

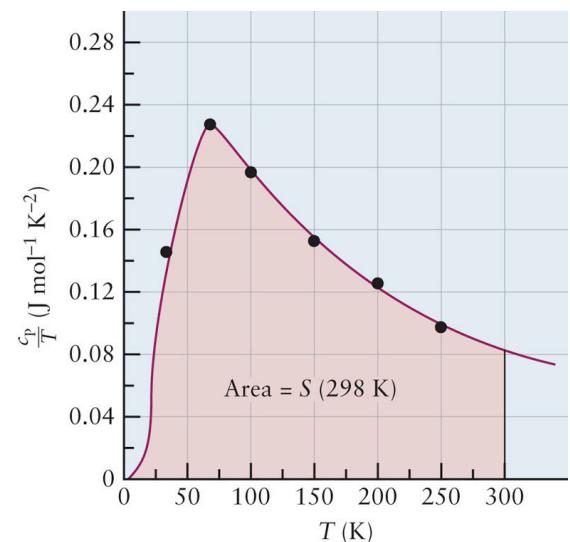
Ch 1b Lecture 14

February 7th, 2013

Next few lectures – Still on the road to chemical reactivity, circa mid-1800s.

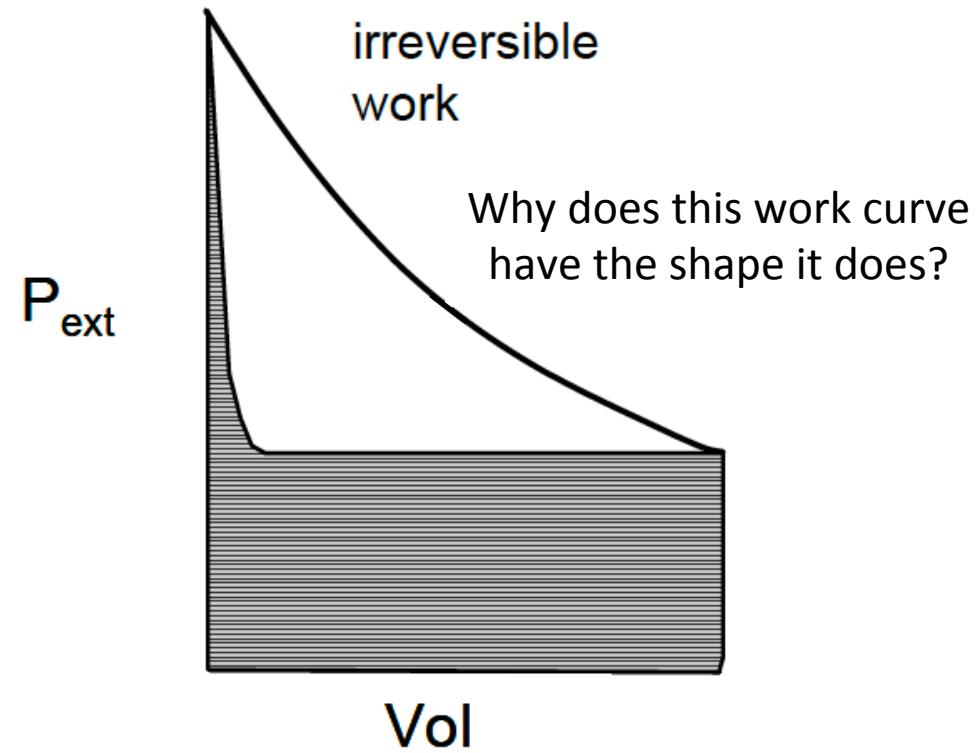
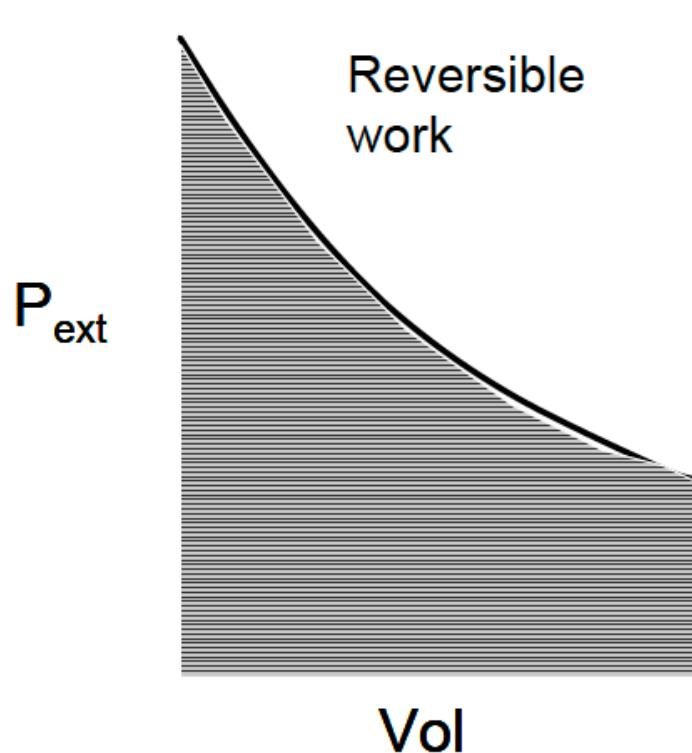
Today: Entropy & the 2nd Law of Thermodynamics

Reading: OGC Chapter 13



Last time:

Reversible & Irreversible Processes:

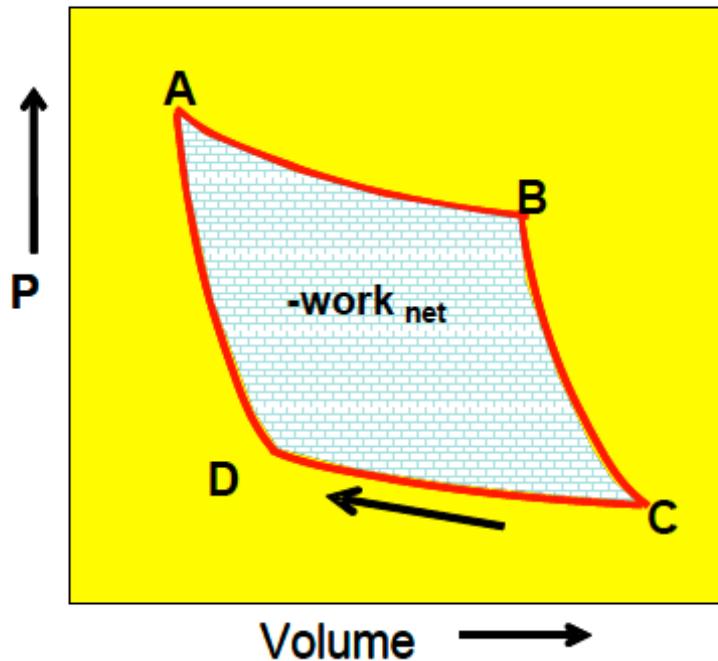


Work done in a reversible process is always greater than work done in an irreversible process. In an irreversible expansion of a gas, for example, the volume and/or pressure is altered abruptly, rather than incrementally. However, the various state functions that describe the initial and final state are unchanged.

Entropy & the 2nd Law:

Recall the efficiency of the Carnot Engine

$$eff = \frac{-w_{net}}{|q_{AB}|} = \frac{nR(T_H - T_L) \ln\left(\frac{V_B}{V_A}\right)}{nRT_H \ln\left(\frac{V_B}{V_A}\right)}$$



$$eff = \frac{-w_{net}}{|q_{AB}|} = 1 - \frac{T_L}{T_H}$$

It is impossible to make a 100% efficient engine

This provided the origins of the 2nd Law of Thermodynamics

Entropy & the 2nd Law:

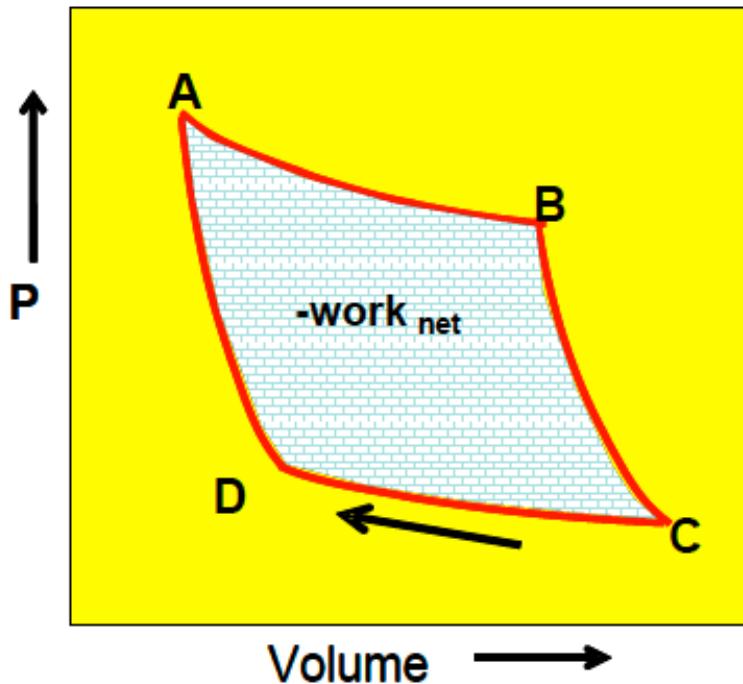
For the isothermal pathways:

$$w_{AB} = -q_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

$$w_{CD} = -q_{CD} = -nRT_L \ln\left(\frac{V_D}{V_C}\right)$$

Recall that the above equations imply:

$$\left(\frac{V_C}{V_D}\right) = \left(\frac{V_B}{V_A}\right)$$



Entropy & the 2nd Law:

For the isothermal pathways:

$$w_{AB} = -q_{AB} = -nRT_H \ln\left(\frac{V_B}{V_A}\right)$$

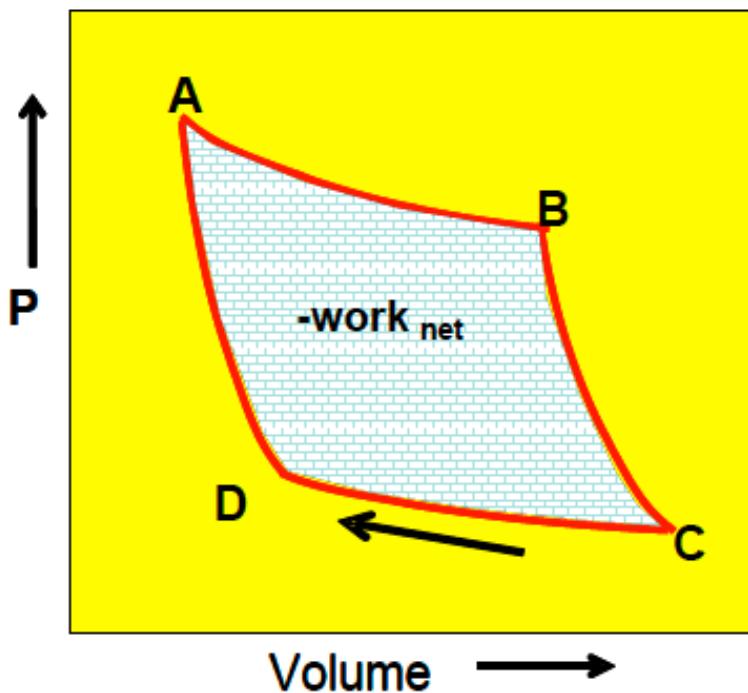
$$w_{CD} = -q_{CD} = -nRT_L \ln\left(\frac{V_D}{V_C}\right)$$

$$\left(\frac{V_C}{V_D}\right) = \left(\frac{V_B}{V_A}\right)$$

These relationships further imply that

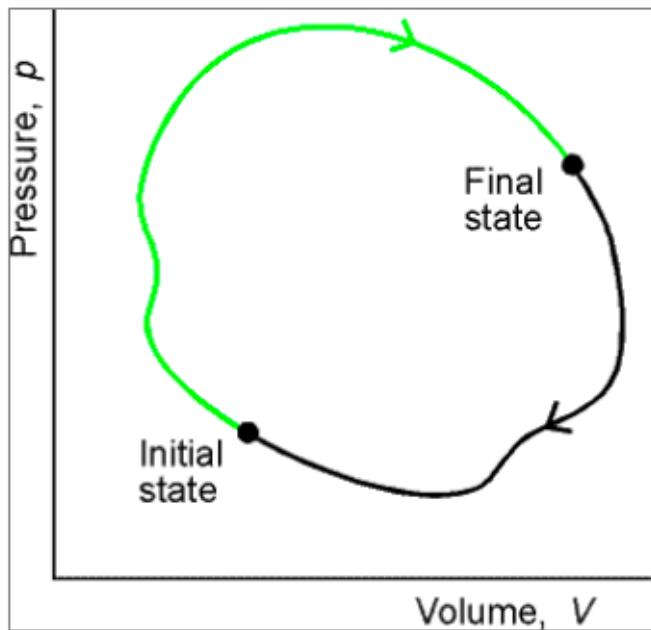
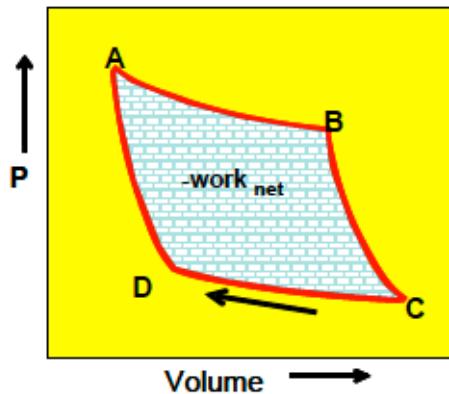
$$\frac{q_f}{T_h} + \frac{q_b}{T_l} = 0$$

f denotes forward pathway $A \rightarrow B \rightarrow C$
b denotes return pathway $C \rightarrow D \rightarrow A$



Show this to yourself!

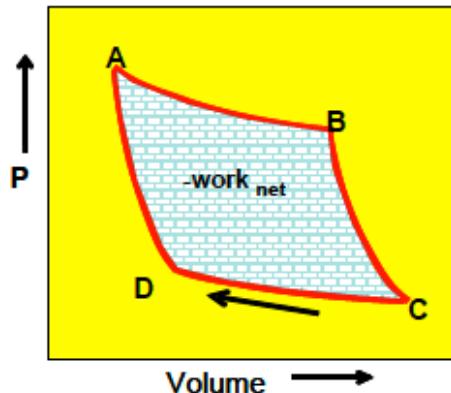
Entropy & the 2nd Law:



Consider the loop drawn below and the Carnot cycle drawn above

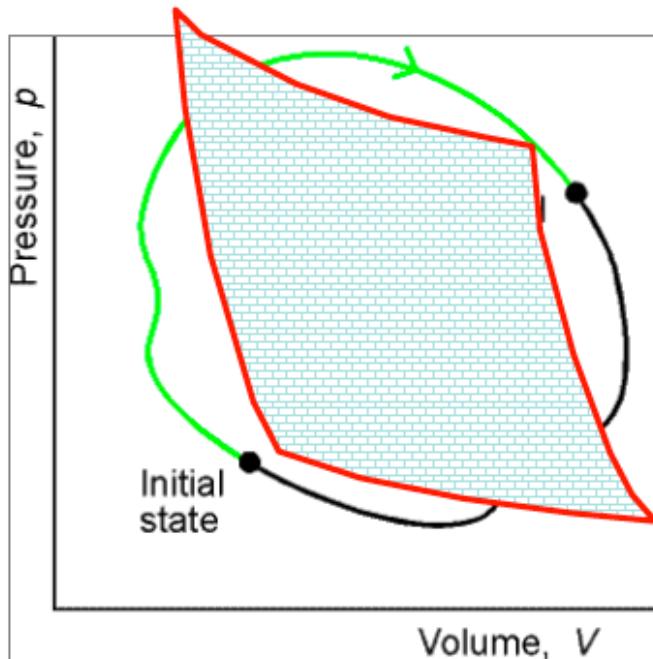
Can we hypothesize reversible adiabatic and isothermal pathways around this loop?

Entropy & the 2nd Law:



Recall that state functions don't care about the path taken around the loop

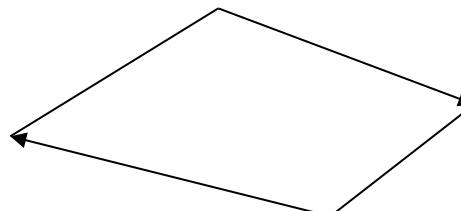
In a thermodynamic cycle, the overall change in a state function (from the initial state to the final state and then back to the initial state again) is zero.



Approximate the loop with 1 Carnot Cycle (not a very good approximation)

Exact differentials:

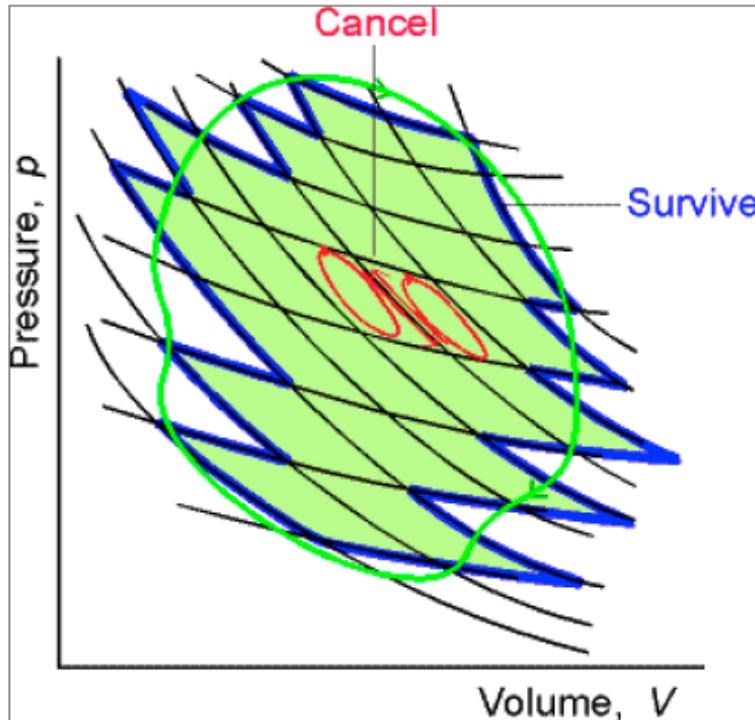
A



B

$$\oint dU = 0$$

Entropy & the 2nd Law:



A general cycle can be divided into many small Carnot cycles.
The match is exact in the limit of infinitesimally small cycles.
Paths cancel in the interior of the collection of cycles
Only the perimeter, an increasingly good approximation to the true cycle as the number of cycles increases, survives.

Entropy & the 2nd Law:

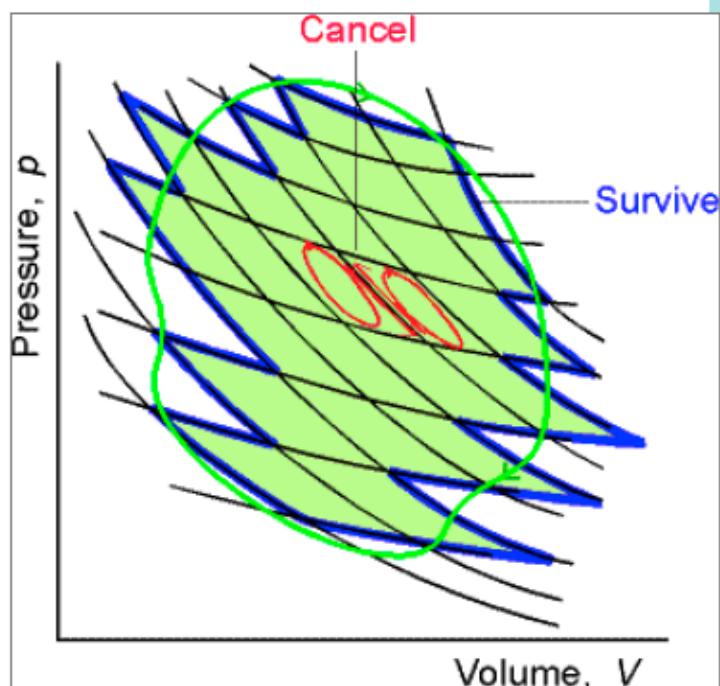
$$\frac{q_f}{T_h} + \frac{q_b}{T_l} = 0$$

No matter how we traverse this loop, this equation holds. Thus:

The implication is that q/T is a state function

f denotes forward pathway A→B→C

b denotes return pathway C→D→A



More generally, Clausius defined entropy as:

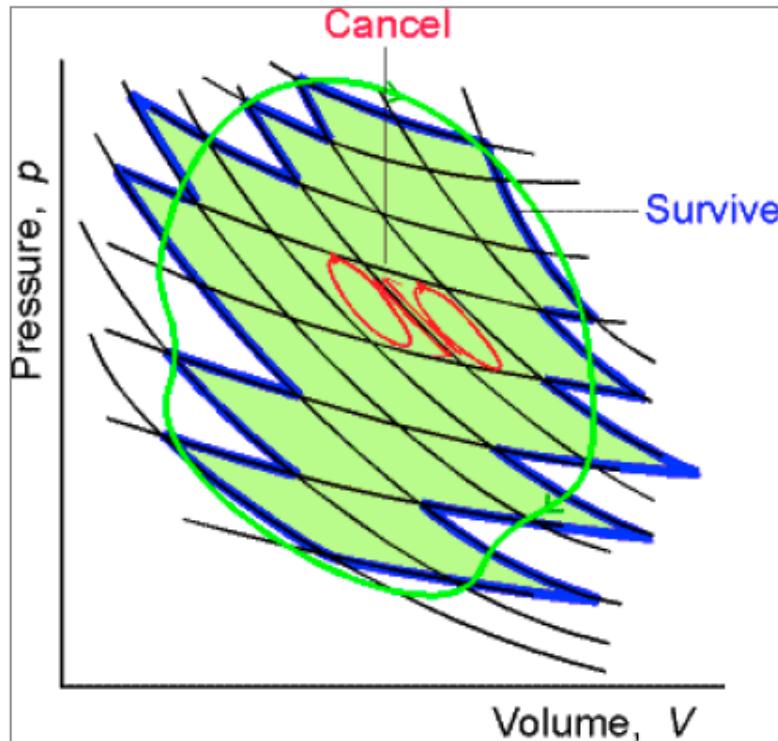
$$\Delta S \equiv \int_i^f \frac{dq_{rev}}{T}$$

Units J·K⁻¹

'i , f' here mean initial and final

Entropy & the 2nd Law:

Carnot Cycle - Generalized

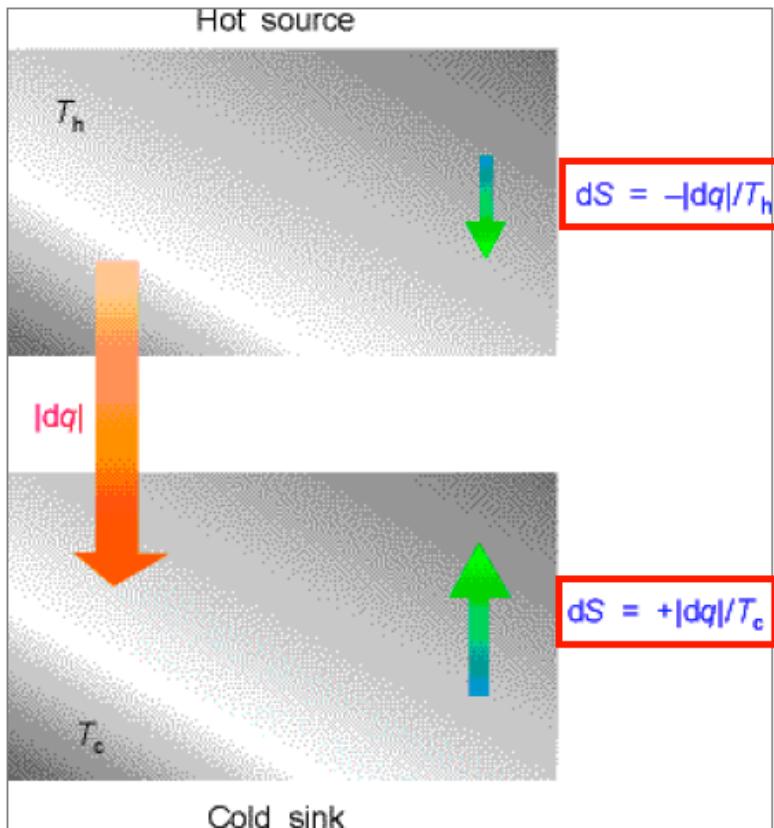


Because the entropy change around every individual cycle is zero, the integral of the entropy around the perimeter is zero too.

$$\Delta S = \oint_{perimeter} \frac{dq_{rev}}{T} = 0$$

Entropy & the 2nd Law:

The heat flow from a hot body to a cold body is not a reversible process.



When energy leaves a hot reservoir as heat, the entropy (S) of the reservoir decreases
When the same quantity of energy enters a cooler reservoir, the entropy increases by a larger amount.

Overall $\Delta S > 0$

Because $T_c < T_h$

Entropy & the 2nd Law:

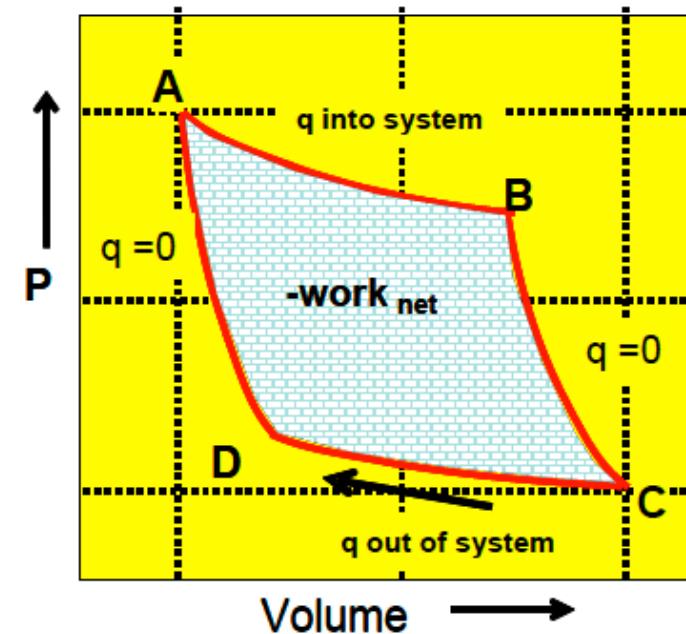
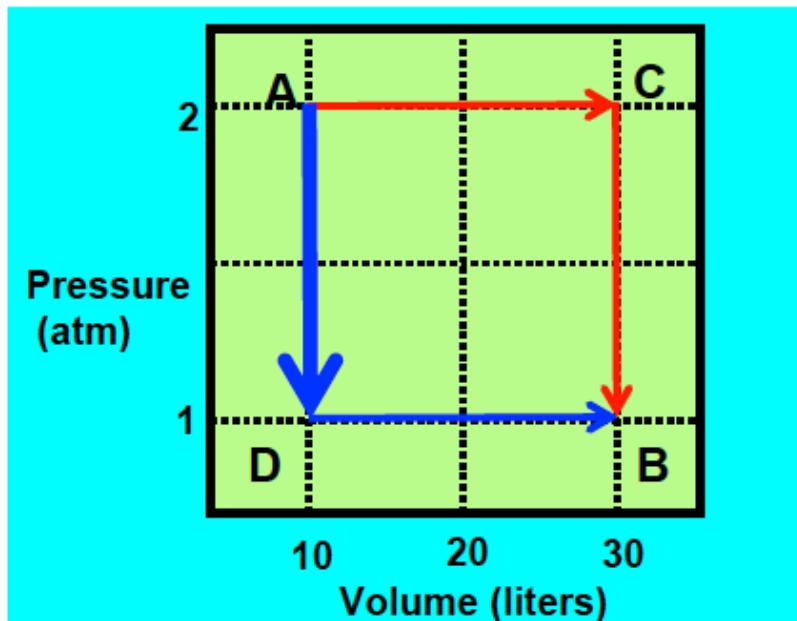
The Second Law

The second law originated from an analysis of the efficiency of steam engines by Carnot in which he concluded that unrecoverable losses of energy to the environment cannot be eliminated. This eventually became stated as the second law of thermodynamics:

In a real, spontaneous process the entropy of the universe (the system plus its surroundings) must increase:

$$\Delta S_{univ} > 0.$$

Entropy & the 2nd Law:



Think about engines – heat engines, thermoelectric engines, computational machines, etc.

Making them more efficient means making their cycles more reversible
 This means minimizing entropy changes –
 if $\Delta S_{\text{cycle}} \rightarrow 0$, then that engine cycle is approaching reversibility.

Entropy & the 2nd Law:

Because the second law is a bit more abstract, it can be stated many ways.

Another is: There is a quantity S , called entropy, which is a state function. In an irreversible process, the entropy of the system and its surroundings increases. For a reversible process, the entropy of the system and its surroundings remains constant. Mathematically:

$$dS = dq_{rev}/T$$

where the differentials are again meant to emphasize infinitesimal changes.

Reversible processes are those in which the driving force (a difference in P , T , etc.) is infinitesimal. Any other change is called irreversible or spontaneous.

Reversible		Irreversible
$\Delta S = S_A - S_B = \int dq_{rev}/T$	or	$S_A - S_B > \int dq_{irrev}/T$

Given the formulation above, the first and second laws can be combined to yield the well known perfect gas equation:

$$dU = TdS - PdV \quad (\text{heat} + \text{work})$$

A couple of worked examples, Entropy:

Entropy for an Isothermal Processes

$$\text{Temp}_{\text{initial}} = 300\text{K} \quad n_{\text{initial}} = 0.37 \text{ moles}$$

$$\text{Volume}_{\text{initial}} = 3 \text{ liters} \quad \text{Volume}_{\text{final}} = 10 \text{ liters}$$

$$\text{Pressure}_{\text{initial}} = 3 \text{ atmospheres} \quad T_{\text{final}} = 300 \text{ K} = T_i$$

$$w = -nRT \ln\left(\frac{V_2}{V_1}\right) = -q = -1111J$$

$$\frac{1111J}{300K} = \Delta S = 3.7 J \cdot K^{-1}$$

A couple of worked examples, Entropy:

Entropy (reversible, non-isothermal process)

$$\Delta S = \int_i^f \frac{dq_{rev}}{T}$$

$\Delta V=0$
Isochoric process

$$dq_{rev} = n c_v dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = n c_v \ln\left(\frac{T_2}{T_1}\right)$$

$\Delta P=0$
Isobaric process

$$dq_{rev} = n c_p dT$$

$$\Delta S = \int_{T_i}^{T_f} \frac{dq_{rev}}{T} = n c_p \ln\left(\frac{T_2}{T_1}\right)$$

A couple of worked examples, Entropy:

Entropy (reversible, non-isothermal process)

Reversible processes

$$\Delta S \text{ of system + surroundings} = 0$$

Example (ideal gas): $n = 2$; $V=10$ Liters; $T=300K$

For a reversible, isobaric compression to 5 Liters

ΔS_{gas} and $\Delta S_{\text{surrounding}} = ?$

$$\Delta P = 0$$

$$V_2/V_1 = 0.5$$

$$T_2/T_1 = 0.5$$

$$\text{So } T_2 = 150K$$

$$\begin{aligned}\Delta S_{\text{gas}} &= \int_{T_1}^{T_2} \frac{dq_{\text{rev}}}{T} = n c_P \ln\left(\frac{T_2}{T_1}\right) = 2\left(\frac{5}{2} \cdot 8.314 J \cdot mol^{-1} K^{-1}\right) \ln\left(\frac{150}{300}\right) \\ &= -29 J K^{-1}\end{aligned}$$

$$\Delta S_{\text{surroundings}} = 29.1 J \cdot K^{-1}$$

Where are we going with all this?



$$\Delta S_{univ} > 0$$

Spontaneous Processes and
Thermodynamic Equilibrium

Entropy

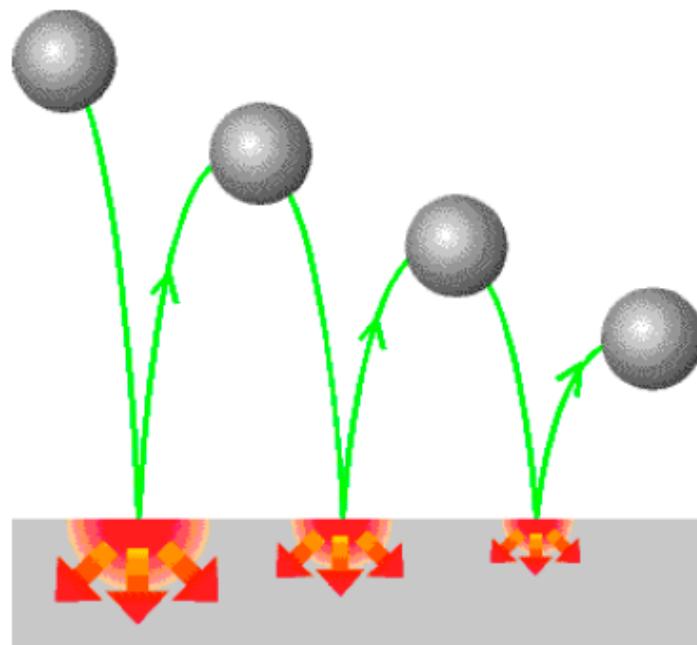
The Second Law of
Thermodynamics

The Gibbs Free Energy

Chemical Equilibrium

That is, we want to be able to predict the macroscopic behavior of chemical systems using what we know about molecules.

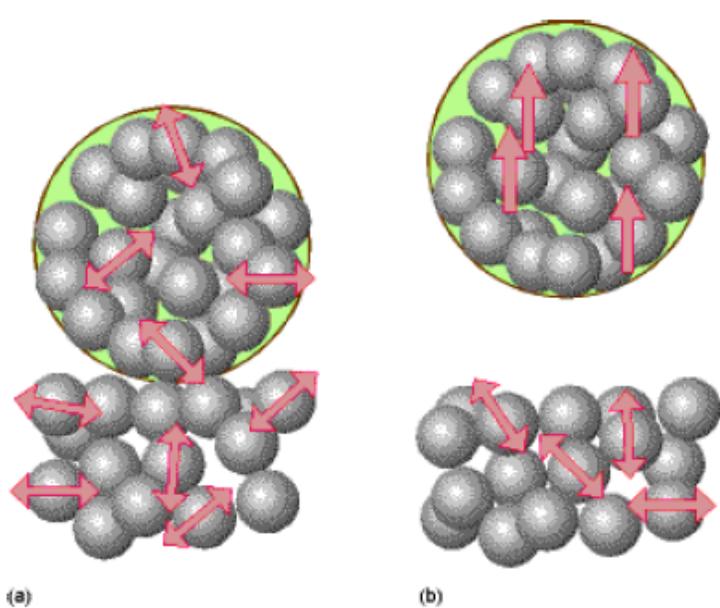
The Second Law Applied to Macroscopic Objects



The direction of spontaneous change for a ball bouncing on a floor. On each bounce some of its energy is degraded into the thermal motion of the atoms of the floor, and that energy disperses. The reverse has never been observed to take place on a macroscopic scale.

Entropy & the 2nd Law:

The molecular interpretation of the irreversibility expressed by the Second Law.

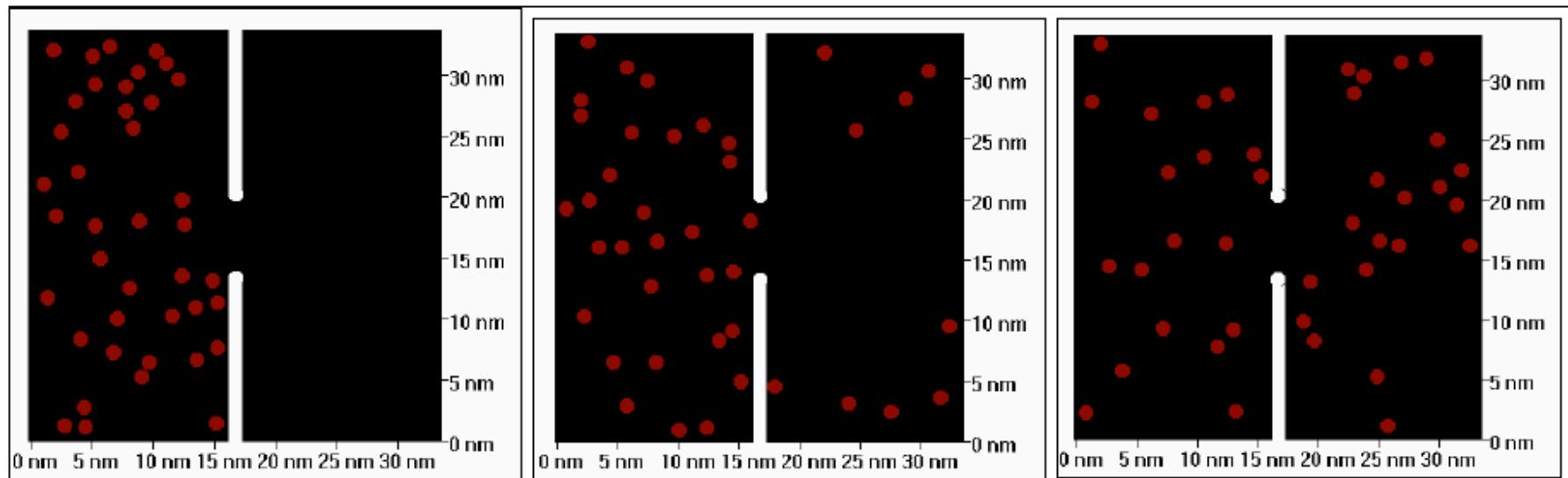


- (a) A ball resting on a warm surface; the atoms are undergoing thermal motion (chaotic vibration, in this instance), as indicated by the arrows.
- (b) For the ball to fly upwards, some of the random vibrational motion would have to change into coordinated, directed motion. Such a conversion is highly improbable (except during earthquakes).

Entropy & the 2nd Law:

Key concept -

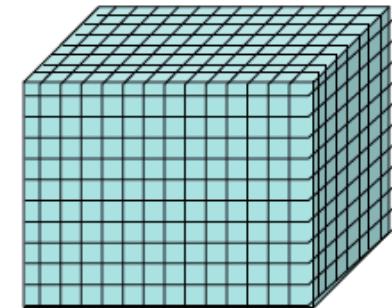
Entropy is a measurement of the disorder within a system



These images represent a molecular dynamics simulation of an ideal gas, and illustrate the concept of entropy. At time=0 the valve between the two chambers is opened. Within 100 picoseconds (10^{-10} seconds) the atoms have effectively moved to make the pressure between the two regions the same.

A microscopic approach to Entropy

$$S = k_B \ln \Omega$$



How does this definition relate to the Carnot Cycle definition?

$$\Omega = \frac{Z(Z-1)(Z-2)\dots(Z-(N-1))}{N!}$$

Since $Z \gg N$

$$\Omega = \frac{Z^N}{N!} = \frac{(V/v)^N}{N!}$$

Z cells for putting atom 1 into
 $(Z-1)$ cells for putting atom 2 into

Etc.

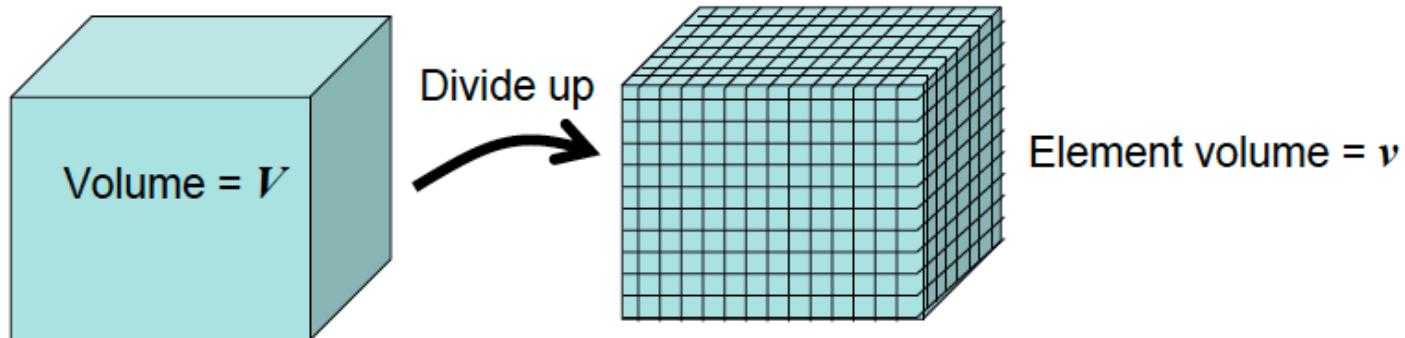
$N!$ permutations of the N molecules
that yield identical distributions

$Z \gg N$

V = volume of vessel; v = volume of individual cells

Ω (or W) refers to the number of microstates

A microscopic approach to Entropy



- Take a vessel containing an ideal gas
- Divide into individual volume elements
- # of elements \gg # of gas atoms

$$S = k_B \ln \Omega$$

Assert for now. Tie to 2nd Law?

A state of the system corresponds to a particular arrangement of gas atoms within the individual elements

Ω (or W) refers to the number of microstates – i.e. # of ways to arrange the atoms into the cubes in the above box

Statistical Thermodynamics (a quick overview)

First Postulate of Statistical Thermodynamics: In an isolated system all of the possible quantum states consistent with specified values of the number of particles, the volume, and the energy are equally probable. This is *the principle of equal a priori probabilities*.

Second Postulate of Statistical Thermodynamics: The time average of a mechanical property for a single system is equal to the average of this property over all the systems of the *ensemble* (idealized copies, each of which represents a possible state in which the system can exist).

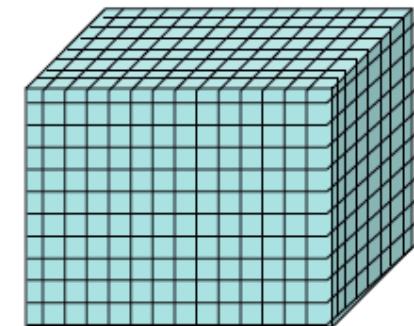
With some math (Lagrange multipliers and the like), these postulates lead directly to the Boltzmann expressions we have been using and a tie between quantum mechanics and thermodynamics.

A microscopic approach to Entropy (cont'd)

$$\Omega = \frac{Z^N}{N!} = \frac{\left(\frac{V}{v}\right)^N}{N!}$$

imagine we do a Pressure/Volume expansion of an ideal gas.

$$V_1 \rightarrow V_2$$



Then we can calculate ΔS

$$\Delta S = k_B \cdot \ln \frac{\Omega_2}{\Omega_1} = k_B \cdot \ln \left(\frac{\left(\frac{V_2}{v} \right)^{N_A}}{N_A!} \cdot \frac{N_A!}{\left(\frac{V_1}{v} \right)^{N_A}} \cdot \frac{N_A!}{N_A!} \right)$$

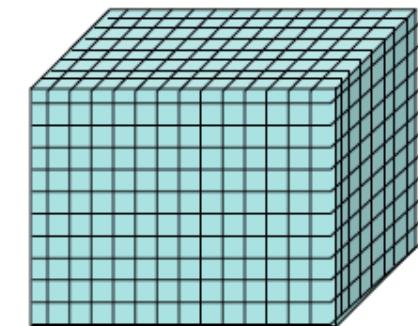
Z cells for putting atom 1 into
 $(Z-1)$ cells for putting atom 2 into
 Etc.
 $N!$ permutations of the N molecules
 that yield identical distributions
 $Z \gg N$

A microscopic approach to Entropy

$$\Omega = \frac{Z^N}{N!} = \frac{(V/v)^N}{N!}$$

Assume we do a Pressure/Volume expansion of an ideal gas.

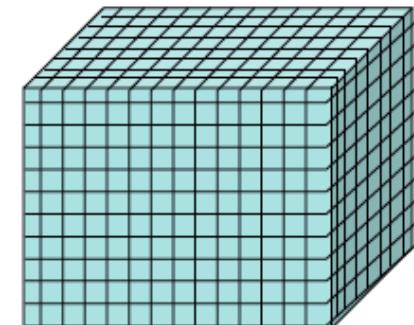
$$V_1 \rightarrow V_2$$



Then we can calculate ΔS

$$\Delta S = k_B \cdot \ln \frac{\Omega_2}{\Omega_1} = k_B \cdot \ln \left(\frac{\frac{\left(\frac{V_2}{v} \right)^{N_A}}{N_A!}}{\frac{\left(\frac{V_1}{v} \right)^{N_A}}{N_A!}} \right)$$

A microscopic approach to Entropy



$$\Delta S = k_B \cdot \ln \frac{\Omega_2}{\Omega_1} = N_A k_B \ln \frac{V_2}{V_1}$$

Calculations of Entropy Using $S = k_B \ln W$ Isothermal Gas Expansion

Boltzmann analysis

$$\Delta S = N_A k \ln \frac{V_2}{V_1} = nR \ln \frac{V_2}{V_1}$$

Note how these all relate!!!

Reversible Isothermal expansion

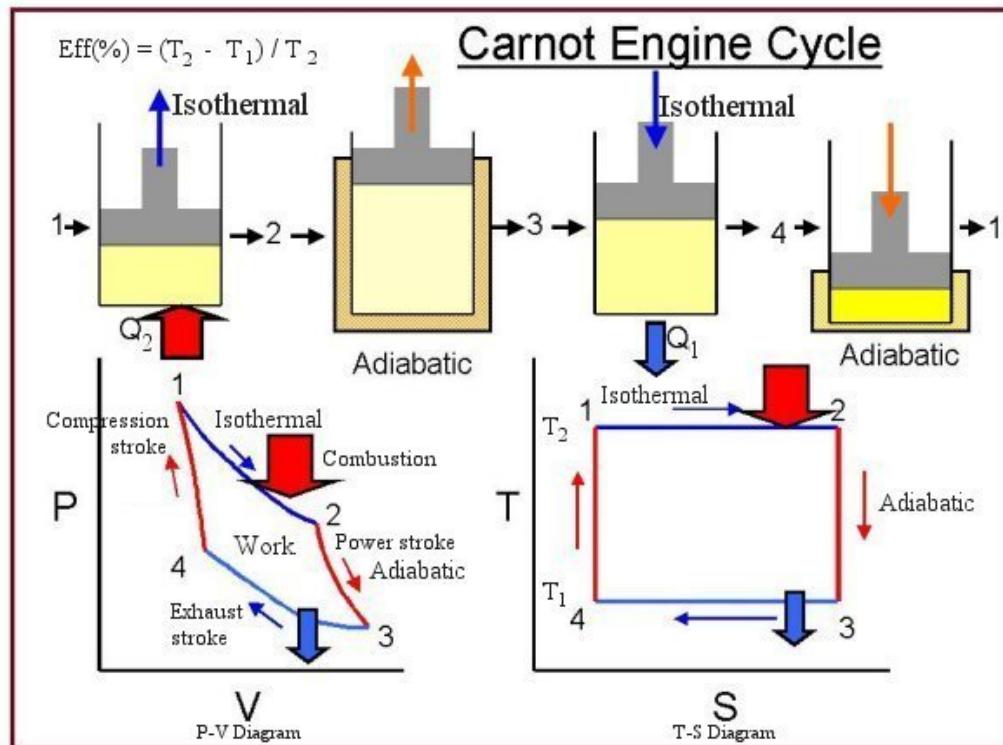
$$w_{12} = -q_{12} = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Clausius definition of entropy

$$\Delta S \equiv \int_1^2 \frac{dq_{rev}}{T} = nR \ln \left(\frac{V_2}{V_1} \right)$$

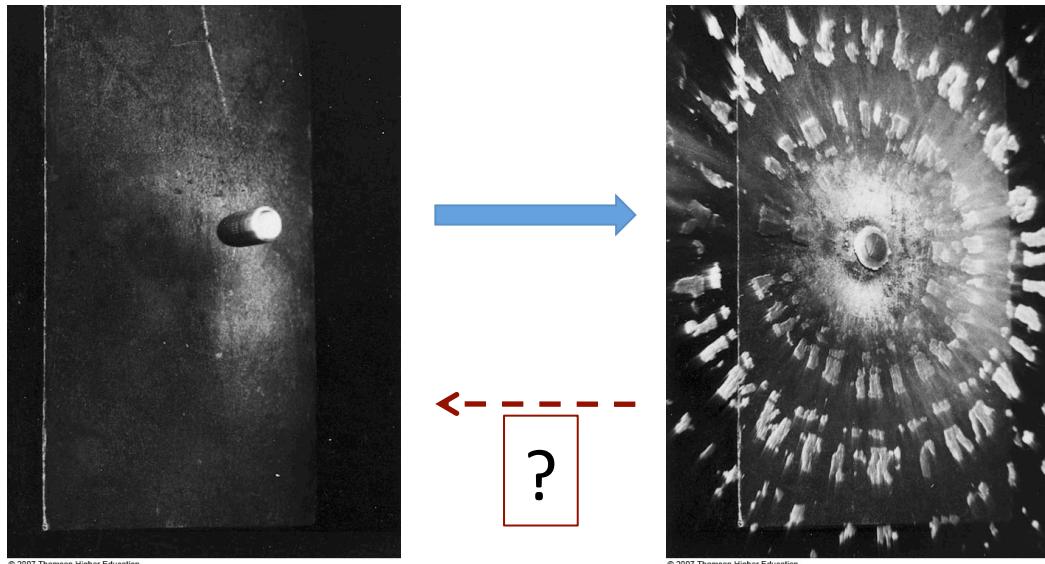
A microscopic approach to Entropy

These same approaches can also be applied to information theory (the so-called Shannon Entropy (1948), where the entropy of a random variable is defined in terms of its probability distribution) and the limits of lossless compression...



The Carnot cycle can also be viewed in entropy, temperature (S,T) space, which are natural coordinates for isothermal & adiabatic processes operating on an ideal gas.

A microscopic approach to Entropy

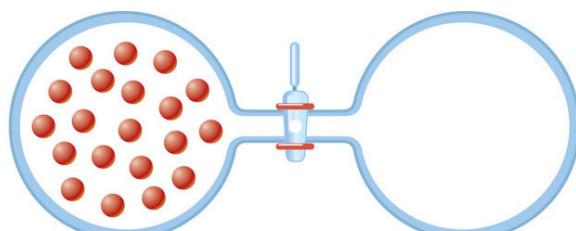


Hey, you've not
really told us about
directionality.
What's up with
that?

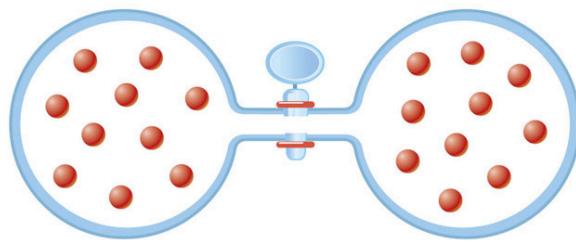
A critical part of the answer, with apologies to Douglas Adams, is:

“[Avogadro’s number] is big, really big. You may think it’s a long way down to the chemist’s shop, but that’s just peanuts to $[N_A]$.”

A microscopic approach to Entropy



(a)



(b)

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OGC gives a couple of simple, small number examples, such as noting that only once out of sixteen tries are you likely to get all heads (or tails) in four tosses of a coin.

We need to think about MUCH larger numbers, and so will need a relationship called Stirling's Approximation:

$$\ln(N!) = \sum_{m=1}^N \ln(m) \approx \int_1^N \ln(x) dx = N \ln(N) - N \quad (N \text{ large})$$

A microscopic approach to Entropy

Let's examine what the so-called binomial distribution looks like for very large numbers of trials ($N_1 + N_2 = N$)...

$$f(N_1) = N!/N_1!(N - N_1)! \quad \text{Probability distribution}$$

$$[(d \ln f(N_1))/dN_1] = 0 \quad \text{Peak of distribution}$$

$$N_1^* = N/2 \quad \text{Most likely outcome}$$

What does the binomial distribution look like near the most likely outcome? ($N_1^* = N_2^* = N/2$)

$$\ln[f(N_1)] = \ln[f(N_1^*)] + \frac{1}{2} \left(\frac{d^2 \ln[f(N_1)]}{dN_1^2} \right)_{N=N_1^*} (N_1 - N_1^*)^2 + \dots$$

Taylor expansion... Why is the first derivative term zero?

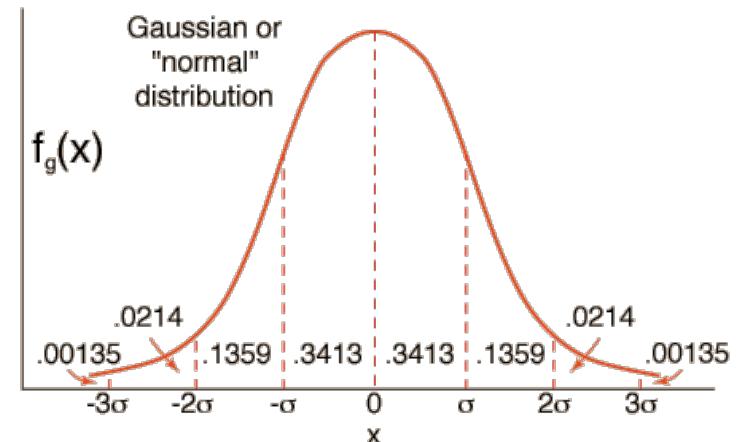
A microscopic approach to Entropy

$$\ln[f(N_1)] = \ln[f(N_1^*)] + \frac{1}{2} \left(\frac{d^2 \ln[f(N_1)]}{dN_1^2} \right)_{N=N_1^*} (N_1 - N_1^*)^2 + \dots$$

It turns out the second derivative is $-4/N$, and so the distribution function around N_1^* is:

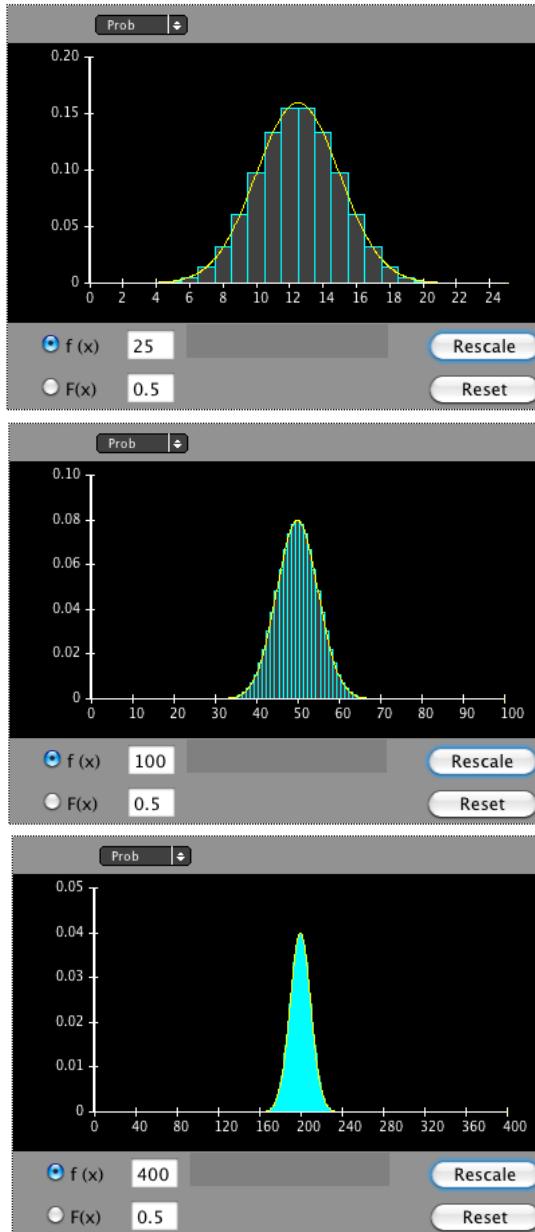
$$f(N_1) = f(N_1^*) \exp \left\{ -\frac{2(N_1 - N_1^*)^2}{N} \right\}$$

This is clearly a Gaussian function with a mean of $N/2$ and a standard deviation σ of order $N^{1/2}$.



What does this mean for large N ?

A microscopic approach to Entropy

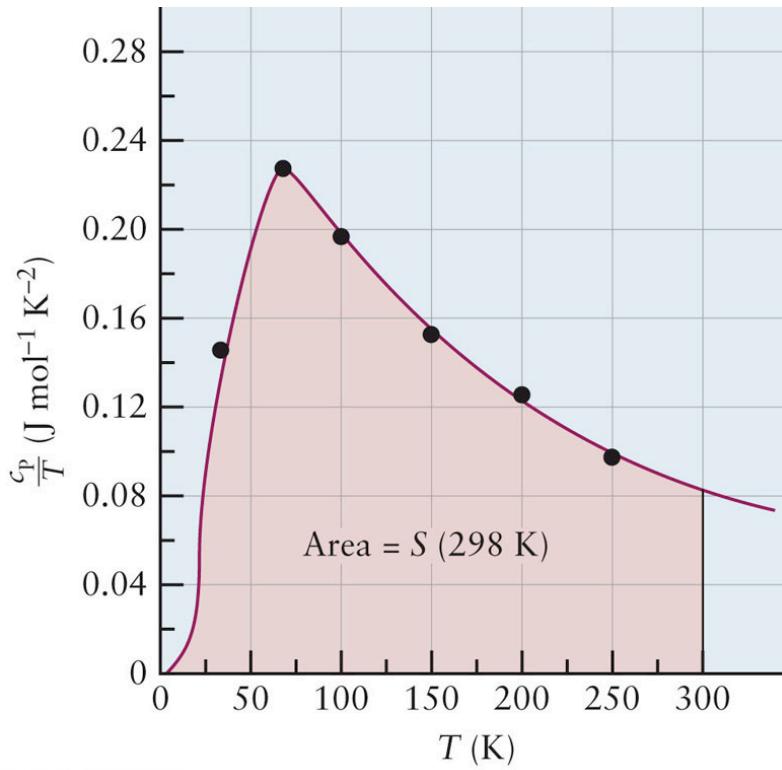


As the number of trials increases, both the mean and the dispersion go up...

But the width of the distribution *relative* to the mean decreases...

Thus, for ensembles of order N_A , fluctuations that measurably depart from the most likely outcome are insignificant!

A microscopic approach to Entropy



System cannot access
the excited state

$$\Delta E/kT \gg 1$$

Heat capacities of metals
cannot be understood
classically, but a two
level quantum approach
is illuminating:

System saturated and
cannot respond

$$\Delta E/kT \ll 1$$



Ch 1b - The Third Law of Thermodynamics (Nernst Heat Theorem)

The second law relates the infinitesimal change in entropy, an exact differential, to that in the infinitesimal change in the heat exchanged (which is inexact since it depends on the path of the system) under isothermal conditions. The integral needed to calculate the change in entropy, however, has an additive constant associated with its calculation. The third law, which can be written in several forms, deals with this constant. One formulation is:

In any system in internal equilibrium undergoing an isothermal process between two states, the entropy change of the process approaches zero as the temperature of the system approaches zero. This enables us to calculate the absolute entropy of a substance via the expressions

$$S - S_0 = \int dq_{rev}/T \quad \text{and} \quad S_0(T=0) = 0$$

where the integral runs from 0 to T. The restriction to states of internal equilibrium is important. Frequently, during the approach to $T = 0$, a system develops internal constraints that prevent the achievement of internal equilibrium (glasses cannot turn into crystalline solids, for example, at low T).

Entropy & Computation?

Logically, a function is reversible if there is a one-to-one mapping of the input to output state(s).

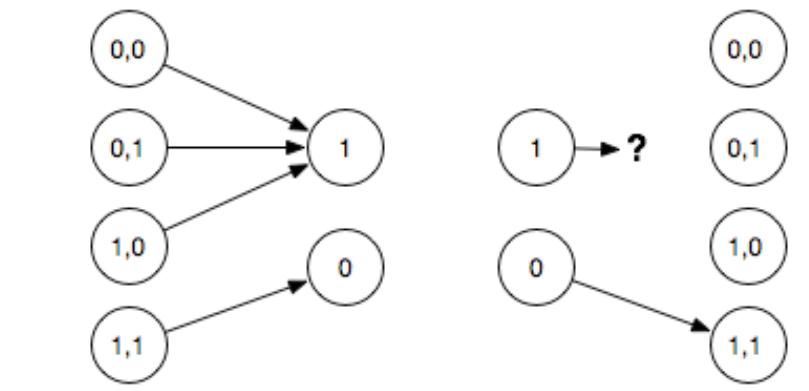
It is possible to reversibly embed irreversible steps in computation, but we are often concerned about the speed and throughput of computers.

Is there a limit to irreversible computation?

Experimental realization (2012):

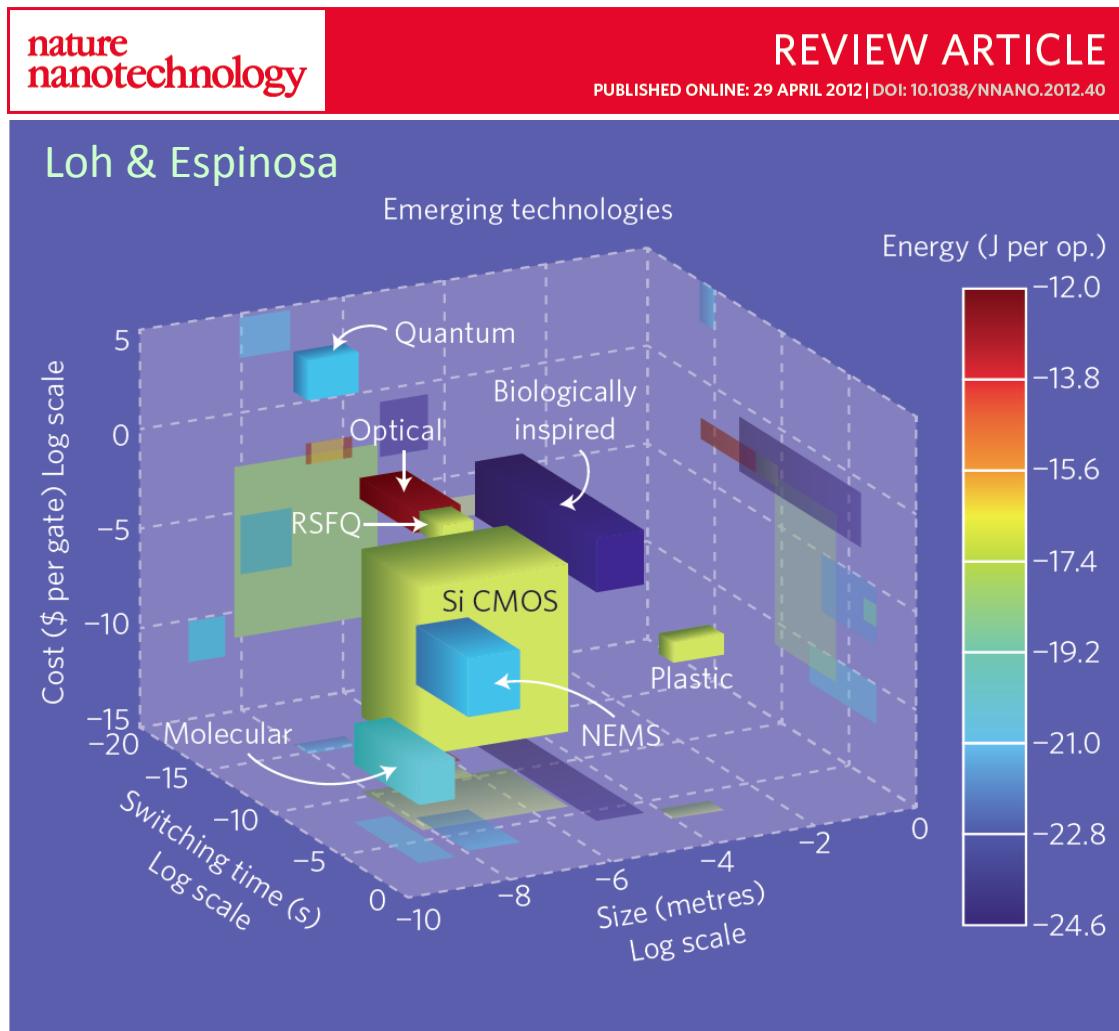
<http://www.nature.com/news/the-unavoidable-cost-of-computation-revealed-1.10186>

NAND Truth Table



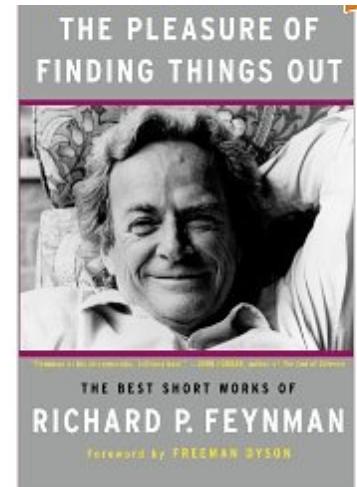
Landauer's Conjecture (1961): If a physical system performs a logically irreversible classical computation, then it must increase the entropy of the environment with an absolute minimum of heat release of $kT \times \ln(2)$ per lost bit.

Entropy & Computation?

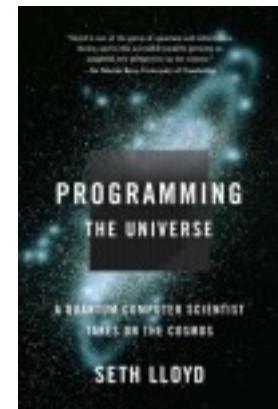


At 300 K, the Landauer limit is close to 3×10^{-21} J/operation. How close are we?

More? See...



Chapter 2



and Lloyd, S. 2000,
Nature 406 : 1047–1054

To Summarize:

In many cases, we will care about the possibilities that are associated with chemical reactions taking place under constant pressure and temperature.

Reversible processes

ΔS of system + surroundings = 0

Irreversible processes

ΔS of system + surroundings > 0

A situation where

ΔS of system + surroundings < 0

Is not possible

This will lead us to consider a new state function, the Gibbs Free Energy, or G , defined as:

$$G = H - TS$$

The midterm covers material through this lecture and Problem Set #5.