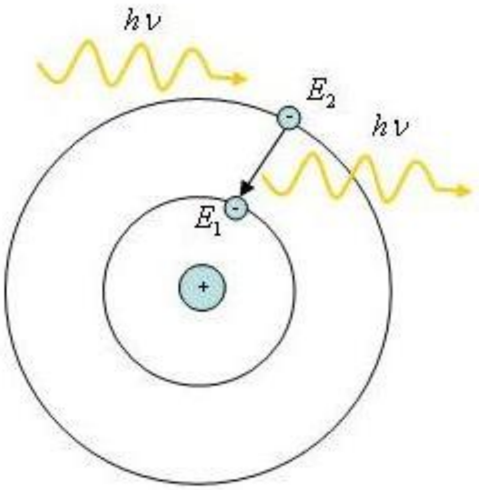
Chemistry 163B
Heuristic Tutorial
Second Law,
Statistics and Entropy

“Lower energy states are more stable”

Systems naturally go to lower energy ????

falling apples

http://www.sciencemuseum.org.uk/onlinestuff/snot/
if_the_earths_a_big_ball_why_dont_we_fall_off_the_bottom_of_it.aspx



excited state → ground state

http://www.thespectroscopynet.com/
images/PI_AS_EB_StE.jpg

chemistry 163B students

http://www.moonbattery.com/
sleeping_student.jpg

But ………………..   ???   First Law of Thermodynamics

The energy lost has to go somewhere ???

Energy lost by system means energy gained by surroundings.

First Law of Thermodynamics

$\Delta U_{sys} = -\Delta U_{surr}$

$\Delta U_{universe} = 0$ (also consider $E = mc^2$)

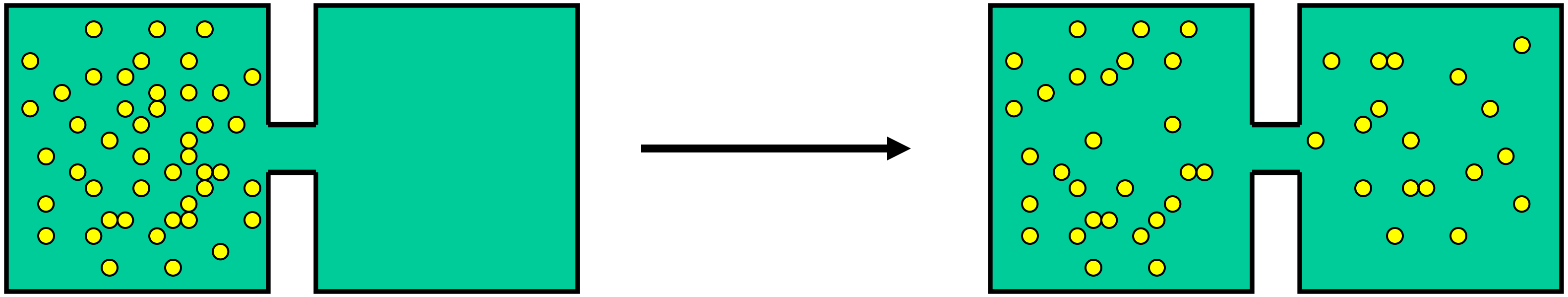
The second law of themodynamics

- Why do things happen?

- What are the limitations on things that do occur spontaneously?

- $\Delta H < 0$ was considered by Berthelot to be the driving principle for spontaneity

- But: some salts cool when dissolving
  and why do gasses diffuse if no energy difference



SADI CARNOT

RÉFLEXIONS

SUR LA

PUISSANCE MOTRICE

DU FEU

ET

SUR LES MACHINES

PROPRES A DÉVELOPPER CETTE PUISSANCE.

PAR S. CARNOT,

ANCIEN ÉLÈVE DE L'ÉCOLE POLYTECHNIQUE.

A PARIS,

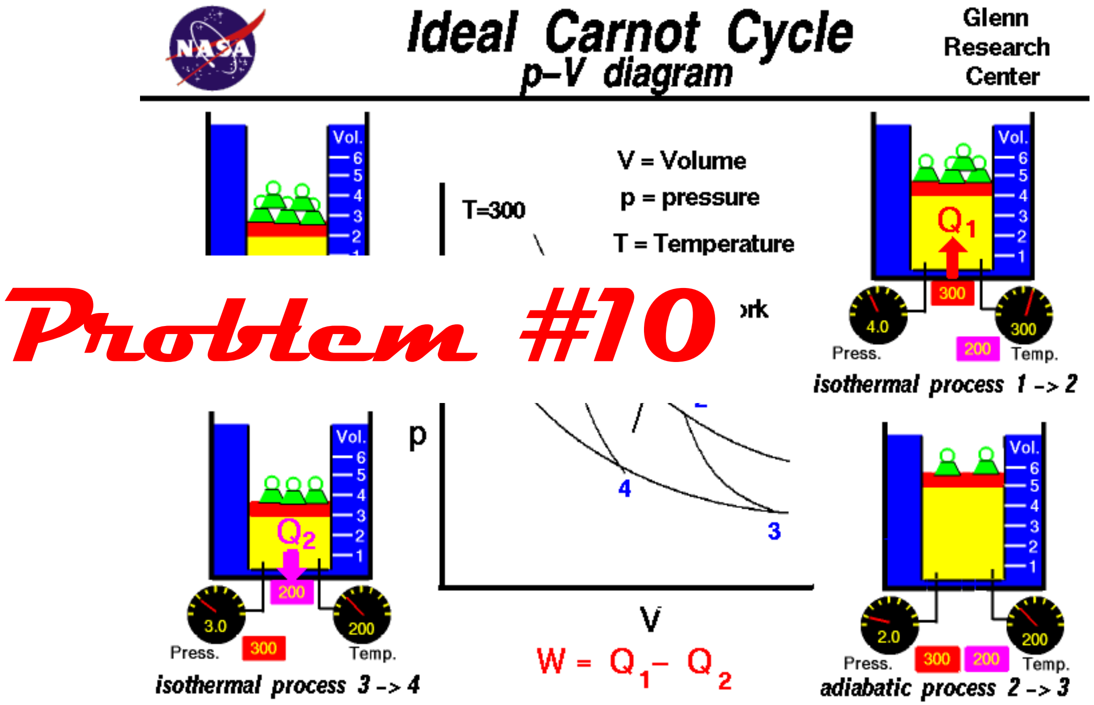
CHEZ BACHELIER, LIBRAIRE,

QUAI DES AUGUSTINS, nº. 55.

1824.

- born 1796, son of Lazare Carnot and antimonarchist
- named Sadi after Persian poet and mystic
- went to Polytechnique Ecole whose faculty included Lagrange, Fourier, Laplace, Berthelot, Ampere, duLong and had as classmates Cauchy, Coriolis, Poisson, Petit, Fresnel
- 1814 went into Corps of Engineers and when monarchy reestablished was sent to boondocks outpost
- 1824 wrote “Reflections on the Motive Power of Heat and Machines Adapted for Developing this Power”

Carnot cycle (E&R. pp. 80-85 and HW2 prob #10)



Problem #10

1→2 isothermal reversible expansion at T_1 (300K)
2→3 adiabatic reversible expansion $T_1 \rightarrow T_2$ (200K)
3→4 isothermal compression at T_2 (200K)
4→1 adiabatic compression $T_2 \rightarrow T_1$ (300K)

Carnot cycle (graphical interpretation; $w_{sys} = -\int P_{ext}\, dV$; review)

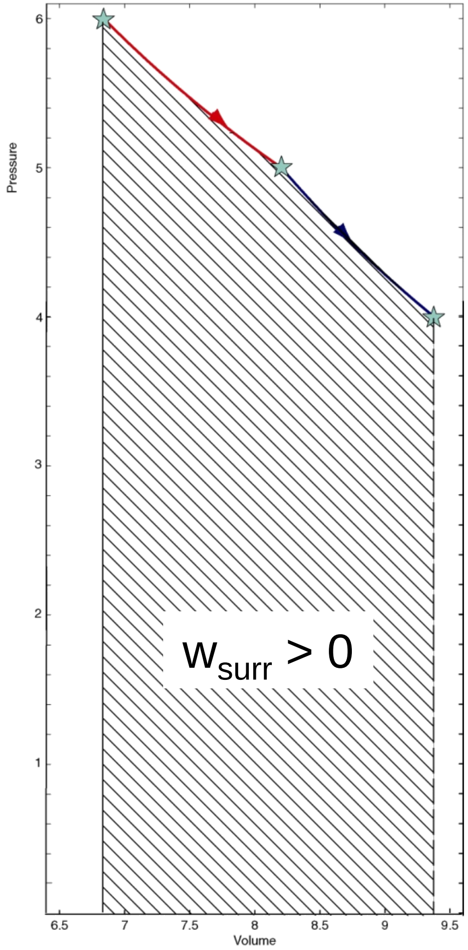
net work for cycle:

$w_{surr} > 0$

engine DOES work on surroundings

expansions, steps I-II

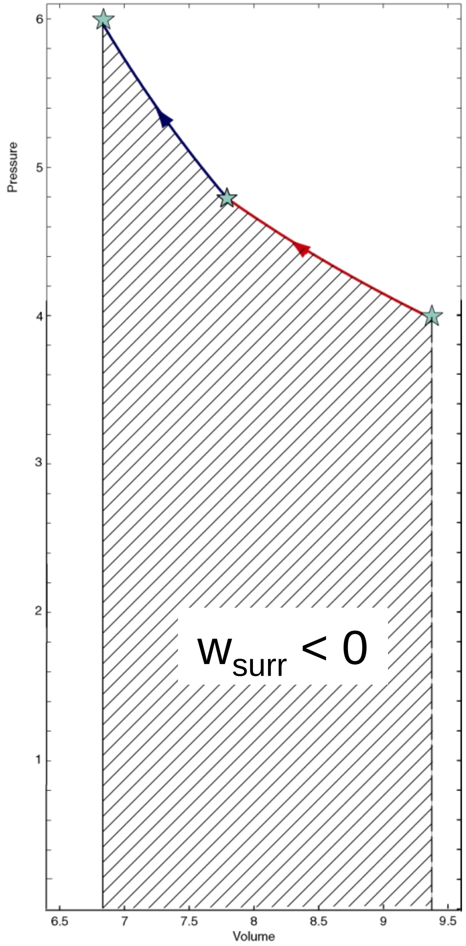
$w_{sys} < 0$, $w_{surr} > 0$ $T_{iso} = T_U$



$w_{surr} > 0$

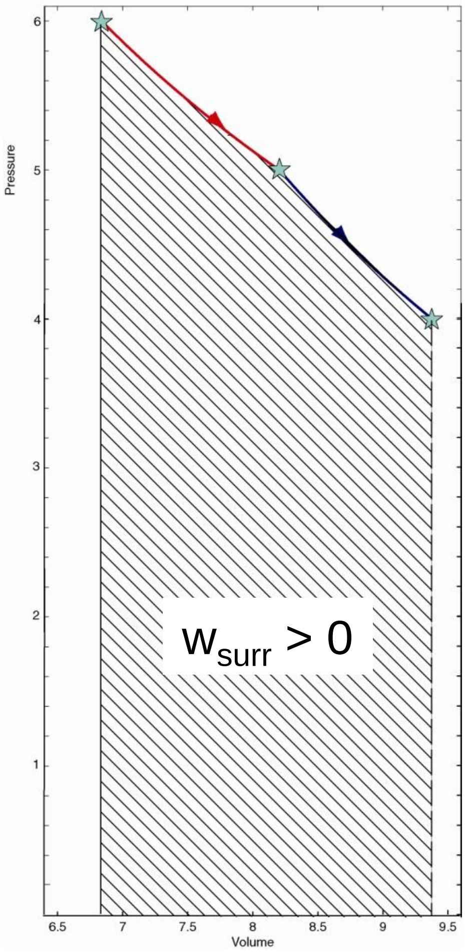
compressions, steps III-IV

$w_{sys} > 0$, $w_{surr} < 0$ $T_{iso} = T_L$



$w_{surr} < 0$

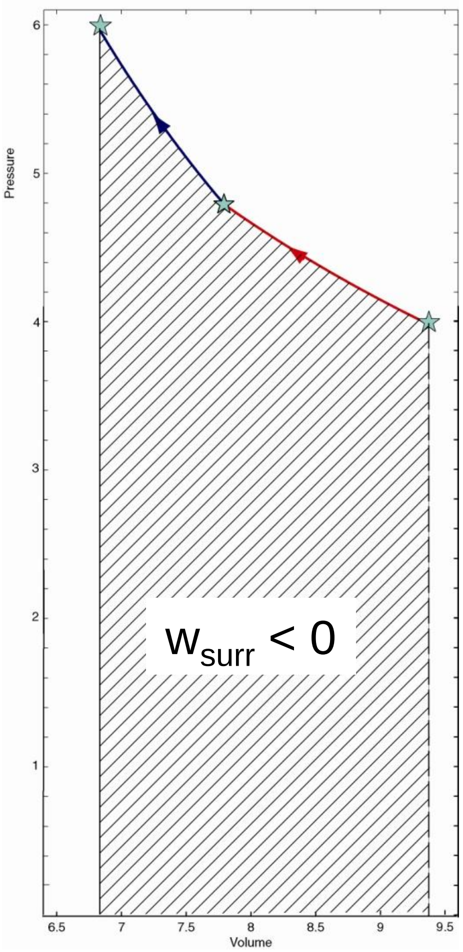
Carnot cycle: (graphical interpretation; $w_{sys}=-\int P_{ext}\, dV$; review)



expansions, steps I-II

$w_{sys} < 0$, $w_{surr} > 0$ $T_{iso} = T_U$

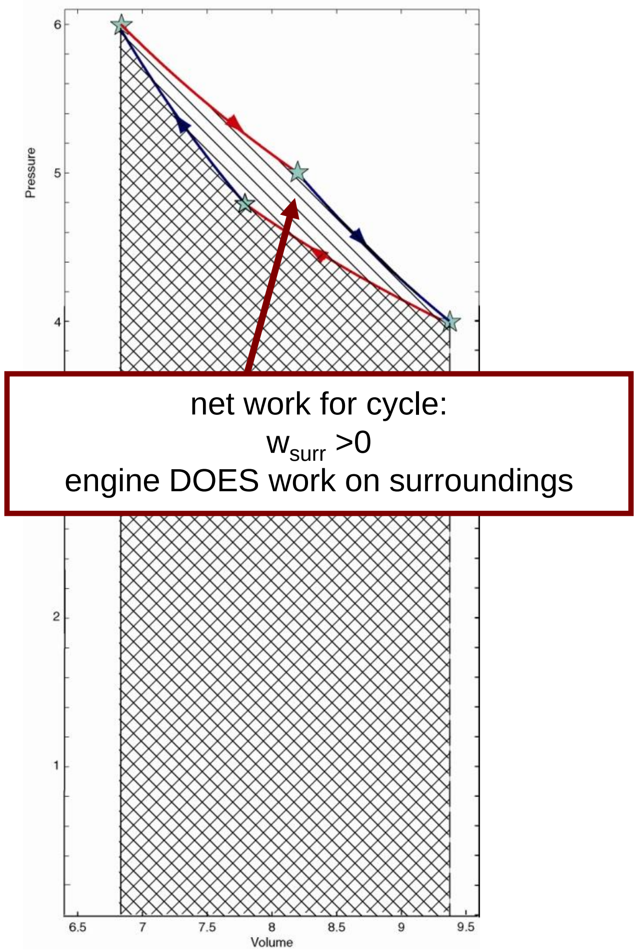
+



compressions, steps IIII-IV

$w_{sys} > 0$, $w_{surr} < 0$ $T_{iso} = T_L$

=



net work for cycle:
$w_{surr} > 0$
engine DOES work on surroundings

Carnot cyclic engine
net work ON surroundings

from Carnot cycle

for system in complete cycle:
$\Delta U=0$; $q > 0$; $w < 0$ (work DONE on surr) **(#10E)**

$q > 0$ (q_{in}) at higher T_1; $q < 0$ (q_{out}) at lower T_2

efficiency= $-w/q_{1\to 2}$
(how much net **work out** for **heat in** 1→2)

efficiency will depend on T_1 and T_2

HW prob #22 ε is εfficiency

$$\varepsilon = \frac{T_H - T_C}{T_H} \quad or \quad \varepsilon = \frac{T_U - T_L}{T_U}$$

H=HOT C=COLD or U=UPPER L=LOWER

statements of the Second Law of Thermodynamics

1. Macroscopic properties of an isolated system eventually assume constant values (e.g. pressure in two bulbs of gas becomes constant; two block of metal reach same T) [*Andrews. p37]*

2. It is impossible to construct a device that operates in cycles and that converts heat into work without producing some other change in the surroundings. *Kelvin's Statement [Raff p 157]; Carnot Cycle*

3. It is impossible to have a natural process which produces no other effect than absorption of heat from a colder body and discharge of heat to a warmer body. *Clausius's Statement, refrigerator*

4. In the neighborhood of any prescribed initial state there are states which cannot be reached by any adiabatic process
   ~ Caratheodory's statement [Andrews p. 58]

Tolman’s perpetual motion machine

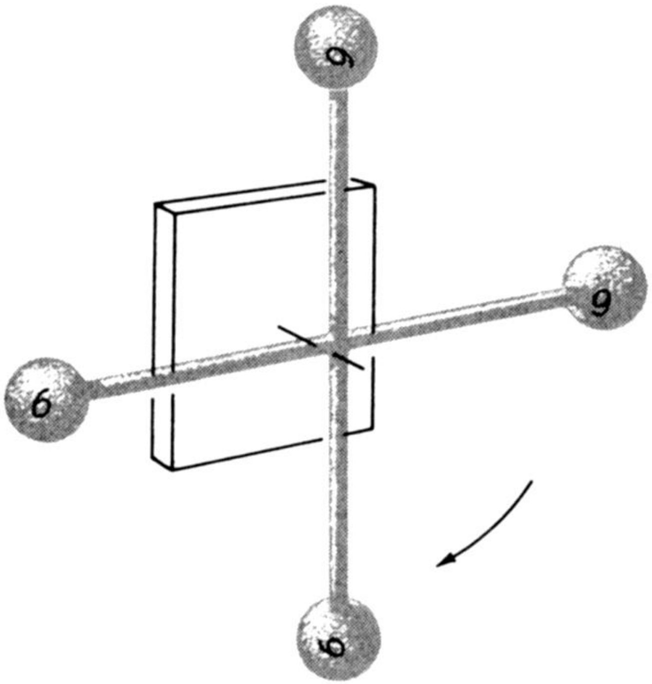


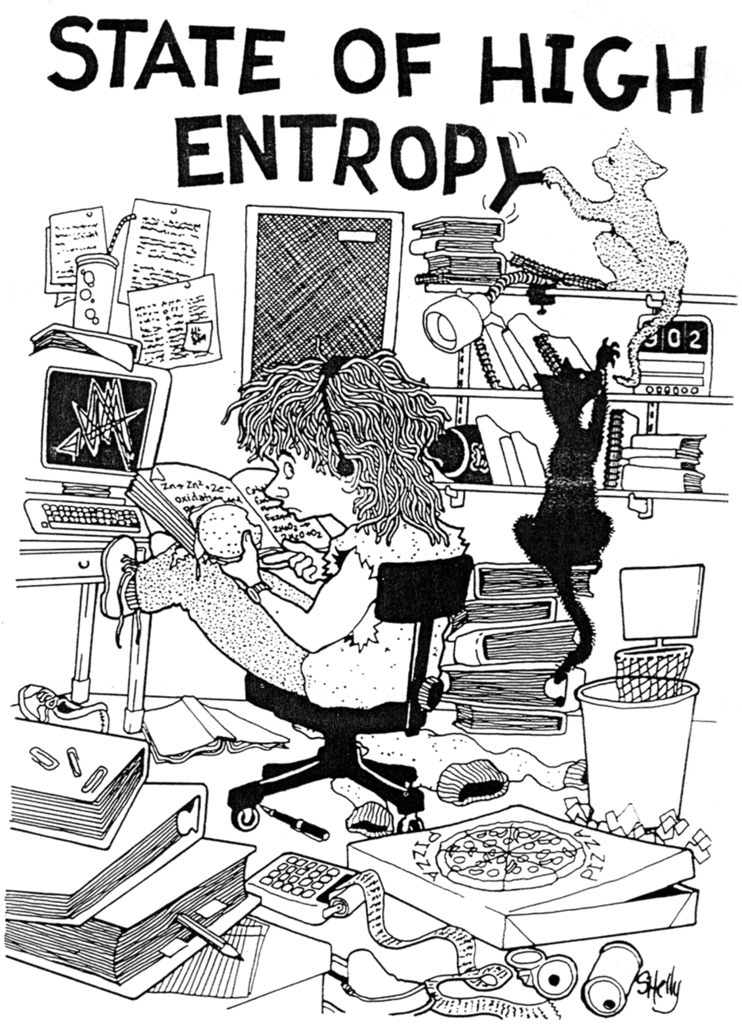
Figure 2–1 Tolman’s perpetual motion machine. In his lectures on thermodynamics Professor R. C. Tolman used to delight in presenting this tongue-in-cheek example of a perpetuum mobile of the first kind. The numbers indicate weights, in arbitrary units.

first a look at disorder and its relation to entropy and 2nd Law

$S = k \ln W$

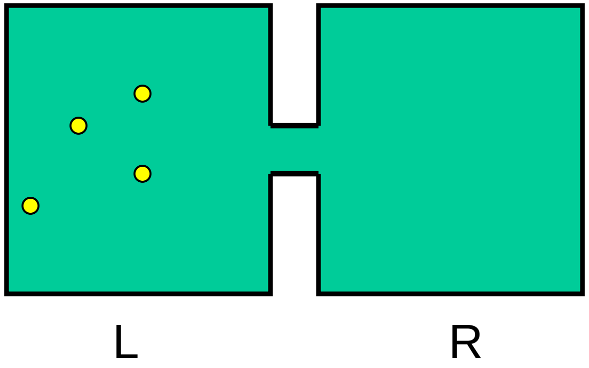
Boltzmann

disorder and entropy



microstates and macrostates

configuration 1 2 3 4	macrostate **L** **R**	W no. of microstates

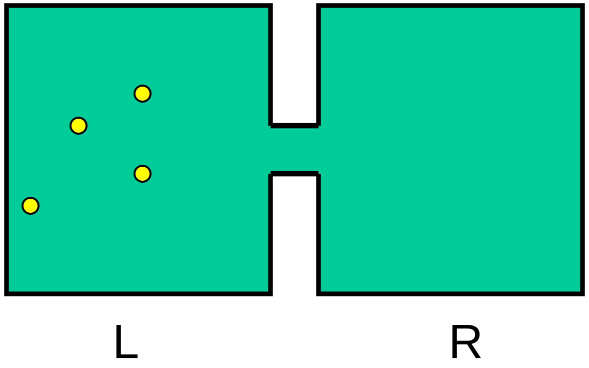


etc.

$$W = \frac{(n_{total})!}{(n_L)!\,(n_R)!}$$

microstates and macrostates

configuration	macrostate		W no. of microstates
1 2 3 4	**L**	**R**	
L L L L	**4**	**0**	**1**
L L L R L L R L L R L L R L L L	**3**	**1**	**4**
L L R R L R L R R L L R L R R L R L R L R R L L	**2**	**2**	**6**
~	**1**	**3**	**4**
~	**0**	**4**	**1**



etc.

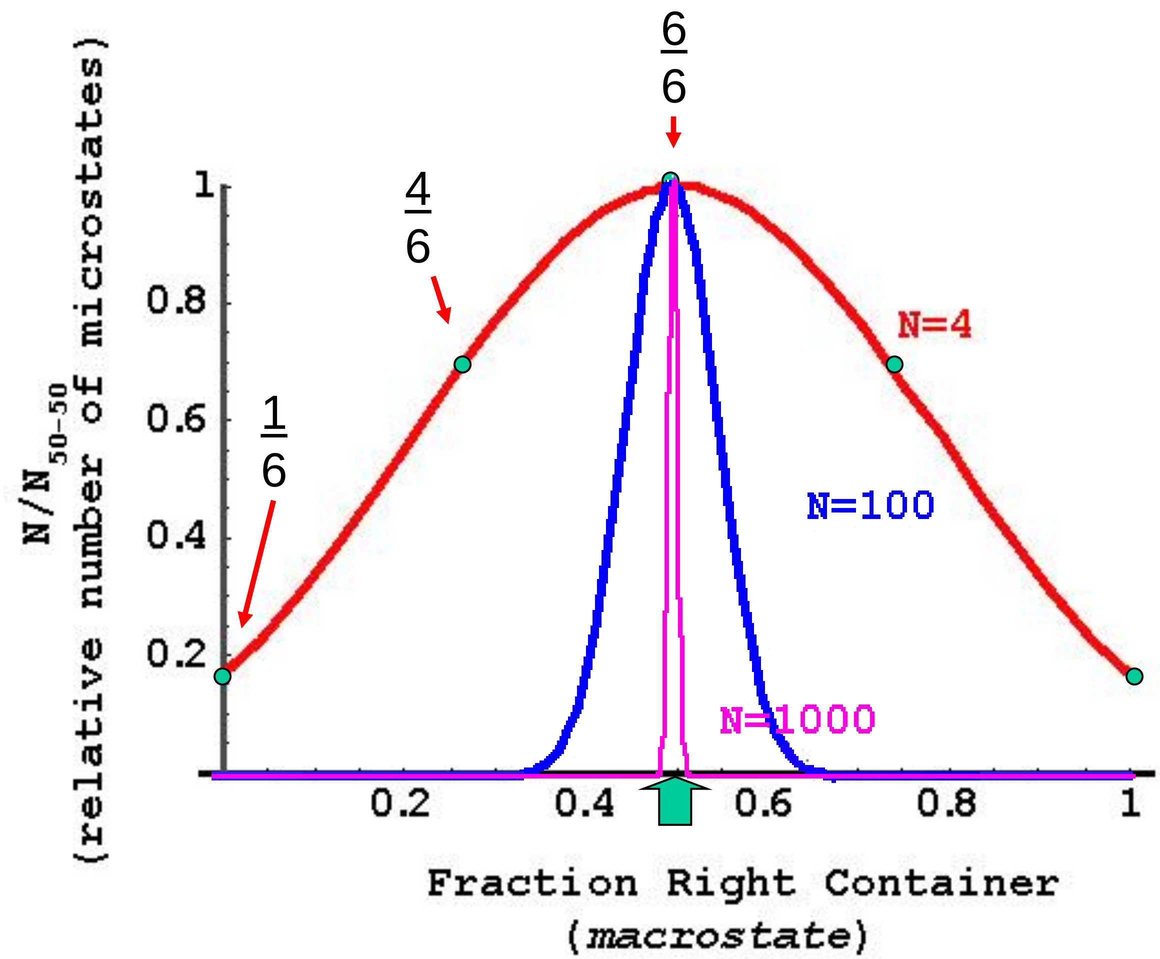
$$W = \frac{(n_{total})!}{(n_L)!\,(n_R)!}$$

macrostates and microstates

microstate: one of the **EQUALLY PROBABLE** configurations
of molecules (e.g. LLLL vs LRLR)

macrostate: state with specific macroscopic properties
e.g. L=2 R=2

macrostates for large numbers



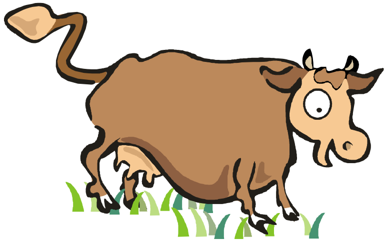
moral of the story

although each allowed microstate (e.g. LLRR or LLLL) is equally probable

the overwhelming number of microstates correspond
to macrostates with almost identical macroscopic
properties (e.g. ~ 50-50 RvsL)

W, the number of microstates corresponding to
the macrostate, is a measure of the DISORDER
of the system in that macrostate

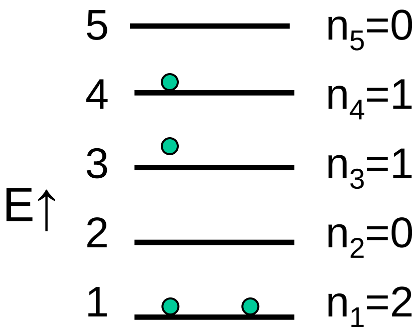
a system “meanders” through all available microstates;
but you are only likely to observe it in one of the overwhelming
number that correspond to the equilibrium macrostate



famous quote

“ disorder happens”

how energy changes affect disorder



5 $n_5=0$

4 $n_4=1$

E↑ 3 $n_3=1$

2 $n_2=0$

1 $n_1=2$

$$\mathrm{n_i} = \text{number of molecules in energy state } \varepsilon_\mathrm{i}$$

$$\sum_\mathrm{i} \mathrm{n_i} = \mathrm{n_{total}}$$

$$W = \frac{n_{total}!}{n_1!n_2!n_3!\cdots} \text{ number of ways of arranging with } \mathrm{n_1}, \mathrm{n_2}, \ldots$$

NOTE : W depends only on the $\mathrm{n_i}$'s, i.e. the distribution of molecules among quantum states

how energy changes affect disorder

$$U = E_{\text{total}} = \sum_i n_i \varepsilon_i$$

$$dE = \sum_i n_i d\varepsilon_i + \sum_i \varepsilon_i dn_i$$

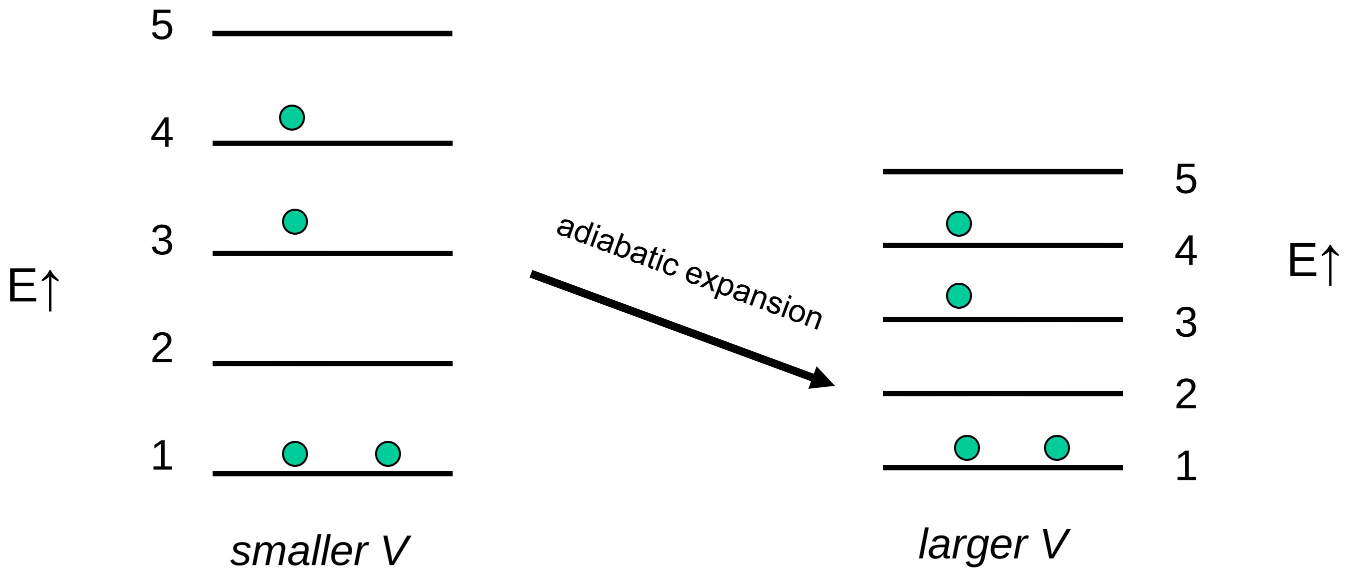
change in energy due to change in energy levels, e.g. 3D quantum p.i.b. change in energy levels as box changes size

change in energy due to change redistribution of molecules among energy levels, e.g. put in more total energy to fixed size 3D quantum p.i.b.

heat

work

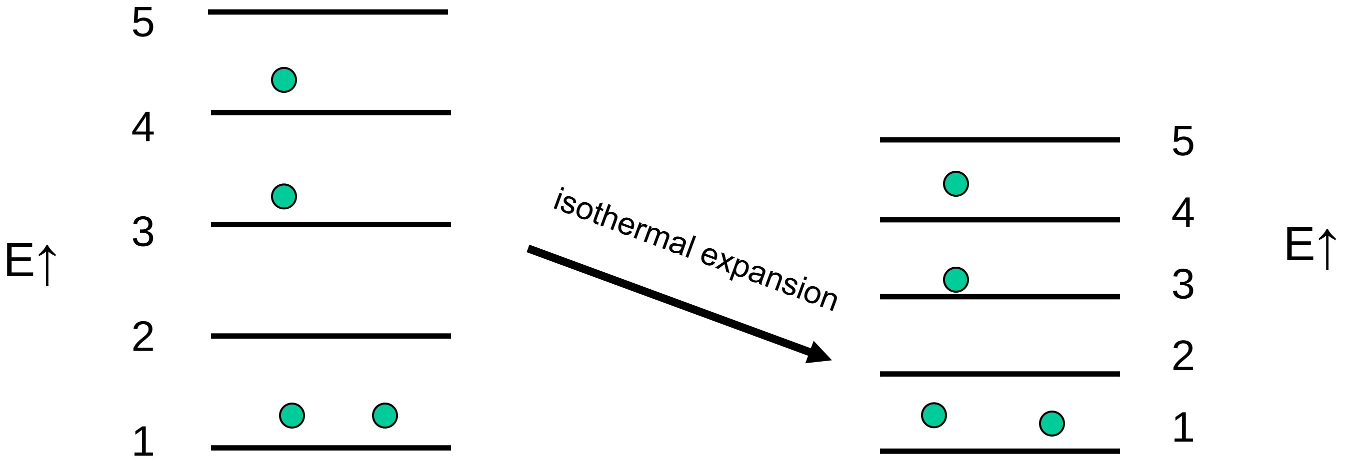
reversible adiabatic expansion ($\Delta U_{sys} < 0$; $q_{rev} = 0$)



quantum: expansion, bigger box, energy levels more closely spaced

- Total energy of system decreases ($\Delta U_{sys} < 0$ for adiabatic expansion)
- NO CHANGE IN LEVEL POPULATIONS if expansion done slowly, reversibly
- $q_{rev} = 0$; NO CHANGE IN DISORDER (**W**)

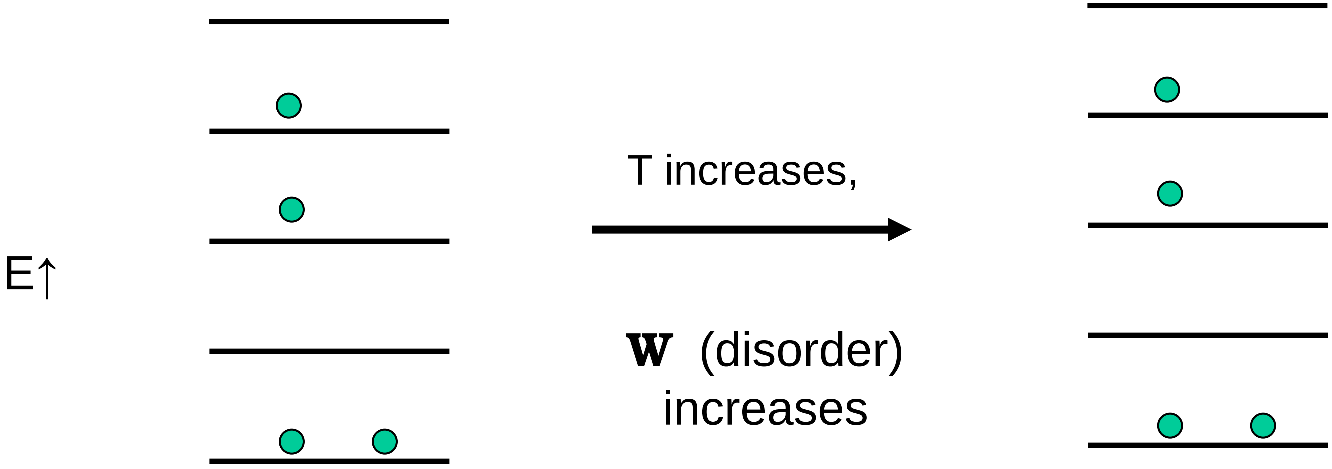
reversible isothermal expansion ideal gas (ΔU$_{sys}$ = 0 ; q$_{rev}$> 0; w=–q)



to maintain ΔU = 0 need to put in heat

- Levels get closer due to ΔV > 0 ; w < 0
- To maintain ΔU = 0, q>0 and the level populations have to change and thus W changes
- q_{rev} > 0 ; INCREASE IN **W**, INCREASE IN DISORDER

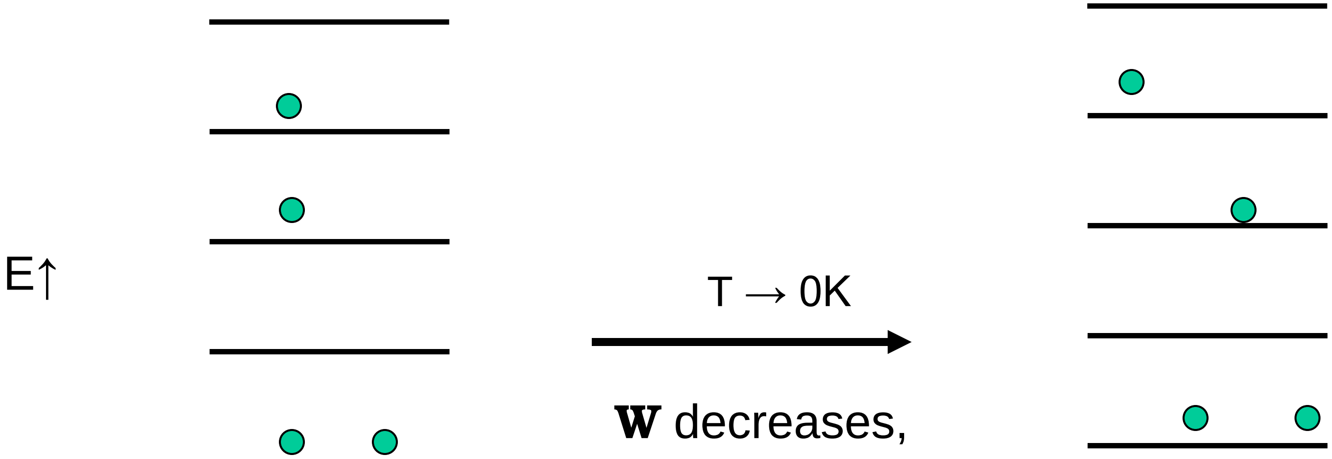
What happens to W as thermal energy raised?



T increases,

W (disorder) increases

What happens to W as thermal energy goes to zero (T→0K) ?



W decreases,
in fact **W**→ 1
only ‘one way to distribute at 0ºK

Boltzmann and Entropy

$$S = k \ln \mathbf{W}$$

S is entropy

k=Boltzmann’s constant= 1.3807×10^{-23} J K^{-1}

disorder increases ⇔ entropy increases

take home messages

- Disorder, $\mathbf{W}$, did not change during an adiabatic reversible expansion ($q_{rev} = 0$)

- Disorder, $\mathbf{W}$, increased in isothermal reversible expansion ($q_{rev} > 0$)

- Disorder, $\mathbf{W}$, increased with T increase ($q > 0$)

- Disorder, $\mathbf{W}$, decreased with T decrease ($q < 0$)

- As $T \rightarrow 0$, $\mathbf{W} \rightarrow 1$

take home messages

A sample problem†:

Two bodies 500 molecules each
one at $T_A = .63 \times T_f$,
the other at $T_B = 1.37 \times T_f$

COLD		HOT	W (microstates)
$T_A = .63\ T_f$	+	$T_B = 1.37\ T_f$	$\approx 10^{202}, 10^{354}$

bring into thermal contact

⇩

STAY COLD-HOT ??

.63 T_f	1.37 T_f

$\approx 10^{556} = 10^{202} \times 10^{354}$

or

or

☑ EQUILIBRIUM ??

$T_E = T_f$

$\approx 10^{594}$

† *adapted from Nash, <u>ChemThermo</u>, Addison Wesley, pp 175-176*

take home message continued†

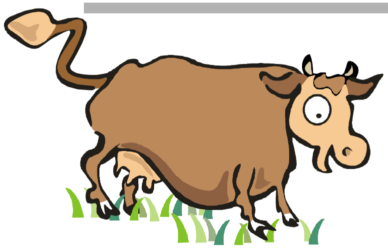
The equilibrium macrostate is $\frac{10^{594}}{10^{556}} = 10^{38}$ time more likely than the hot-cold state, even though every (microstate)$_{\text{hot-cold}}$ has the same likelihood as a (microstate)$_{\text{equilibrium}}$.

No more than one time in 10^{38} a measurement will find the blocks in a half-hot and half-cold configuration.

If you had observed the microstate of the system 10^{6} times a second constantly (without a msec of rest!) from the beginning of the universe until your midterm Friday (10^{10} years) **the odds against ever seeing a (microstate)$_{\text{hot-cold}}$ are 1:10^{15} !!!**

† adapted from Nash, ChemThermo, Addison Wesley, pp 175-176

take home message continued[†]



… ….. a progressive increase in “disorder” necessarily accompanies an approach to equilibrium characterized by the assumption of macrostates with ever-increasing values of W. And **what may at first appear to be a purposeful “drive” towards states of maximal disorder**, can now be seen to arise from **the operation of blind chance in an assembly** where all microstates remain equally probable, but where the overwhelming proportion of microstates is associated with the maximally disordered (nearly identical) macrostates corresponding to equilibrium macroscopic properties.

† adapted from Nash, ChemThermo, Addison Wesley, p 26.

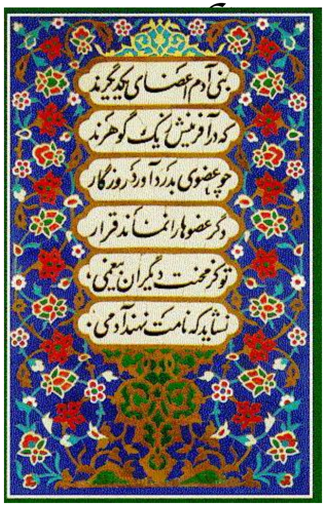
MUCH MORE

much more molecules, probability, statistical mechanics

CHEMISTRY 163C

End Of Introductory Lecture on Second Law and Disorder

بنی آدم اعضاء یک پیکرند
که در آفرینش زیک گوهرند
چو عضوی بدرد آورد روزگارد
دگر عضوها را نماند قرار



بنی آدم اعضای یکدیگرند
که در آفرینش ز یک گوهرند
چو عضوی بدرد آورد روزگار
دگر عضوها را نماند قرار
تو کز محنت دیگران بیغمی
نشاید که نامت نهند آدمی

literal translation (Farzaneh):

Of one Essence is the human race
thus has Creation put the base
One Limb impacted is sufficient
For all Others to feel the Mace

—Saadi (1184–1283)

interpretative translation on UN building:

Human beings are members of a whole,
In creation of one essence and soul.
If one member is afflicted with pain,
Other members uneasy will remain.
If you have no sympathy for human pain,
The name of human you cannot retain.

Persian Poet 13th Century

Nicolas Léonard Sadi Carnot (1796-1832) in the dress uniform of a student of the [École Polytechnique]

$$\varepsilon = 1 - \frac{T_L}{T_U}$$

French Thermodyamicist

Namesake 19th century

Saadi and Sadi

heuristic

heu·ris·tic [hy*oo*-**ris**-tik *or, often*, *yoo*-] ***adjective***

1. serving to indicate or point out; stimulating interest as a means of furthering investigation.