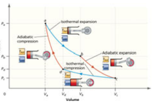
Chemistry 163B
Winter 2020
Heuristic Introduction
Second Law,
Statistics and Entropy

lecture 8 objectives:

When and Why do things happen ??

(an overview of 2nd Law)

- exothermicity ($q<0$) often accompanies spontaneous processes, but not all; not a requirement
- can't find a repeatable (cyclic) process that fully converts heat (disorder) to work (order)



- order and disorder in terms of microstates

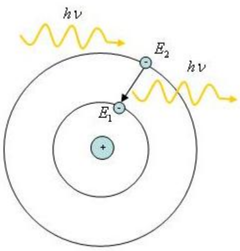
- the Universe meanders through the fields and meadows of microstates only to be observed in the 'state' corresponding to the maximum number of microstates!!

"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.

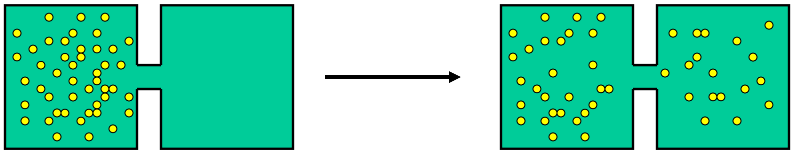
First Law of Thermodynamics

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

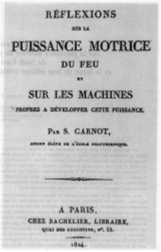
$$\Delta U_{universe} = 0 \quad \text{(also consider } E=mc^2\text{)}$$

The second law of themodynamics

- Why do things happen?
- What are the limitations on things that do occur spontaneously?
- exothermicity, $\Delta H < 0$, was considered by Berthelot to be the driving principle for spontaneity
- but this can’t be true: 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 approach to 'what can happen': engines, work, efficiency

- the 'Carnot Cycle" is a cyclic process (engine) of reversible (ideal) gas expansions and compressions ($\Delta U=0$)
- want process that does net w on surroundings
  i.e. convert heat to work *$[(w_{sys})_{total\ process} < 0;\ q_{sys}>0\ ]$*

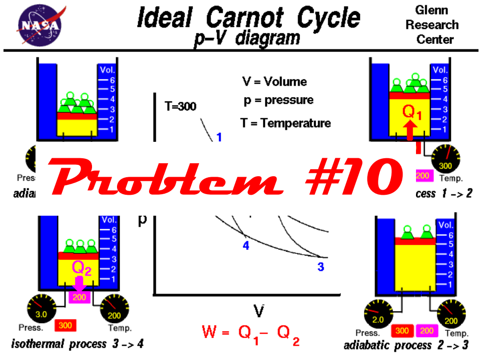
- we will employ Carnot cycle to show that

❖ "net disorder of universe" limits efficiency of the engine

❖ analysis of the process will lead to a **NEW STATE FUNCTION**

defined by $\dfrac{đq_{rev}}{T}$ **an exact differential !!!**

Carnot cycle (E&R_{4th} pp. 124-129 and HW2 prob #10)



1→2 isothermal reversible expansion at T_1 (500K)
2→3 adiabatic reversible expansion $T_1 \rightarrow T_2$ (457K)
3→4 isothermal compression at T_2 (457K)
4→1 adiabatic compression $T_2 \rightarrow T_1$ (500K)

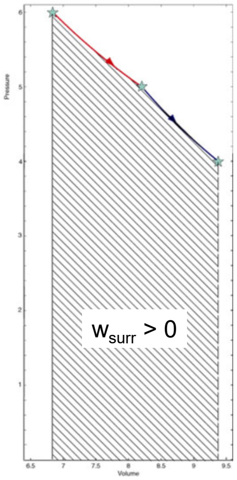
Carnot cycle (graphical interpretation; $w_{sys}=-\int P_{ext}\,dV$; review)

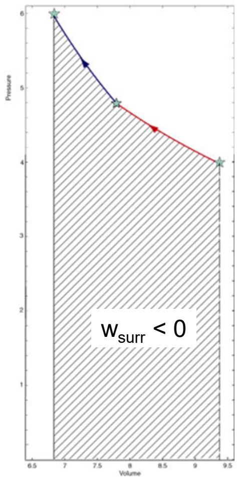
expansions, steps I-II

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

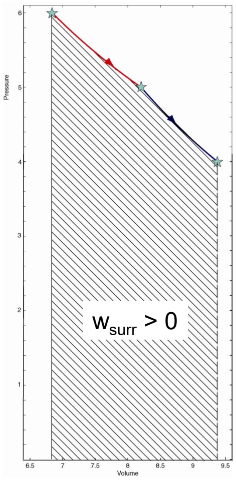
compressions, steps III-IV

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





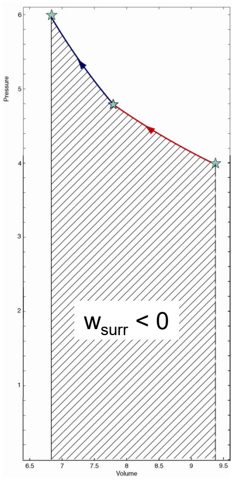
Carnot cycle: (graphical interpretation; $w_{sys}= -\int P_{ext}\,dV$; review)



expansions, steps I-II

$w_{sys} < 0$, $w_{surr} > 0$
q_{in} at $T_{iso} = T_{Upper}$

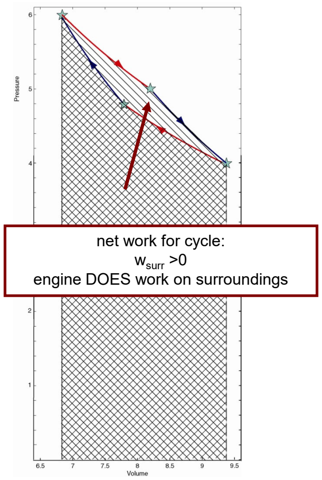
+



compressions, steps IIII-IV

$w_{sys} > 0$, $w_{surr} < 0$
q_{out} at $T_{iso} = T_{Lower}$

=



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= $-w/q_{1\rightarrow 2}$
(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 *(also see handout)*

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

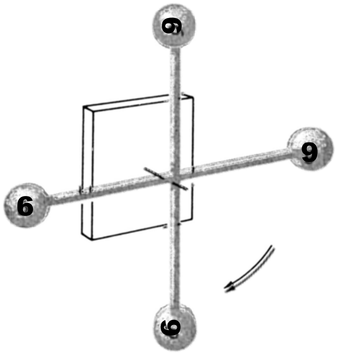
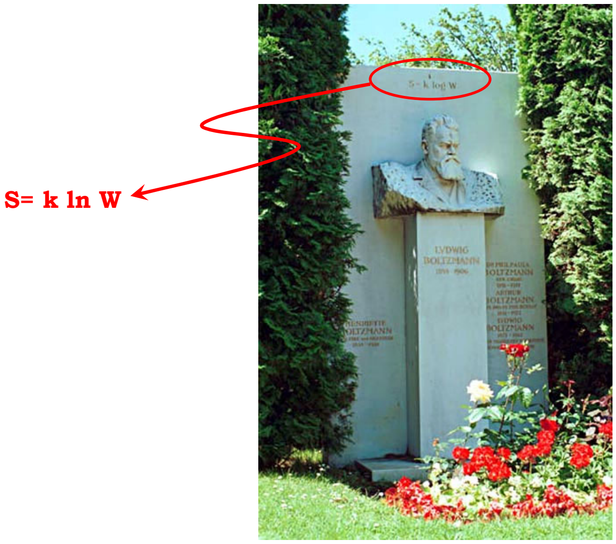


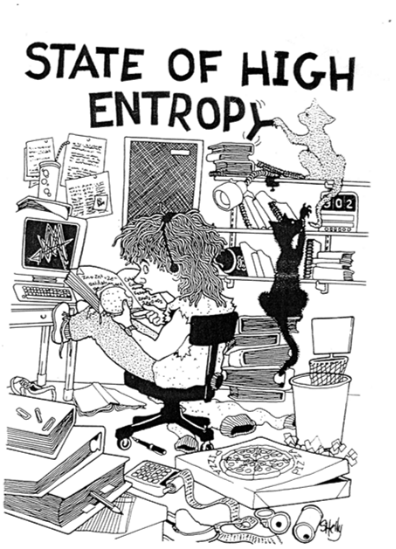
Figure 2–1 Tolman's perpetual motion machine. In his lectures on thermodynamics Professor R. C. Tolman used to delight in presenting this tongue-in-cheek example of a perpetuum mobile of the first kind. The numbers indicate weights, in arbitrary units.

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



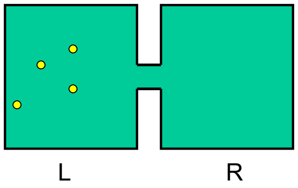
Boltzmann

disorder and entropy



microstates and macrostates

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

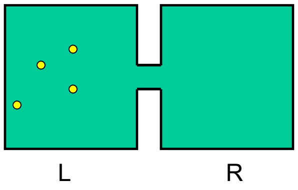


etc.

$$W=\frac{(n_{total})!}{(n_L)!\,(n_R)!}=\frac{24}{(n_L)!\,(n_R)!}$$

microstates and macrostates

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

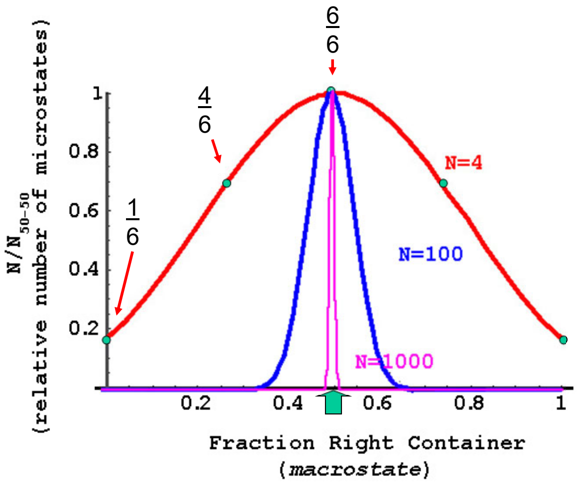
$$W = \frac{(n_{total})!}{(n_L)!\,(n_R)!} = \frac{24}{(n_L)!\,(n_R)!}$$

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



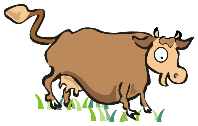
moral of the story

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”

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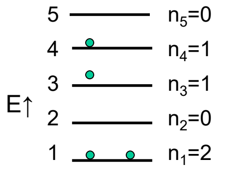
how energy changes affect disorder



n_i = number of molecules in energy state ε_i

$$\sum_i n_i = n_{total}$$

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

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

how energy changes affect disorder

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

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

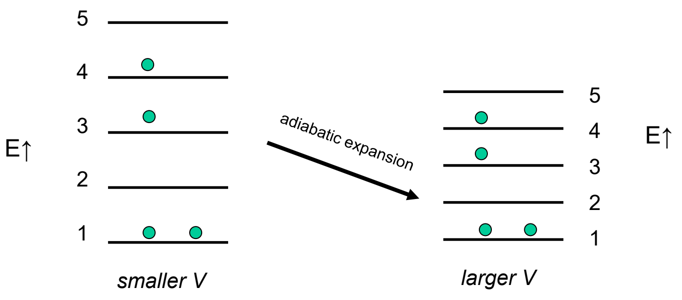
change in energy due to change in energy levels, e.g. 3D quantum p.i.b. change in energy levels as box changes size

work

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

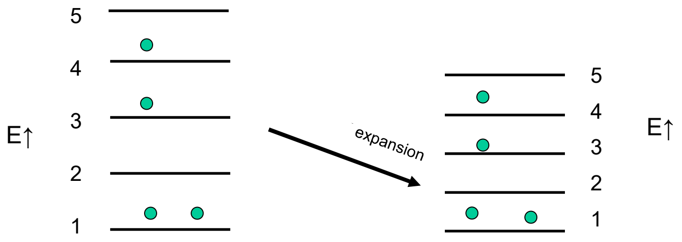
reversible adiabatic expansion ($\Delta U_{sys} < 0$; $q_{rev} = 0$)



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 (   )

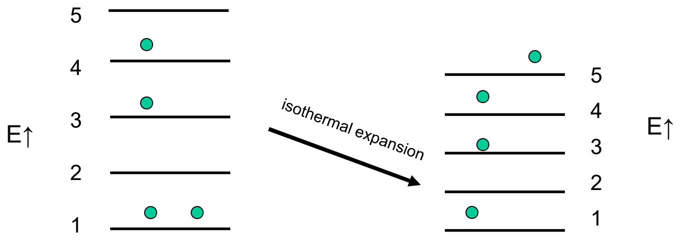
reversible isothermal expansion ideal gas ($\Delta U_{sys} = 0$; $q_{rev} > 0$; $w = -q$)



to maintain $\Delta U = 0$, $\Delta T = 0$ need to put in heat

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

reversible isothermal expansion ideal gas ($\Delta U_{sys} = 0$; $q_{rev} > 0$; $w = -q$)



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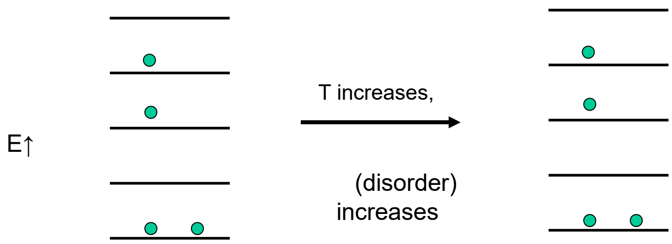
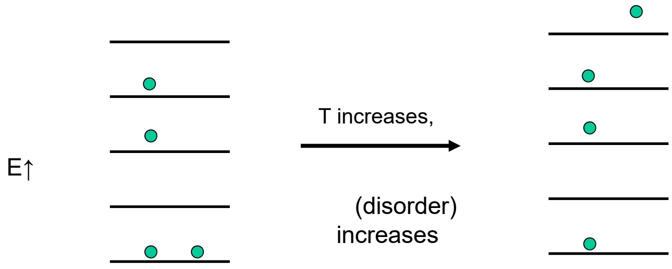
- To maintain $\Delta U = 0$, $q > 0$ and the level populations have to change and thus W changes
- $q_{rev} > 0$; INCREASE IN , INCREASE IN DISORDER

What happens to   as thermal energy raised?

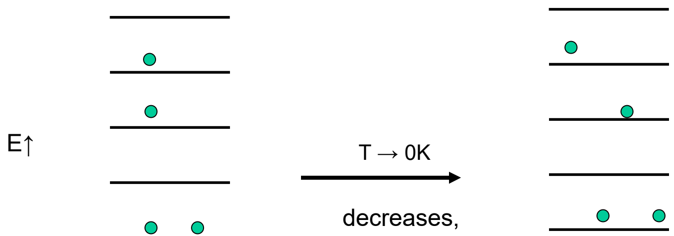


What happens to   as thermal energy raised?



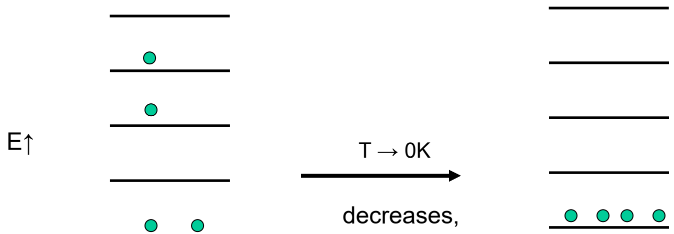
- $q_{rev} > 0$; INCREASE IN   , INCREASE IN DISORDER

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



decreases,
in fact → 1
only 'one way to distribute at 0ºK

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



decreases,
in fact → 1
only 'one way to distribute at 0ºK

Boltzmann and Entropy

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

disorder increases ⇔ entropy increases

take home messages

- Disorder, Y , did not change during an adiabatic reversible expansion (q_{rev} =0)
- Disorder, Y , increased in isothermal reversible expansion (q_{rev} >0)
- Disorder, Y , increased with T increase (q>0)
- Disorder, Y , decreased with T decrease (q<0)
- As T → 0, Y →1

take home messages

A sample problem†:

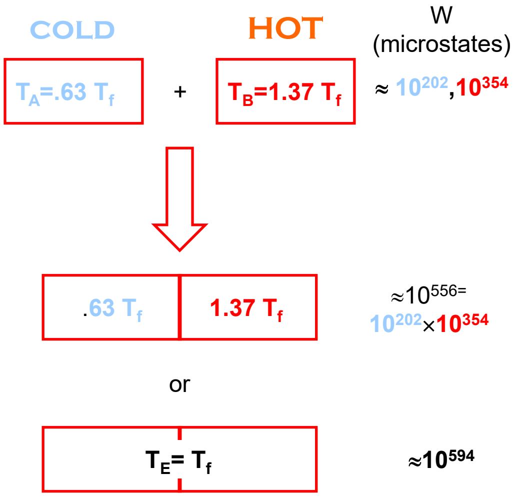
Two bodies 500 molecules each
one at T_A=.63 × T_f,
the other at T_B=1.37 × T_f

bring into thermal contact

STAY COLD-HOT ??

or

☑ EQUILIBRIUM ??



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

take home message continued†

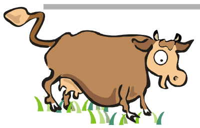
The equilibrium macrostate is $\frac{10^{594}}{10^{556}}=10^{38}$ time more likely than the hot-cold state, even though every $(\text{microstate})_{\text{hot-cold}}$ has the same likelihood as a $(\text{microstate})_{\text{equilibrium}}$.

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 $(\text{microstate})_{\text{hot-cold}}$ 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

q_{rev} vs q_{irrev} : some examples from 1^{st} Law Calculations

from lectures 2-3-4

Process **10 atm → 1atm** **300K → T_f**	q_{rev}	q_{irrev}	$(T_f)_{rev}$	$(T_f)_{irrev}$
isothermal				
adiabatic				

q_{rev} vs q_{irrev} : some examples from 1^{st} Law Calculations

from lectures 2-3-4

Process **10 atm → 1atm** **300K → T_f**	q_{rev}	q_{irrev}	$(T_f)_{rev}$	$(T_f)_{irrev}$
isothermal	**5743J**	**2244 J**	300 K	300K
adiabatic	0	0 192K→119K ($C_p\Delta T$) **-1517J**	119K	192K ↓ 119K

for these expansions:
same initial and final states

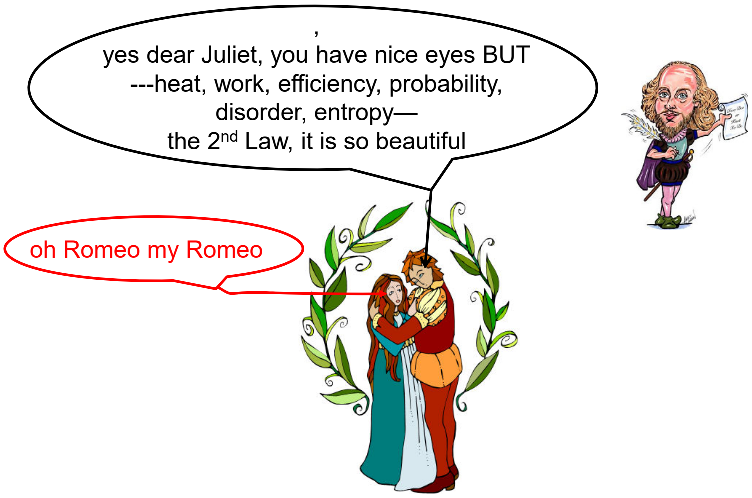
$q_{rev} > q_{irrev}$

lecture 8 objectives:

When and Why do things happen ??

(an overview of 2nd Law)

- ✓ exothermicity ($q<0$) often accompanies spontaneous processes, but not all; not a requirement
- ✓ can't find a repeatable (cyclic) process that fully converts heat (disorder) to work (order)
- ✓ order and disorder in terms of microstates
- ✓ the Universe meanders through the fields and meadows of microstates !!



End Of Introductory Lecture on
Second Law and Disorder

بنی آدم اعضای یک پیکرند
که در آفرینش ز یک گوهرند
چو عضوی بدرد آورد روزگار
دگر عضوها را نماند قرار

literal translation
(thank you 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.

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

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

Persian Poet 13th Century

French Thermodyamicist
Namesake 19th century

Saadi and Sadi