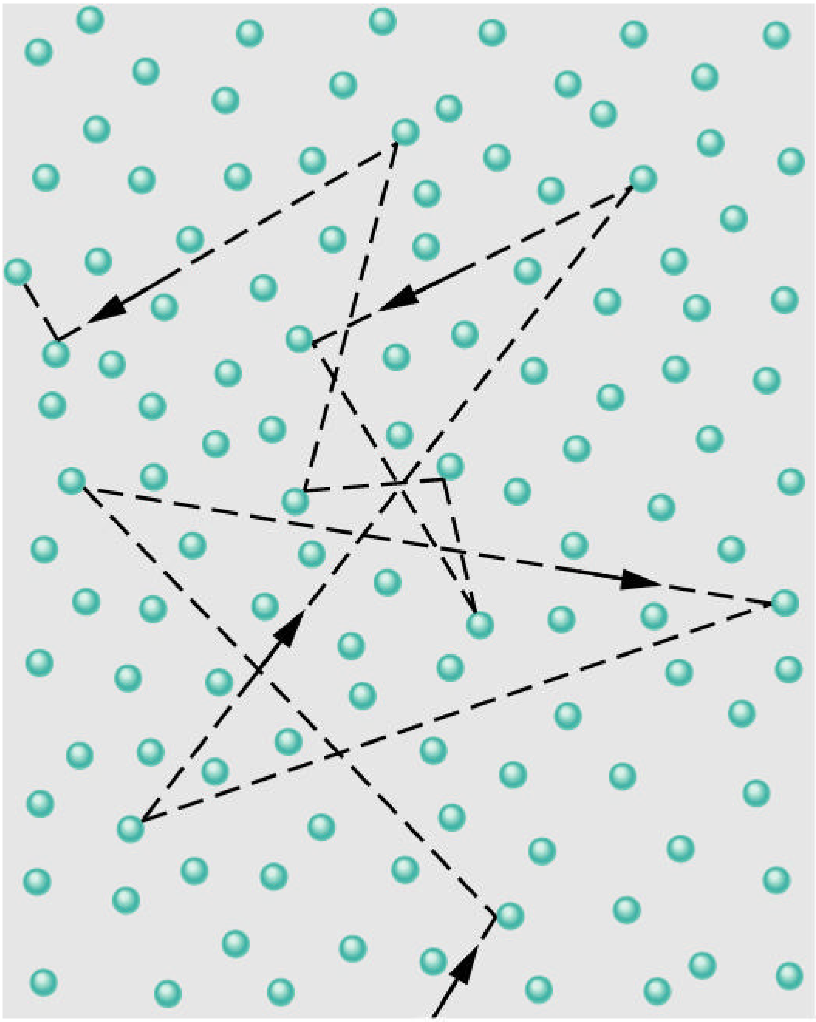
Macroscopic vs Microscopic for Gases

- Gas is said to be in a specific "macrostate"
- Entropy is a measure of the gas "state probability"
- A specific macrostate may have many microstates (different ways of arranging atoms to get same macrostate)

- **Macroscopic Quantities**
  - temperature
  - pressure
  - volume
  - internal energy
  - entropy=$\Delta Q/T$
  - Specific macroscopic "state" of gas can have many configurations or microstates

- **Microscopic States**
  - velocity vector each molecule
  - position vector each molecule
  - Specific "microstates", with definite values for p_x, p_y, p_z, x, y, z for each particle will contribute to the macrostate
  - w = number of different "microstates", or configurations, in the macrostate

Bouncing Atoms



- **For gas, as one specific time in a particular macrostate, the status of each molecule is described by parameter values of**
  - x, y, z
  - v_x, v_y, v_z
- **The gas molecules are characterized by a probability distribution for each parameter**
- **Wider range of probability for these six parameters necessarily implies more microstates available to the molecules**
- **Examples:**
  - twice the volume = 2 X # pos states
  - increase temp = large # velocity states

Boltzmann's Ansatz

Many "microstates" or combinations of particles may give same macrostate

Statistical mechanics: all microstates are equally probable

Formula for entropy:

$$S_{molecule} = k \ln w$$

$$w = \#\ \text{microscopic states in macrostate}$$

$$S_{gas} = \sum_{\substack{all \\ molecules}} S_{molecule}$$

- Statistical mechanics: not on exam (later courses will discuss more fully)
- Do simple illustrations here
- We choose for illustration an analogy with "discrete" states available to *N* coins
- If these were atoms, the number of different microstates would give the entropy of the macrostate (which will be discussed)

Boltzmann applied

- More microstates = more entropy
- For atoms and microstates, the number of states are delineated by
  - Position possibilities
  - Velocity possibilities
- for each atom, enormous number of possibilities … return to this later
- Total entropy = Sum over all atoms (also enormous number)
- Look first at <u>simpler physical system</u>: limited number of coins

$$S_{molecule} = k \ln w$$

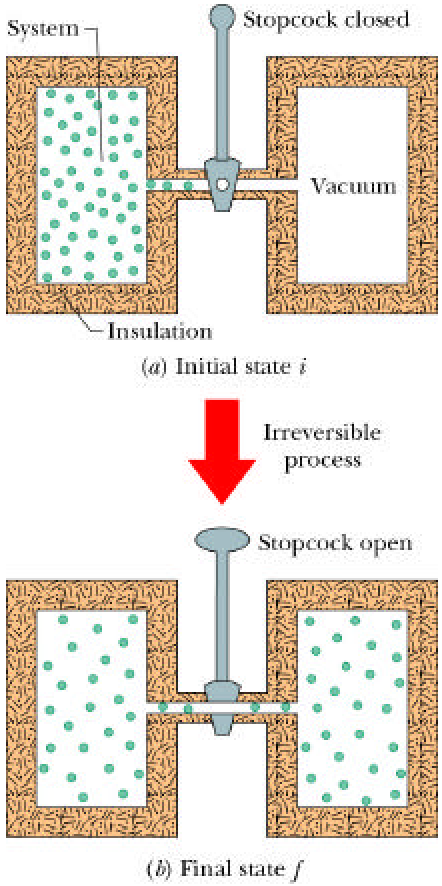
$$w = \#\ \text{microscopic states in macrostate}$$

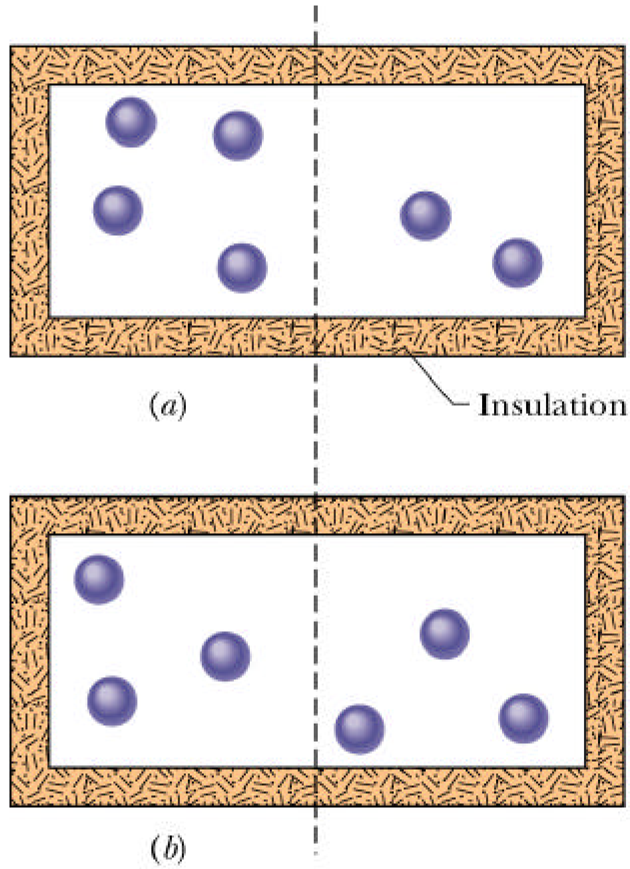
$$S_{gas} = \sum_{\substack{all \\ molecules}} S_{molecule}$$

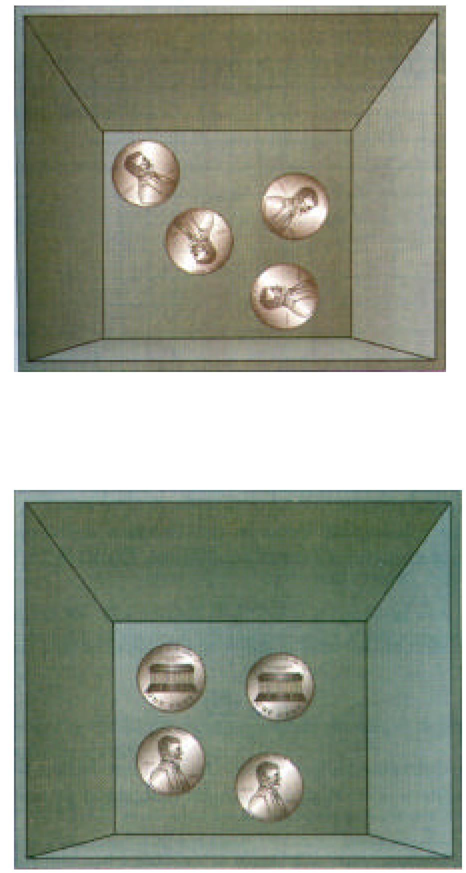
Order vs Disorder

More ordered

Less ordered

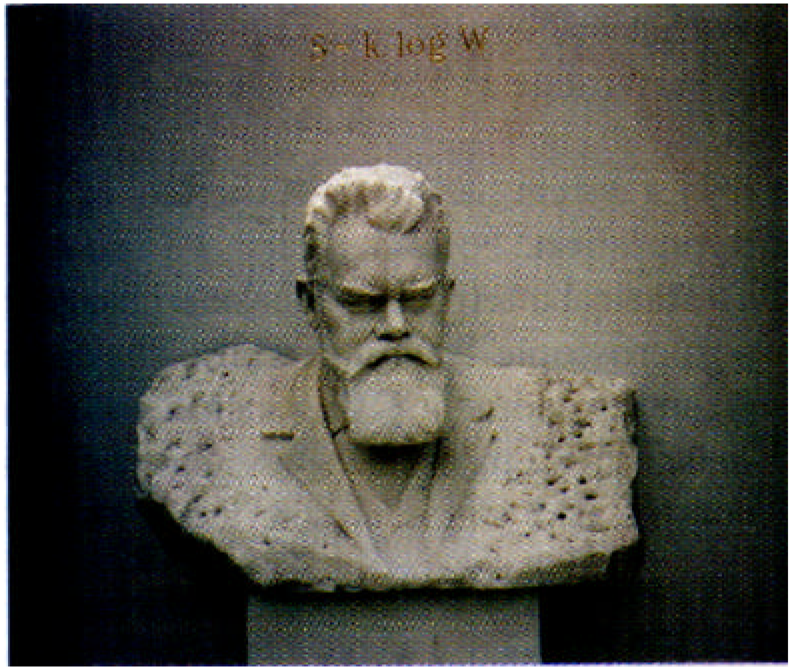




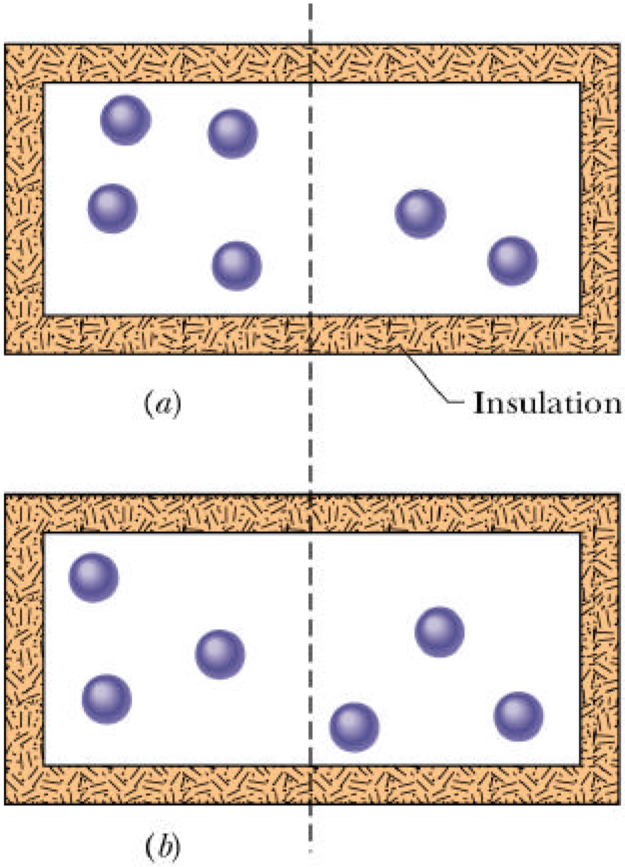


- Order implies that the system is in a state with very few microstates (or a state of very low probability)
- Disorder=system is in a highly probable state (many microstates)

Boltzmann: Macrostates (and Microstates)



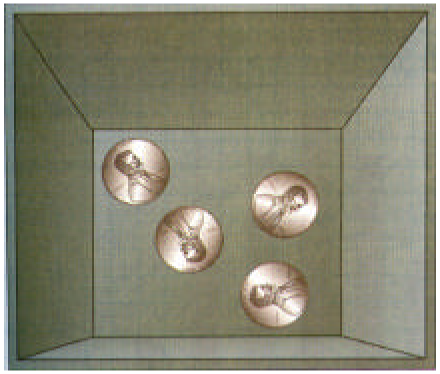
- **Two scenarios at right**
  - each has several possible microstates
  - depend on which molecules are on which side
- **Analyze with coins**



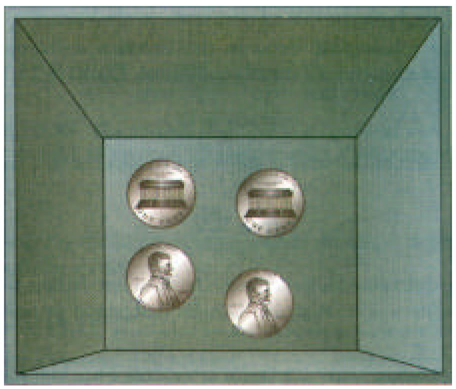
$$S = k \ln W$$

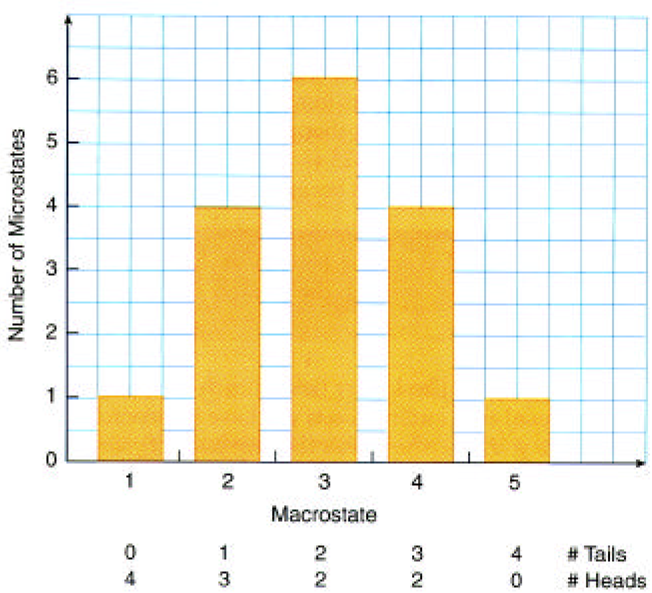
$$W = \begin{pmatrix} \text{number of} \\ \text{microstates} \end{pmatrix}$$

4 pennies-macrostates and microstates



- all heads: one microstate
- One tail: 4 microstates
- 2 heads, 2 tails: six microstates
- In total: 16 microstates
- Pix shows relative probabilities





Four-Penny Macrostates and Microstates

Macrostate (1): 4 heads (H) and 0 tails (T)			
Penny 1	*Penny 2*	*Penny 3*	*Penny 4*
H	H	H	H
(1 microstate)			
Macrostate (2): 3 heads and 1 tail			
Penny 1	*Penny 2*	*Penny 3*	*Penny 4*
H	H	H	T
H	H	T	H
H	T	H	H
T	H	H	H
(4 microstates)			
Macrostate (3): 2 heads and 2 tails			
Penny 1	*Penny 2*	*Penny 3*	*Penny 4*
H	H	T	T
H	T	T	H
T	T	H	H
T	H	H	T
T	H	T	H
H	T	H	T
(6 microstates)			
Macrostate (4): 1 head and 3 tails			
Penny 1	*Penny 2*	*Penny 3*	*Penny 4*
H	T	T	T
T	H	T	T
T	T	H	T
T	T	T	H
(4 microstates)			
Macrostate (5): 0 heads and 4 tails			
Penny 1	*Penny 2*	*Penny 3*	*Penny 4*
T	T	T	T
(1 microstate)			

Binomial Coefficients

- **Binomial Coefficients give a formula for the number of ways in which to combine N coins to have n tails and (N-n) heads**

$$\binom{N}{n} \equiv \frac{N!}{n!(N-n)!}$$

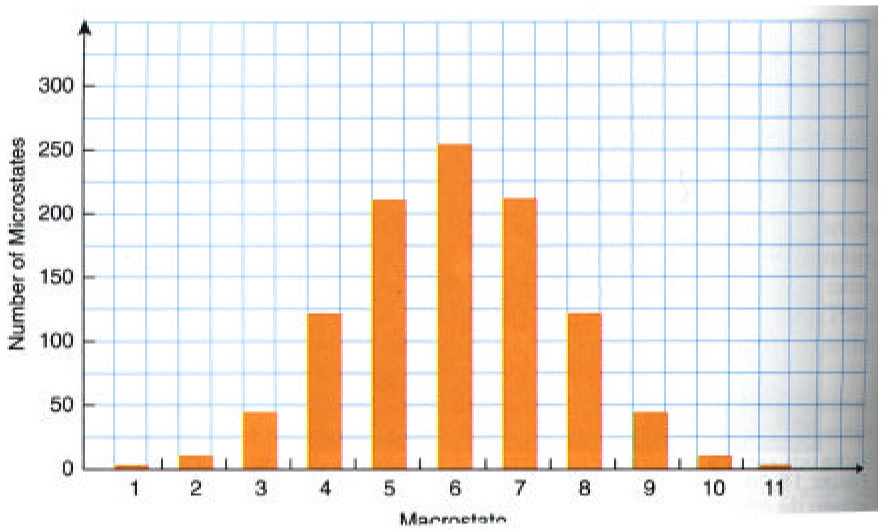
$$\binom{4}{0} \equiv \frac{4!}{0!(4)!} = \frac{4\cdot3\cdot2\cdot1}{4\cdot3\cdot2\cdot1} = 1$$

$$\binom{4}{2} \equiv \frac{4!}{2!(2)!} = \frac{4\cdot3\cdot2\cdot1}{2\cdot1(2\cdot1)} = 6$$

Four-Penny Macrostates and Microstates

Penny 1	Penny 2	Penny 3	Penny 4
Macrostate (1): 4 heads (H) and 0 tails (T)			
H	H	H	H
(1 microstate)			
Macrostate (2): 3 heads and 1 tail			
H	H	H	T
H	H	T	H
H	T	H	H
T	H	H	H
(4 microstates)			
Macrostate (3): 2 heads and 2 tails			
H	H	T	T
H	T	T	H
T	T	H	H
T	H	H	T
T	H	T	H
H	T	H	T
(6 microstates)			
Macrostate (4): 1 head and 3 tails			
H	T	T	T
T	H	T	T
T	T	H	T
T	T	T	H
(4 microstates)			
Macrostate (5): 0 heads and 4 tails			
T	T	T	T
(1 microstate)			

10 coins -contrast



crostate	H	T	# microstates Ω
1	10	0	1
2	9	1	10
3	8	2	45
4	7	3	120
5	6	4	210
6	5	5	252
7	4	6	210
8	3	7	120
9	2	8	45
10	1	9	10
11	0	10	1
		Total	$1024 = 2^{10}$

- **5 each is 252 times more probable than all heads**
- **as more coins are added, equal partitioning=equal numbers heads and tails gets more probable relative to all other possibilities**
  - **especially those near the extremes (list top and bottom)**

Thermodynamics and Gases

Today

- 2nd Law of Thermodynamics
- Entropy
- Uses in engines, heat pumps, refrigerators

Next Time (not on final)

- Continue discussing origin of Entropy
  - measure of system disorder
  - statistical mechanics

General Points

- **Finished required material today**
- **Next lecture will continue expanded discussion of section 21-7 (on entropy) … not on final**
- **Will have regular office hours on Monday**
- **Will have one additional office hour session later next week (to be announced)**
- **By Monday (Dec 8), will post sample final exam**
- **Real final on Monday, December 15, 1 PM here**
  - **Must be taken**
  - **You may bring your own double-sided handwritten formula sheet (8½ X 11 inch).**