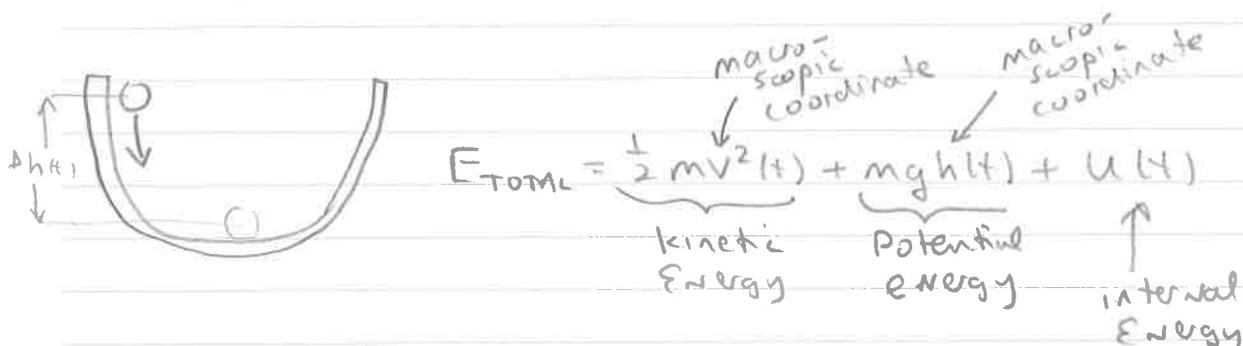


Second Law of Thermodynamics

(75)

The 1st law of Thermodynamics tells us that energy is conserved (i.e., it cannot be created nor destroyed). If we do proper bookkeeping of energy, we can account for all of it at all times.

Let's go back to our earlier example of the marble in a bowl.



We know from experience that the work (energy) I put into the marble by lifting it Δh_{max} and releasing will move back & forth between kinetic & potential energy involving the macroscopic coordinates, but eventually all that energy gets dissipated into the internal energy of both marble and bowl. The marble will stop rolling, and the temperature of marble & bowl is slightly higher.

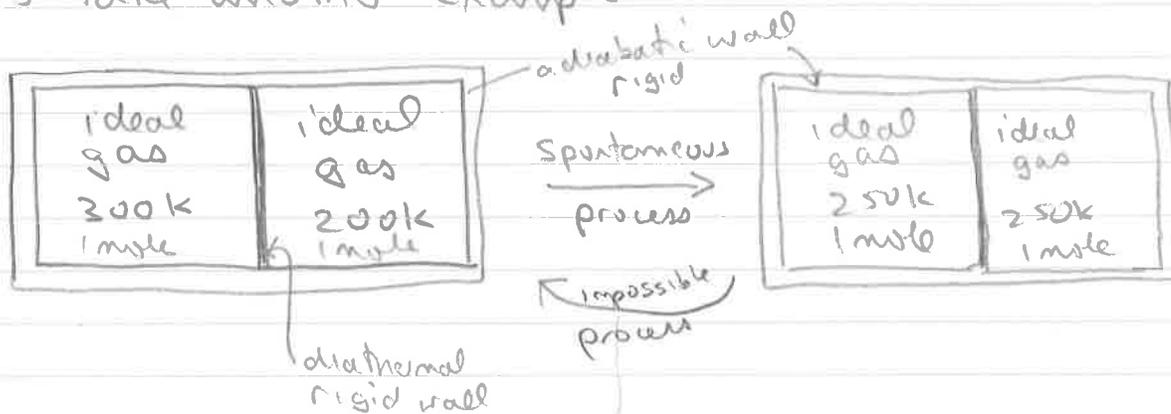
On the other hand, according to 1st law, it would be perfectly fine if the marble continued rolling forever, and there was no energy dissipated into the internal energy of marble & bowl. This would NOT violate the 1st law at all.

The 1st law doesn't require energy to be dissipated.

Even worse, The 1st law doesn't even forbid the internal energy of the marble and bowl to be transferred into the potential and kinetic energy involving the macroscopic coordinates.

Imagine the marble rolling higher and higher as the marble and bowl get colder!
Even this would be perfectly acceptable according to the 1st law, as long as the total energy remains constant.

Let's take another example

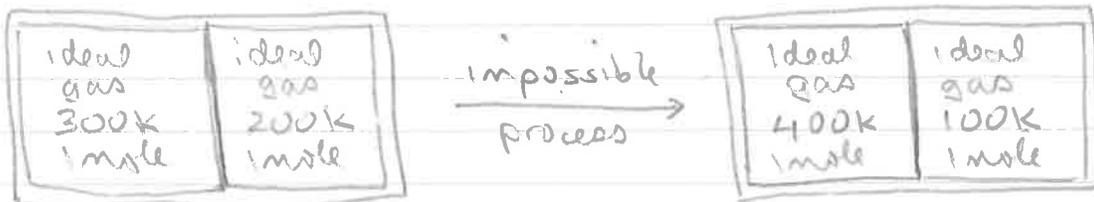


$$U_{\text{TOTAL}} = \frac{3}{2}R(300K) + \frac{3}{2}R(200K)$$

$$= 2 \times \frac{3}{2}R(250K)$$

$$U_{\text{TOTAL}} = \frac{3}{2}R(250K) + \frac{3}{2}R(250K)$$

$$= 2 \times \frac{3}{2}R(250K)$$



$$U_{\text{TOTAL}} = \frac{3}{2}R(300K) + \frac{3}{2}R(200K)$$

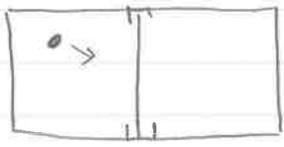
$$= 2 \times \frac{3}{2}R(250K)$$

$$U_{\text{TOTAL}} = \frac{3}{2}R(400K) + \frac{3}{2}R(100K)$$

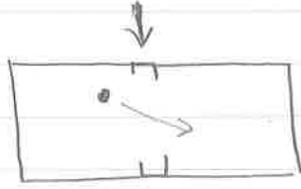
$$= 2 \times \frac{3}{2}R(250K)$$

As far as 1st law is concerned, both processes are valid, that is, energy is constant (conserved).

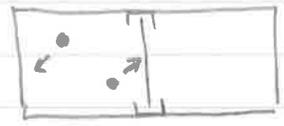
Imagine a box containing a single atom on the left side separated from a vacuum on the right by a Partition.



Before we remove the partition the probability of finding the atom on the left half is 100% or 1



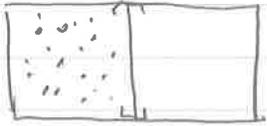
If we remove the partition, then the atom can move freely between both sides, and the probability of finding the atom on the left half is 50% or $\frac{1}{2}$



If we do the same with 2 atoms, then as before, the probability of finding both on the left half is 100% or 1

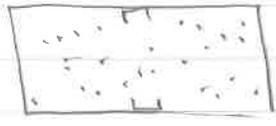


After removing the partition, the probability of finding both on the left half is 25% or $(\frac{1}{2})(\frac{1}{2}) = \frac{1}{4}$



Now, imagine N atoms on the left. Before removing the partition the probability that all N atoms are on the left half is 100%

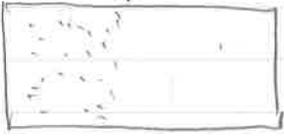
Spontaneous process



After removing the partition, the probability that all N atoms are on the left half is

$(\frac{1}{2})^N$
If $N = 6 \times 10^{23}$

Impossible process



Then
 $(\frac{1}{2})^N \approx 10^{-2 \times 10^{23}}$

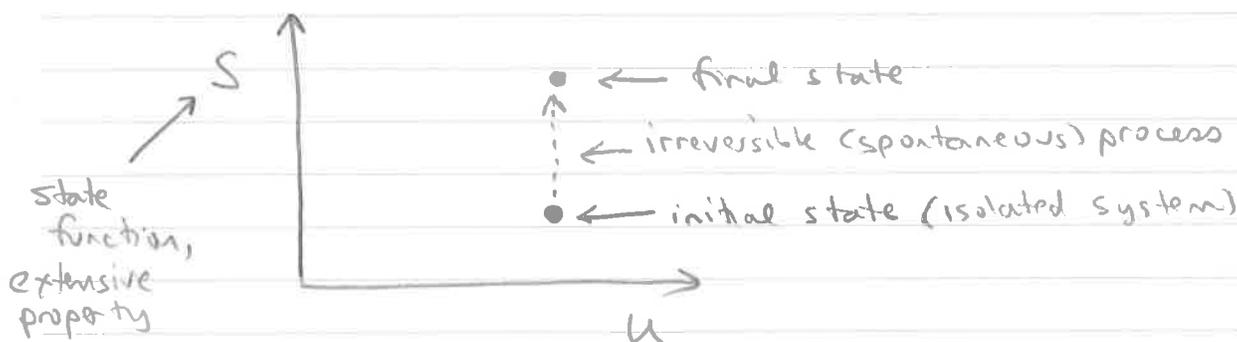
allowed according to 1st law of thermodynamics, but probability of occurring is too low to ever happen.

How do we predict the new equilibrium state?

Clearly, the 1st law isn't enough.

2nd Law of Thermodynamics proposes the existence of a function, S , called Entropy, which increases monotonically until it reaches its maximum value at the state of thermodynamic equilibrium.

$$\text{irreversible process} \rightarrow \frac{d_i S}{dt} \geq 0 \quad \text{isolated system} \quad \left(\begin{array}{l} \text{e.g.} \\ \text{the} \\ \text{universe?} \end{array} \right)$$



Entropy is a measure of how the energy of atoms & molecules is dispersed across its energetically accessible degrees of freedom.

So, the 2nd law tells us that energy will spread out into the maximum number of degrees of freedom consistent with the total energy.

Why would this happen? It's just a matter of probabilities.

For an ideal monatomic gas with N atoms the total energy would be given by The sum of kinetic energy of each atom

$$E_{\text{TOTAL}} = \sum_{i=1}^N \frac{P_{x_i}^2 + P_{y_i}^2 + P_{z_i}^2}{2m}$$

with each atom having its own unique position in the box

As you can imagine, there are many different ways to place all N atoms in the box and adjust their momenta so their kinetic energies add up to E_{TOTAL} .

Each unique way we do this is called a microstate

microstate - state with unique set of atomic position and momentum coordinates consistent with the total Energy.

In contrast, we also speak of macrostates as

macrostate - state with unique macroscopic coordinates, e.g. volume, consistent with the total Energy.

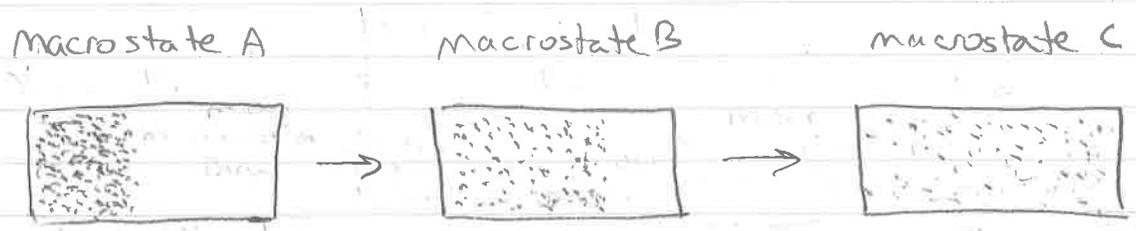
A macrostate can arise from any microstate that has that same macroscopic coordinates.

For a given macrostate, the system can be in any one of a very large number of possible microstates.

Some macrostates, however, can be realized with a much higher number of microstates, than other macrostates.

The more microstates associated with a given macrostate, then the more probable is that macrostate.

We just saw an example where two different macrostates with the same energy had different probabilities, that was simply because one had more microstates than the other.



System Volume $V = \frac{1}{2} V_{box}$ $V = \frac{2}{3} V_{box}$ $V = V_{box}$

Energy $E_A = E_B = E_C$

microstates $W(E_A) < W(E_B) < W(E_C)$

How do we count # microstates?

We integrate in a $6N$ -dimensional space with coordinates $x_i, y_i, z_i, p_x, p_y, p_z, i=1 \dots N$, only over values that correspond to total Energy $E \pm \frac{1}{2} \delta E$

a point in this space corresponds to a given microstate

microstates for a given macrostate

$$W(E) = \int_{E - \frac{1}{2} \delta E}^{E + \frac{1}{2} \delta E} \int d^3r_1 \dots d^3r_N d^3p_1 \dots d^3p_N$$

where $d^3r = dx dy dz$
 $d^3p = dp_x dp_y dp_z$

For an ideal gas of N atoms

$$W(E) = B V^N E^{3N/2}$$

microstates \nearrow \nearrow \nearrow \nwarrow total energy
 proportionality const. volume macrostate coordinate

At equilibrium the system will be in the macrostate with the largest number of microstates.

You might be tempted to use W as our entropy function, but this wouldn't work because we want our entropy function to be an extensive property.

When you double the size of system the entropy should double. For a monatomic gas we see that W increases by the power of the number of atoms.

To use W properly in our entropy definition we need to take its logarithm

Boltzmann
1872

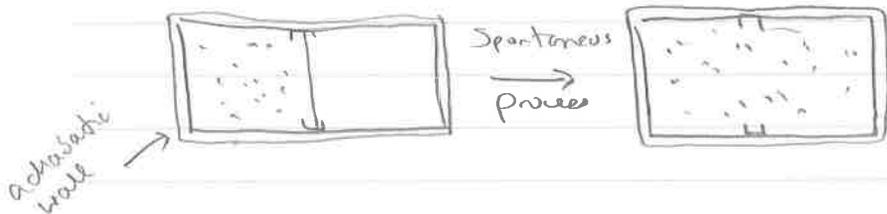
$$S = k_B \ln W$$

← # microstates
Boltzmann constant

Then $S = k_B \ln B(V E^{3/2})^N = k_B \ln B + N k_B \ln V E^{3/2}$

Entropy increases (nearly) with # atoms.
⇒ extensive.

We can now calculate the entropy change associated with removing the partition from the middle of the box.



ideal gas

$$\Delta U = 0$$

← recall gas expanding into vacuum. $w=0$

$$\Delta S = ?$$

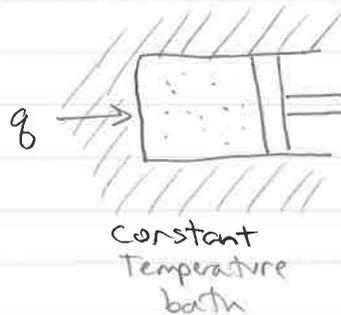
$$\Delta S = S_f - S_i = k_B \ln W_f - k_B \ln W_i$$

$$\Delta S = k_B \ln \frac{W_f}{W_i} = k_B \ln \frac{B V_f^N E^{3N/2}}{B V_i^N E^{3N/2}} = N k_B \ln \frac{V_f}{V_i}$$

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

For an ideal gas, The spontaneous expansion occurs with $\Delta U = 0$, and since $U \propto RT$, Then $\Delta T = 0$.

So, if we obtained the same volume expansion through isothermal reversible expansion we should have the same initial and final states. U and S are state functions



for this process we already saw that

$$q_{rev} = nRT \ln \frac{V_2}{V_1} \quad \leftarrow \text{look familiar?}$$

and we see that

$$\frac{q_{rev}}{T} = nR \ln \frac{V_2}{V_1} = \Delta S$$

from

$S = k_B \ln W$
↑
Boltzmann's definition of entropy
- 1872

we obtain $\Delta S = \frac{q_{rev}}{T}$
↑
Clausius' definition of entropy
1865

It was Clausius who "discovered" Entropy, 7 seven years before Boltzmann's proposed his definition.

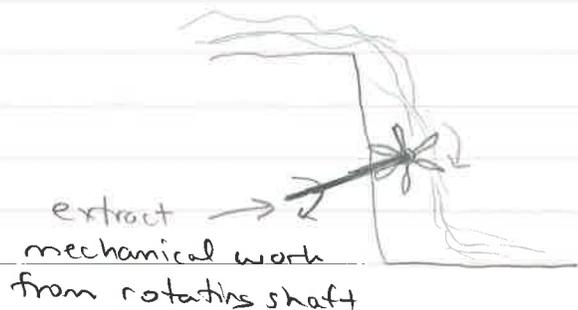
How did Clausius "discover" entropy?

- he was investigating the Thermodynamics of heat engines. In particular, he was interested in something called the Carnot Engine

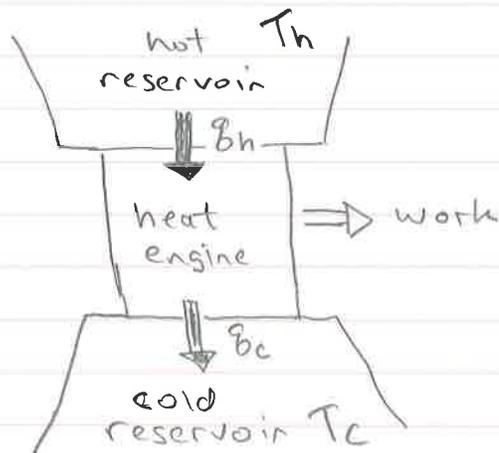
The Carnot Engine was based on The Carnot Cycle invented by Sadie Carnot in 1824

how does a heat engine work?

The process is analogous to how work can be extracted from a waterfall.



A heat engine exploits the flow of heat from a warm object to a cold object to extract mechanical work.

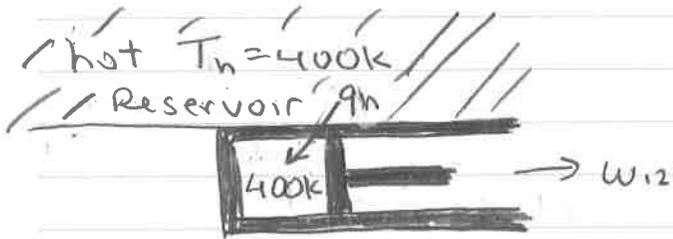


Just as the paddle wheel generates work as water flows over from a high altitude to a lower one, the heat engine generates work as heat flows through it from a hotter object to a colder object.

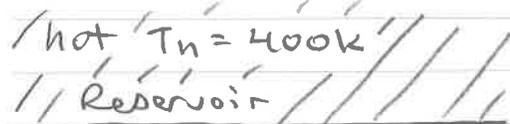
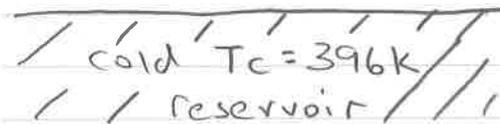
CARNOT ENGINES and CARNOT CYCLES

The Carnot cycle consists of

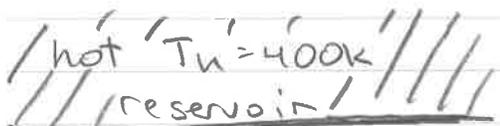
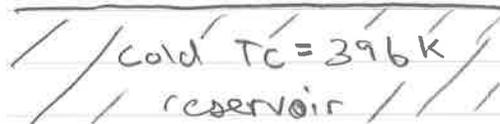
- (A) • isothermal expansion thru contact w/hot reservoir
- (B) • adiabatic expansion,
- (C) • isothermal compression thru contact w/cold reservoir
- (D) • adiabatic compression



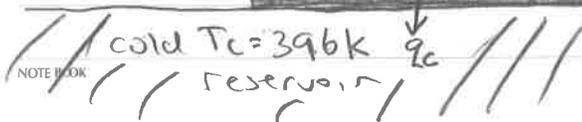
isothermal expansion
thru contact w/hot reservoir

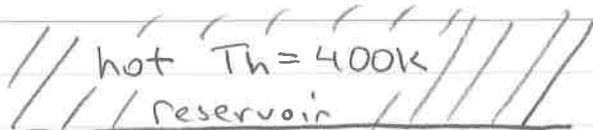


adiabatic expansion

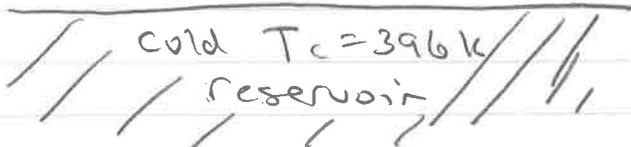


isothermal compression
thru contact w/cold reservoir





adiabatic
compression

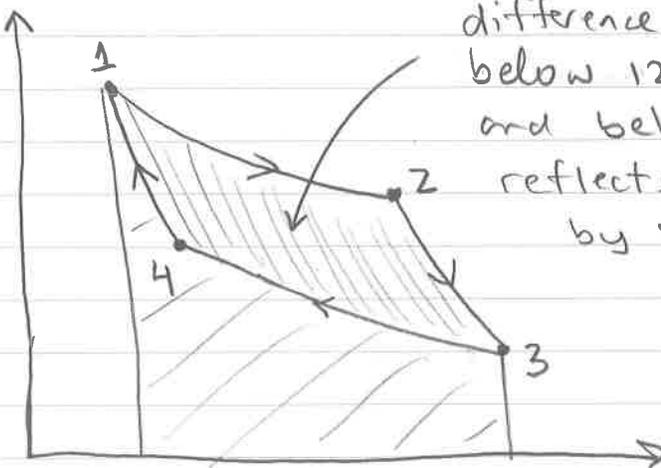


In one cycle, Thermal Energy is transferred as heat from hot reservoir through system to cold reservoir with some fraction of energy flowing out of system as work.

Work occurs in each step, but net work by system is negative

$W_{123} = 1 \rightarrow 2 \rightarrow 3$
system does
work on
surroundings

$W_{341} = 3 \rightarrow 4 \rightarrow 1$
surroundings do
work on system

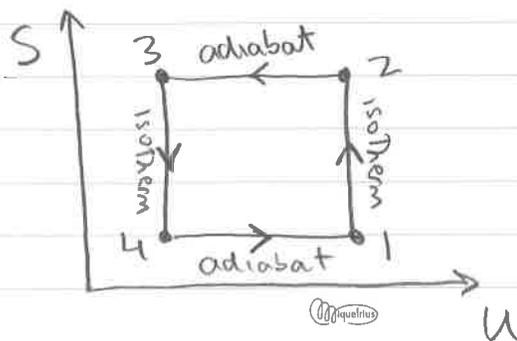


difference of areas
below 123 curve
and below 143 curve
reflects work done
by system

$$W_{net} = W_{123} - W_{341} = -nR(T_h - T_c) \ln \frac{V_2}{V_4}$$

Prove
this
at
home.

Can also
view Carnot
cycle in
S, U. diagram



Efficiency of a Carnot Engine

For one cycle of The Carnot engine we use The 1st law and obtain

$$q_h + q_c + w = 0 \quad \text{after one full engine cycle}$$

we define efficiency as fraction of heat input, q_h , that becomes work.

$$e = \frac{-w \leftarrow \text{net work}}{q_h \leftarrow \text{heat input}}$$

substitute $w = -e q_h$ into 1st law above

$$q_h + q_c - e q_h = 0$$

-or-

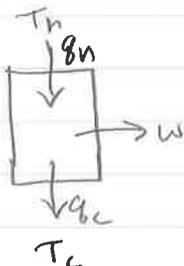
$$e = 1 + \frac{q_c}{q_h}$$

This can never be greater than 1, since $q_h > 0$, $q_c < 0$ and $|q_h| > |q_c|$

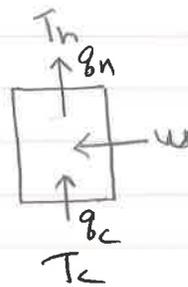
Reversible heat engines operating between same two temperature reservoirs must have the same efficiency, regardless of substance used in engine.

Why?

Imagine a Carnot engine with its cycle run in reverse: work is put into the Carnot engine and heat flows from cold reservoir to hot reservoir. Such a device is called a heat pump

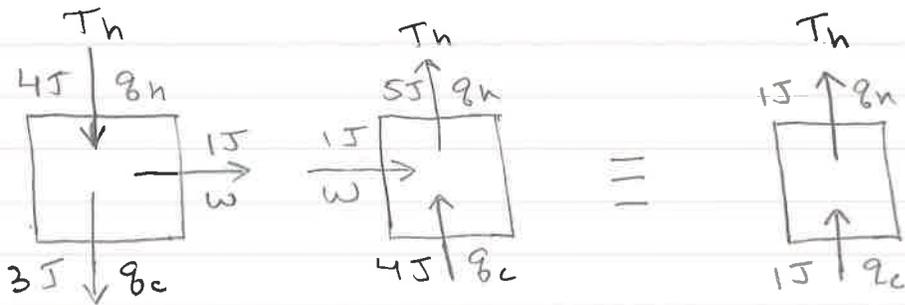


heat engine



heat pump

If a heat engine and a heat pump, each having different efficiencies, were coupled together and operated between the same two temperature reservoirs, you could make a heat pump that required no work to operate.



but this is impossible. heat will never flow spontaneously from cold to hot.

heat engine
 $\epsilon = 1/4$

heat pump
 $\epsilon = 1/5$

If efficiency doesn't depend on substance inside reversible engines then it must only depend on temperature of two reservoirs.

In that case, what is true for an ideal gas is true for all substances.

Let's use the ideal gas to learn how the Carnot engine efficiency depends on the reservoir temperatures.

For each step of Carnot cycle we can use ideal gas law

$$dw = -pdV = -\left(\frac{nRT}{V}\right)dV$$

combined with the 1st law

← ideal gas law

$$dU = dw + dq = -\left(\frac{nRT}{V}\right)dV + dq$$

also recall that $\frac{dU}{dT} = C_V$ so $dU = C_V dT$

$$\text{so } C_V dT = -\left(\frac{nRT}{V}\right)dV + dq$$

For the two adiabatic steps of The Carnot Cycle
we have $dq=0$

$$\text{so } C_v dT + \frac{nRT}{V} dV = 0$$

integrate for step 2 \rightarrow 3 of Carnot cycle

$$\int_{T_h}^{T_c} \frac{C_v dT}{T} + nR \int_{V_2}^{V_3} \frac{dV}{V} = 0$$

integrate for step 4 \rightarrow 1 of Carnot cycle

$$\int_{T_c}^{T_h} \frac{C_v dT}{T} + nR \int_{V_4}^{V_1} \frac{dV}{V} = 0$$

Same integral
except limits
are reversed $\Rightarrow \int_a^b f(x) dx = - \int_b^a f(x) dx$

so, if we add both expressions for the 2 Carnot cycle steps we get

$$nR \left[\int_{V_2}^{V_3} \frac{dV}{V} + \int_{V_4}^{V_1} \frac{dV}{V} \right] = 0$$

which becomes

$$\ln \frac{V_3}{V_2} + \ln \frac{V_1}{V_4} = 0 \quad \text{or} \quad \boxed{\ln \left(\frac{V_3}{V_2} \right) = - \ln \left(\frac{V_4}{V_1} \right)}$$

we'll use this later.

For the two isothermal steps of Carnot Cycle

we have $dT = 0$

and for an ideal gas $U \propto RT$, so if $dT = 0$

Then $dU = 0$

1st law requires $dq = -dw$

integrate step 1 \rightarrow 2

$$q_h = -\int dw = nRT_h \int_{V_1}^{V_2} \frac{dV}{V} = nRT_h \ln \frac{V_2}{V_1}$$

integrate step 3 \rightarrow 4

$$q_c = -\int dw = nRT_c \int_{V_3}^{V_4} \frac{dV}{V} = nRT_c \ln \frac{V_4}{V_3}$$

take ratio of q_c/q_h

$$\frac{q_c}{q_h} = \frac{T_c \ln(V_4/V_3)}{T_h \ln(V_2/V_1)} = -\frac{T_c}{T_h}$$

= -1 (previous page)

so

$$\epsilon = 1 - \frac{T_c}{T_h}$$

Carnot Engine Efficiency

assumes reversible processes. lower ϵ results w/ irreversible steps.

The efficiency cannot equal nor exceed 1,

if $T_c = 0\text{K}$, then $\epsilon = 1$, but 3rd law says 0K is unattainable

if $T_h = \infty\text{K}$, then $\epsilon = 1$, but molecular speeds can only approach speed of light, c .

absolute hot or

Planck Temperature

$m_p \equiv$ Planck mass

$$T_p = \frac{m_p c^2}{k_B} \approx 10^{32}\text{K}$$

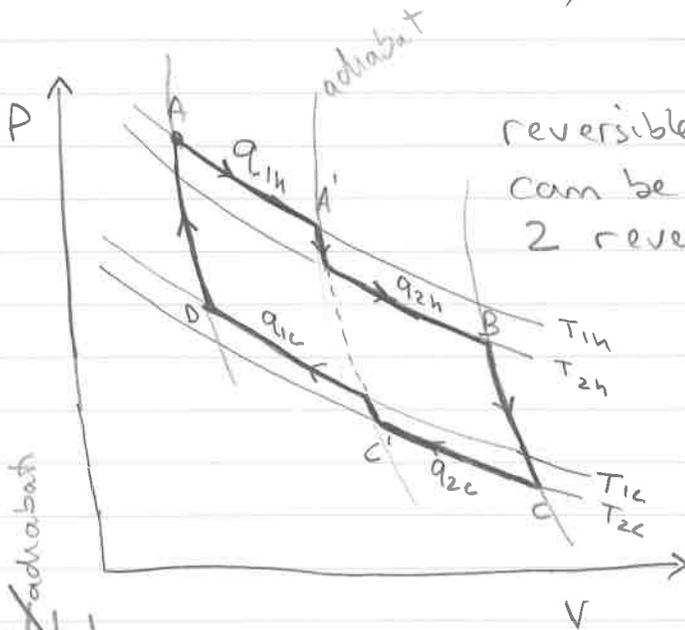
We also learned that

$$\frac{q_h^{rev}}{T_h} = - \frac{q_c^{rev}}{T_c} \quad \text{OR} \quad \boxed{\frac{q_h^{rev}}{T_h} + \frac{q_c^{rev}}{T_c} = 0}$$

Clausius saw
this and thought
...

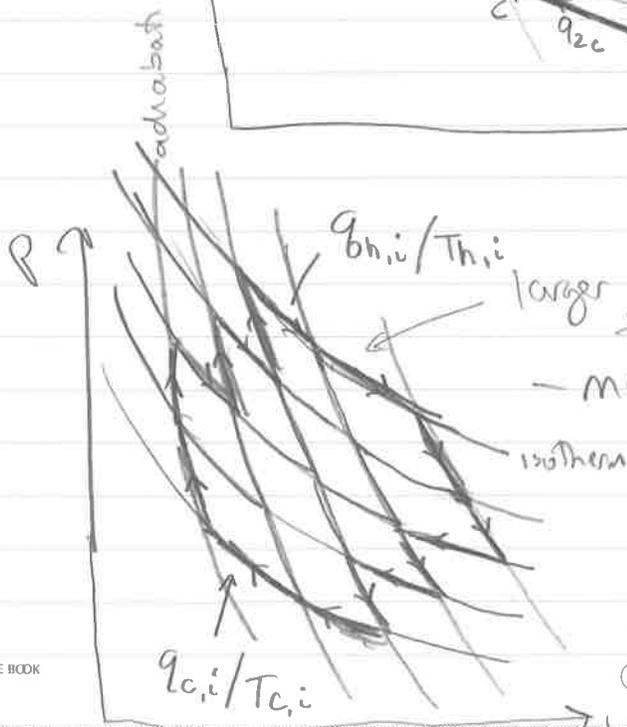
In one Carnot cycle the
reversible heat transfer divided by
temperature will always add to zero.

I can describe any reversible cyclic process
as a series of Carnot cycles,



reversible cycle AA'BCC'DA
can be thought as sum of
2 reversible cycles

$$\frac{q_{1h}}{T_{1h}} + \frac{q_{2h}}{T_{2h}} + \frac{q_{2c}}{T_{2c}} + \frac{q_{1c}}{T_{1c}} = 0$$



larger reversible cycle is equivalent
to many smaller Carnot cycles
- many Carnot cycles infinitesimally
small

$$\sum_i \frac{dq_i^{rev}}{T_i} = 0$$

over full cycle

$$\oint \frac{dq^{rev}}{T} = 0$$

So Clausius realized that for any reversible cyclic process

$$\oint \frac{dq^{REV}}{T} = 0$$

integrate over cyclic path

behaves like a state function. ENTROPY

So, Clausius discovered and named this state function, calling it ENTROPY ↓ Greek for "transformation"

$$dS = \frac{dq^{REV}}{T}$$

in 1865

S = k_B ln W
Boltzmann 1872

While Boltzmann's definition $S = k_B \ln W$ has the advantage of being conceptually easier to understand, Clausius' definition is much more practical definition for measuring entropy.

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

We've already seen the example of isothermal expansion/compression of a gas

where $q_{rev} = nRT \ln \frac{V_2}{V_1}$ } Reversible,
and $\Delta S = nR \ln \frac{V_2}{V_1}$ } isothermal

Phase Transitions

e.g. fusion - solid melts into the liquid phase
 vaporization - liquid vaporizes into the gas phase

These processes occur reversibly at the phase transition temperature, e.g. T_f or T_b .

$$\Delta_{\text{fus}} S = \frac{q_{\text{rev}}}{T_f} = \frac{\Delta H_{\text{fus}}}{T_f}$$

and

$$\Delta_{\text{vap}} S = \frac{q_{\text{rev}}}{T_b} = \frac{\Delta H_{\text{vap}}}{T_b}$$

constant pressure processes

The entropy increases when a solid melts, or a liquid vaporizes, and decreases when the phase transition is in the opposite direction.
 → This should make sense with Boltzmann's interpretation.

Transition	T_b / K	$\Delta_{\text{vap}} H_m / \text{kJ/mole}$	$\Delta_{\text{vap}} S_m / \text{J/kmole}$
$\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$	331.8	30.0	90.4
$\text{C}_6\text{H}_{12}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}(\text{g})$	341.7	28.9	84.6
$\text{CH}_4(\text{l}) \rightarrow \text{CH}_4(\text{g})$	109.	9.2	84.4
$\text{C}_2\text{H}_5\text{OC}_2\text{H}_5(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OC}_2\text{H}_5(\text{g})$	307.6	26.0	84.5
$\text{H}_2\text{O}(\text{l}) \rightarrow \text{H}_2\text{O}(\text{g})$	373	40.79	109.4
$\text{C}_2\text{H}_5\text{OH}(\text{l}) \rightarrow \text{C}_2\text{H}_5\text{OH}(\text{g})$	351.3	29.3	111.9

Most liquids have similar molar entropies of vaporization

$$\Delta_{\text{vap}} S = 88 \pm 5 \text{ J/k-mole} \quad \text{Trouton's Rule}$$

Notice that water & ethanol have higher entropy changes upon vaporization. Why is this?

- H-bonding in liquid state makes liquid structure more ordered (fewer microstates).

ENTROPY Change due to heating

$$dS = \frac{dq_{rev}}{T} \quad \text{or} \quad \Delta S = \int_{T_1}^{T_2} \frac{dq_{rev}}{T}$$

- at constant pressure (isobaric) $dH = dq$

$$\Delta S = \int_{T_1}^{T_2} \frac{dH}{T} \quad \text{and since } dH = C_p dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT = \int_{T_1}^{T_2} C_p d \ln T$$

recall

$$d \ln x = \frac{1}{x} dx$$

$$\Delta S = C_p \ln \frac{T_2}{T_1}$$

assuming C_p is
temperature independent
(valid over certain temp. ranges)

- at constant volume (isochoric)

$$dq_{rev} = C_v dT$$

$$\Delta S = \int_{T_1}^{T_2} \frac{C_v}{T} dT = \int_{T_1}^{T_2} C_v d \ln T = C_v \ln \frac{T_2}{T_1}$$

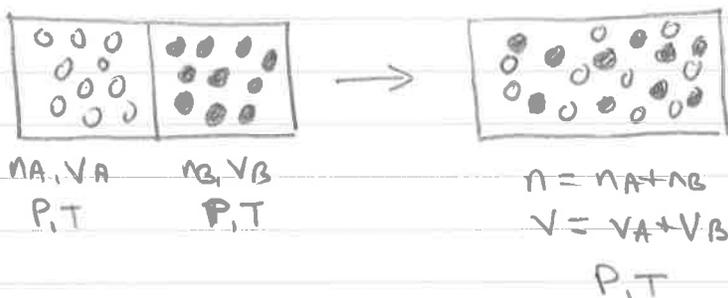
const. vol.
assuming
 C_v is T
independent
over integral
range

Entropy always increases with temperature.

How do we explain this in terms of Boltzmann's definition $S = k_B \ln W$?

Entropy change due to mixing

Ideal Gases



for gas A $\Delta S_A = n_A R \ln \frac{V_A + V_B}{V_A}$

for gas B $\Delta S_B = n_B R \ln \frac{V_A + V_B}{V_B}$

since $V = n \left(\frac{RT}{P} \right)$

$\Delta_{mix} S = n_A R \ln \frac{n_A + n_B}{n_A} + n_B R \ln \frac{n_A + n_B}{n_B}$

change signs

$\Delta_{mix} S = -n_A R \ln \frac{n_A}{n_A + n_B} - n_B R \ln \frac{n_B}{n_A + n_B}$

$x_A = \frac{n_A}{n_A + n_B}$

$x_B = \frac{n_B}{n_A + n_B}$ mole fractions

$\Delta_{mix} S = -R [n_A \ln x_A + n_B \ln x_B]$

3rd Law of Thermodynamics ~ 1906-1912 by NERNST

With state functions like Energy, and particularly enthalpy, we found it convenient to define reference states for substances, e.g. The standard enthalpy of formation, $\Delta_f H^\circ$, of a substance.

Since entropy is a state function, the same would also be useful.

Unlike enthalpy, where the reference state was arbitrarily chosen, with entropy the reference state choice became obvious once it was realized that...

$$\Delta S = \frac{q}{T}$$

↑
 $\Delta S \rightarrow 0$
at
 $T \rightarrow 0$

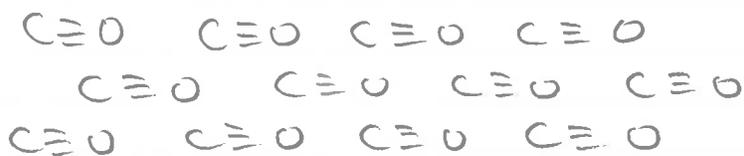
Nernst Heat Theorem [In any thermodynamic process involving only pure phases in their equilibrium state, the entropy change, ΔS , approaches zero as T approaches 0 K.]

[Thus, we define that the absolute entropy of any pure substance (element or compd) in its equilibrium state approaches zero at the absolute zero of temperature.]

3rd law $S = 0$ for pure substance
 $\lim_{T \rightarrow 0K}$ at equilibrium

In practice, equilibrium may be difficult to achieve at low temperatures where molecular motion is quite slow. So, there may be residual entropy due to positional or orientational disorder frozen in.

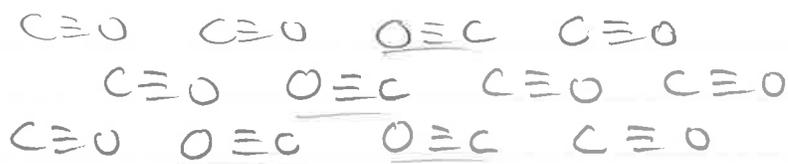
For example, carbon monoxide has an electric dipole moment, and if it was truly at equilibrium at $T=0\text{K}$ all the CO molecules would be ordered like...



$$W=1$$

← only 1 microstate for this macrostate

however, in practice there are always some that are flipped...



If you used Boltzmann's approach and counted the number of microstates, then it would be

$$W = 2^N \leftarrow \begin{array}{l} \# \text{ CO molecules} \\ \# \text{ orientations} \end{array}$$

Simple approach

So, the residual entropy, assuming different orientations are energetically identical would be

$$\begin{aligned} S &= k_B \ln 2^{N_A} = N_A k_B \ln 2 \\ &= R \ln 2 \end{aligned}$$

$$S = (8.314 \text{ J/K-mole}) \ln 2 = 5.8 \text{ J/K-mole}$$

If you took the energy of the electric dipole interactions into account, (more challenging calc) you get

$$S = 4.2 \text{ J/K-mole}$$

Using 3rd law The entropy of a substance in any state (i.e. arbitrary P, T, V) can be calculated by adding up (i.e. integrating) the changes in Entropy from T=0K up to the desired state, through reversible processes.

$$\Delta S = S_0 + \int_0^T C_p d \ln T + \sum \frac{\Delta_{\text{trans}} H}{T_{\text{trans}}}$$

Residual Entropy
Entropy change due to heating.
Entropy change due to phase transitions

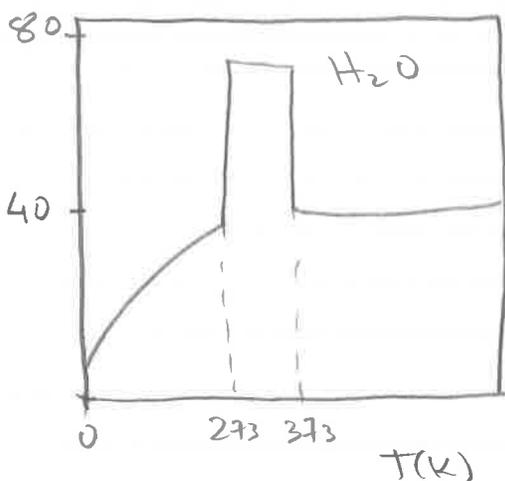
This is more easily done by integrating a plot of the heat capacity as a function of Temperature,

$C_{p,m}$ -vs- T

gives

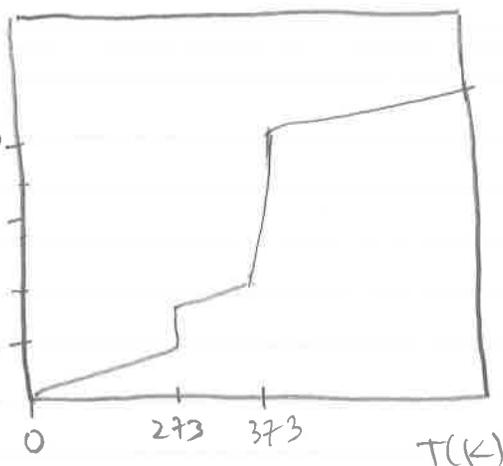
S_m -vs- T

Heat capacity
 $C_{p,m}$
J/K-mole



Entropy

S_m
J/K-mole



at low Temperatures ≤ 30 K measurements of heat capacities can be difficult so statistical mechanics is used to approximate part of the integral

Debye Theory: $C_{p,m} = aT^3$



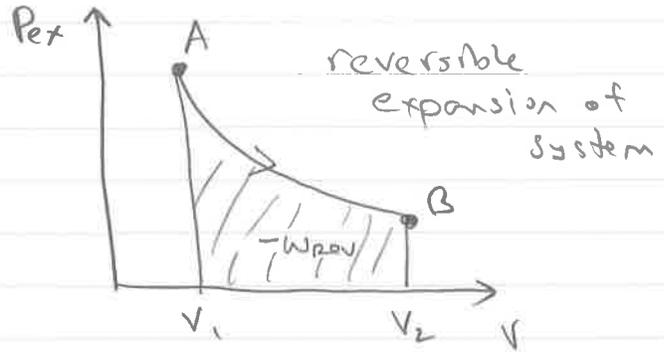
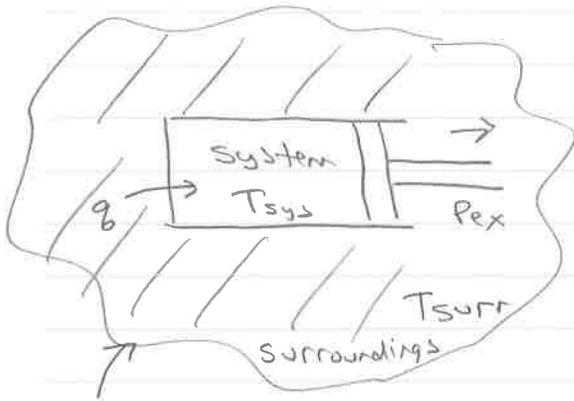
Just like Hess' law, we can calculate the entropy change in a chemical reaction as we would for any state function



$$\Delta_r S^\circ = \left[c S_m^\circ(C) + d S_m^\circ(D) \right] \text{ products} \\ - \left[a S_m^\circ(A) + b S_m^\circ(B) \right] \text{ reactants}$$

$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surrounding}$$

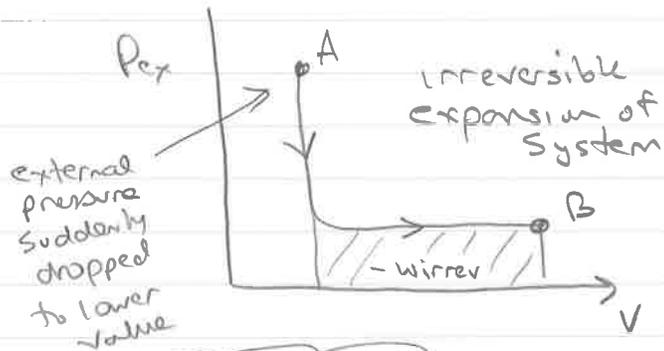
Thermodynamic universe \equiv system + surroundings
(in contact w/ system)



Surroundings will be an infinitely large reservoir, so it will supply or receive energy from system and always be in equilibrium

$$\text{so } \Delta S_{surr} = \frac{q}{T_{surr}}$$

So heat is always transferred reversibly to or from the surroundings.



$$|W_{irrev}| < |W_{rev}|$$

Since initial and final states are the same, the change in energy must be the same for reversible & irreversible expansion.

$$\Delta U_{sys} = \underbrace{W_{irrev}}_{(-)} + \underbrace{q_{irrev}}_{(+)} = \underbrace{W_{rev}}_{(-)} + \underbrace{q_{rev}}_{(+)}$$

if $|W_{irrev}| < |W_{rev}|$ then it must also be true

that $|q_{irrev}| < |q_{rev}|$ if ΔU_{sys} is the same for both reversible and irreversible processes.

Taking signs into account we have

less heat is absorbed by system in irreversible process.

$$q_{rev} > q_{irrev}$$

Divide both sides by T , The temperature at which heat is transferred...

$$\frac{dq_{rev}}{T} > \frac{dq_{irrev}}{T}$$

$$\Delta S_{sys} > \frac{dq_{irrev}}{T}$$

For irreversible process the entropy change is always greater than q_{irrev}/T

So for any process we can write

$$\Delta S_{sys} \geq q/T$$

where equality applies only in the reversible case.

if you don't like inequalities, you can think of this as...

$$\Delta S_{sys} = \frac{q}{T} + \Delta S_{irr}$$

state function, so this difference is same for reversible & irreversible processes.

entropy transferred from surroundings

entropy produced by irreversible processes within the system.

Isolated System, i.e. no work, heat, & matter transfer, then any spontaneous (irreversible) process would have...

$$\Delta U_{sys} = 0 \text{ and } \Delta S_{sys} > 0$$

isolated system spontaneous process

The Thermodynamic Universe \equiv system + surroundings, would by definition be an "isolated system". Therefore we conclude

$$\Delta S_{universe} = 0 \quad \text{for reversible process}$$

$$\Delta S_{universe} > 0 \quad \text{for irreversible (spontaneous) process}$$

$$\Delta S_{universe} < 0 \quad \text{is impossible}$$

Closed System, no matter transfer, but work & heat transfer can occur.

for reversible process, only expansion work, we have

$$dU = dq + dw = Tds - pdv$$

↑
state function

↑ ↑ ↑
state functions

closed system,
reversible process
(only expansion work)

if dU is expressed entirely in terms of state functions, then

$$dU = Tds - pdv$$

- or -

$$\Delta U = T\Delta S - p\Delta V$$

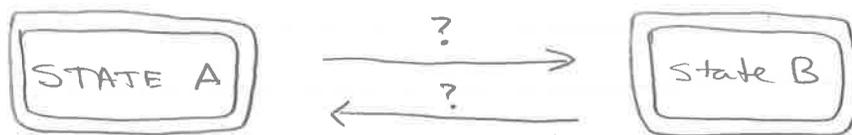
closed system,
any process
(only expansion work)

provide the temperature and pressure of initial and final states are uniform throughout system.

Spontaneous Processes

Consider the following case:

Isolated system ($q=0, w=0$) - no contact w/surroundings



which direction
will it go
spontaneously

Which single Thermodynamic state function, known for both states A & B, will answer this question?

$n, P, V, T, U,$ or S ?

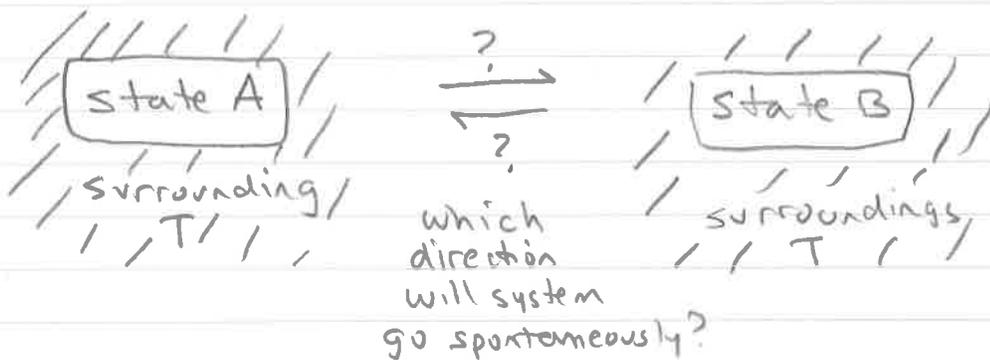
In this case S . if $\Delta S = S_B - S_A > 0$ Then
 $A \rightarrow B$ is
The spontaneous
direction

if $\Delta S = S_B - S_A < 0$ Then
 $B \rightarrow A$ is
The spontaneous
direction

if $\Delta S = S_B - S_A = 0$ Then process is
Reversible

remember this is
isolated
system
where $q=0$
 $w=0$

Now consider another case, isothermal, isochoric
 $\Delta T = 0$ $\Delta V = 0$



In This case, we need to know the total entropy change of system and surroundings, i.e., $\Delta S_{universe}$, since only process with

$\Delta S_{universe} > 0$ will be spontaneous,

So $dS_{univ} = dS_{sys} + dS_{surr} > 0$

and since system and surroundings are in thermal equilibrium,

$T_{sys} = T_{surr} = T$

then $dS_{univ} = dS_{sys} + dq_{surr}/T > 0$

or $dS_{univ} = dS_{sys} - dq_{sys}/T > 0$

and since $\Delta V = 0$ then $du = dq + d\cancel{w}$
 we get

$dS_{univ} = dS_{sys} - \frac{dU_{sys}}{T} > 0$

multiply both sides by T

$TdS_{univ} = TdS_{sys} - dU_{sys} > 0$

condition for determining if process is spontaneous in isothermal, isochoric conditions
 $\Delta T = \Delta V = 0$

We define a new state function

$F \equiv U - TS$ Helmholtz Free Energy

so under isothermal, isochoric condition

$$\boxed{dF = dU - T ds}$$

change in F during $\Delta T = \Delta V = 0$ process.

- or -

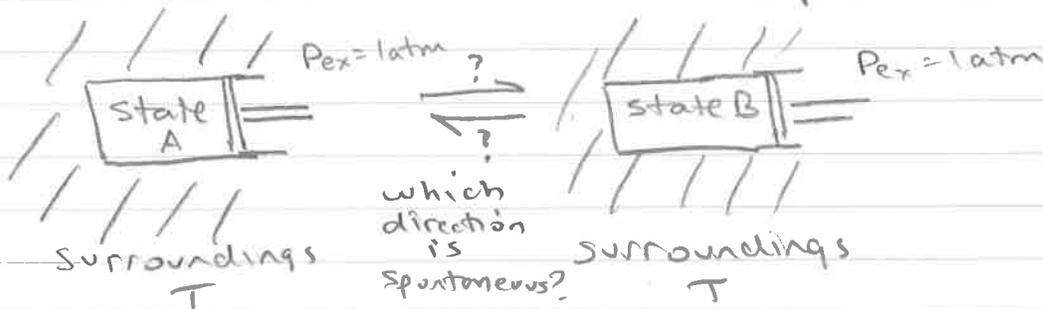
$$\Delta F = \Delta U - T \Delta S$$

Since F is a state function (only depends on state functions), then this expression is true for both reversible & irreversible processes.

- if $\Delta F < 0$ then $A \rightarrow B$ is spontaneous direction
- if $\Delta F > 0$ then $B \rightarrow A$ is spontaneous direction
- if $\Delta F = 0$ then process is reversible,



Let's consider another case: isobaric, isothermal
 $\Delta p = 0$ $\Delta T = 0$



apply same approach

$$dS_{univ} = dS_{sys} + dS_{surr} \geq 0$$

system & surroundings in thermal equilibrium so $T_{surr} = T_{sys} = T$

$$dS_{univ} = dS_{sys} + \frac{dq_{surr}}{T} \geq 0$$

or

$$dS_{univ} = dS_{sys} - \frac{dq_{sys}}{T} \geq 0$$

at constant p we define $dH = dq_p$

so

$$dS_{univ} = dS_{sys} - \frac{dH_{sys}}{T} > 0$$

multiply by T

$$TdS_{univ} = TdS_{sys} - dH_{sys} > 0$$

condition for spontaneous process in isothermal isobaric case

So, we define new state function

$$G = H - TS \quad \text{Gibbs Free Energy}$$

Under isothermal, isobaric process

$$dG = dH - Tds \quad \text{Gibbs Free Energy}$$

Since G is a state function (only depends on state functions), then this expression is true for both reversible & irreversible processes.

if $\Delta G < 0$ Then $A \rightarrow B$ is spontaneous direction

if $\Delta G > 0$ Then $B \rightarrow A$ is spontaneous direction

if $\Delta G = 0$ Then process is reversible

Since many chemical reactions of interest occur at constant pressure in contact with surroundings at constant temperature, then ΔG for a chemical reaction is a thermodynamic state function of great interests to chemists.

Consider the process $A \rightarrow B$

$$\Delta H_{\text{sys}} - T \Delta S_{\text{sys}} = \Delta G_{\text{sys}}$$

\oplus endothermic	\ominus entropy decrease	\oplus Reaction spontaneous in $B \rightarrow A$ direction at all temperatures
\ominus exothermic	\oplus entropy increase	\ominus Reaction spontaneous in $A \rightarrow B$ direction at all temperatures
\oplus endothermic	\oplus entropy increase	\ominus high T, $\Delta G \rightarrow \ominus$ \oplus low T, $\Delta G \rightarrow \oplus$
\ominus exothermic	\ominus entropy decrease	\oplus high T, $\Delta G \rightarrow \oplus$ \ominus low T, $\Delta G \rightarrow \ominus$

Consider the crystallization of an aqueous solution of sodium acetate.



at $T = 350\text{K}$ $\Delta H = -21.8 \text{ kJ/mol}$
 $\Delta S = -65.75 \text{ J/mol-K}$

so $\Delta G = -21.8 \times 10^3 \text{ J/mol} - (350\text{K})(-65.75 \text{ J/mol-K})$
 $= \underline{1,214 \text{ J/mol}}$
 \nwarrow positive, so no crystallization occurs.

at $T = 305\text{K}$ $\Delta H = -15.24 \text{ kJ/mol}$
 $\Delta S = -45.32 \text{ J/mol-K}$

$\Delta G = -15.24 \times 10^3 \text{ J/mol} - (305\text{K})(-45.32 \text{ J/mol-K})$
 $= \underline{-1,417 \text{ J/mole}}$
 \nwarrow negative, crystallizes spontaneously

Armed with tables of standard molar enthalpies, entropies, and heat capacities, you can determine ΔG for any reaction, since it is a state function.



$$\Delta_r G^\circ = [c \Delta_f G_m^\circ(C) + d \Delta_f G_m^\circ(D)] \leftarrow \text{Products}$$
$$- [a \Delta_f G_m^\circ(A) + b \Delta_f G_m^\circ(B)] \leftarrow \text{reactants}$$

where $\Delta_f G_m^\circ = \Delta_f H_m^\circ - T \Delta S_m^\circ$

\uparrow
enthalpy of formation

\nwarrow Calculated from absolute entropies of substances.

Remember, the absolute entropy of an element is NOT zero in its standard state.

Remember enthalpies can be adjusted to different T

$$\int_{H_1}^{H_2} dH = \int_{T_1}^{T_2} C_p dT$$

and likewise entropies can be adjusted

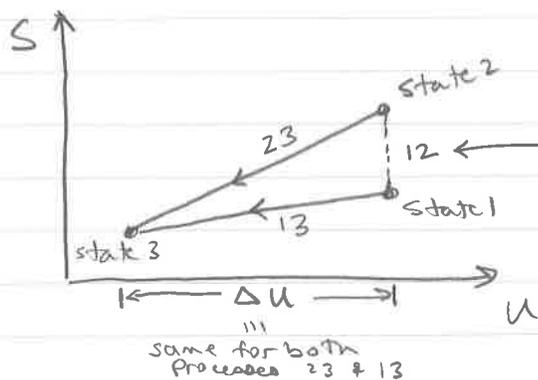
$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} C_p d \ln T$$

NOTE that both ΔH and ΔS depend on C_p . We can exploit this later,

Another way to interpret Entropy

consider...

measure of energy unavailable to do work

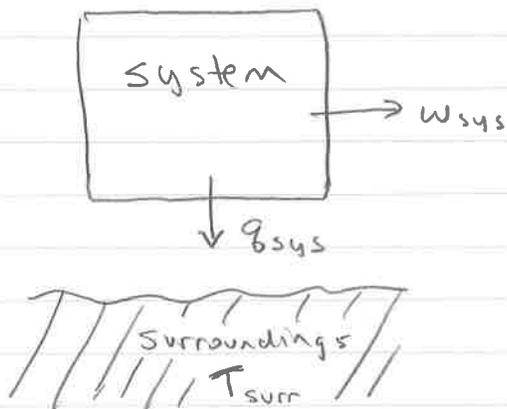


isolated system, irreversible, spontaneous process



Let's compare the maximum work we can extract from state 1 & state 2 in going to a common reference state 3.

$\Delta_{12} S$
↑
entropy change for process 1 → 2 (spontaneous)



$$\Delta U_{sys} = q_{sys} + w_{sys}$$

$$\Delta U_{sys} = T_{surr} \Delta S_{sys} + w_{sys}$$

- or -

$$w_{sys} = \Delta U_{sys} - T_{surr} \Delta S_{sys}$$

We want to find the difference in work output between process 1 → 3 & 2 → 3

$$w_{23} = \Delta_{23} U - T_{surr} \Delta_{23} S$$

$$\& w_{13} = \Delta_{13} U - T_{surr} \Delta_{13} S$$

so

$$w_{23} - w_{13} = (\Delta_{23} U - \Delta_{13} U) - T_{surr} (\Delta_{23} S - \Delta_{13} S)$$

From our plot of S -vs- U , we see that

$$\Delta_{13} U = \Delta_{23} U$$

so

$$w_{23} - w_{13} = -T_{\text{surr}} (\Delta_{23} S - \Delta_{13} S)$$

and since Entropy is a state function

$$\Delta_{12} S = \Delta_{13} S - \Delta_{23} S = (S_3 - S_1) - (S_3 - S_2) = S_2 - S_1$$

Thus

$$w_{23} - w_{13} = T_{\text{surr}} \Delta_{12} S$$

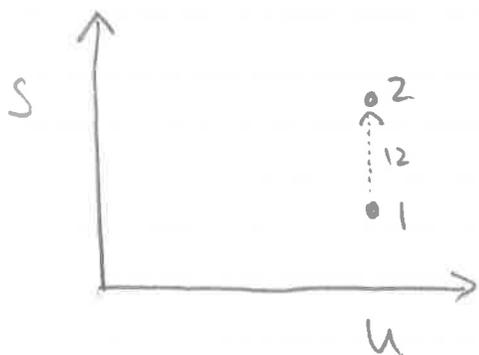
since $\Delta_{12} S$ must be positive for a spontaneous process in an isolated system, then w_{12} will be less negative than w_{23} .

In other words...

$$|w_{23}| = |w_{13}| - T_{\text{surr}} \Delta_{12} S$$

NOTE: As temp is lowered the ability to extract work is improved

An irreversible process in an isolated system reduces the quantity of work that the system can do on the surroundings.



no change in internal energy during spontaneous process but system loses ability to convert internal energy into work

!!!

Principle of energy degradation.