Fundamental theories of physics don't depend on the direction of time

- Newtonian Physics
- Electromagnetism
- Relativity
- Quantum Mechanics

Physics is time symmetric Nature is not

II law of thermodynamics - only law of nature that exhibits direction of time!

The First Law of Thermodynamics:

the only allowed changes for a system are those that do not change the total energy of the Universe.

 $\Delta U = \Delta Q + \Delta W$ $\Delta U_{system} + \Delta U_{surrounding} = 0$

Energy conservation is not a criterion to decide if a process will occur or not !!!!



This rxn occurs in one direction and not in the opposite.

Spontaneous process

A spontaneous process can occur in a system left to itself; no outside action is necessary

A non-spontaneous process cannot take place in a system left to itself

If a process is spontaneous, the reverse process is non-spontaneous and vice versa.

"Spontaneous" *says nothing about how <u>fast</u>* a process occurs

Diamond is thermodynamically favored to convert to graphite, but not kinetically favored.



Irreversible Processes

a change in the thermodynamic state of a system and all of its surroundings cannot be precisely restored to its initial state by infinitesimal changes in some property of the system without expenditure of energy.

All **Real** processes are *irreversible*.



Each state reached during the transition is far more probable than that which preceded it.

$$P_{i+1} >> P_{i-1}$$

Reversible proces

The system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process.

The occurrence of each such step is infinitesimally more probable than its non-occurrence. $P_{i+1} \ge P_{i-1}$

In a reversible process changes are infinitesimally **small**.



Efficiency

Free energy transduction is least efficient when it proceeds by the uncontrolled release of a big constraint.

Free energy transduction is most efficient when it proceeds by the incremental, controlled release of many small constraints.





 $\Delta H = H_{final} - H_{initial}$ State function (path independent)

Enthalpy is an extensive property $\Delta H_{total} = (moles \ reacted) \ \mathbf{x} \ \Delta H_{rxn}$

Standard Enthalpy Change

The standard enthalpy change, ΔH° , of a reaction is the enthalpy change when reactants and products are in their standard states.

$$\Delta H_{rxn}^{o} = \sum n \cdot \Delta H_{products}^{o} - \sum m \cdot \Delta H_{reactants}^{o}$$

(*n* & *m* are stechiometric coefficients)

The change of enthalpy of a reaction is fairly independent of temperature.

Second law of Thermodynamics

"SPONTANEOUS" REACTION

as time elapses





ORGANIZED EFFORT REQUIRING ENERGY INPUT



Entropy

- Rudolf CLAUSIUS (1822-1888)
- 1865: *Definition of entropy for* a process occurring at constant temperature is:

$$dS_I = \frac{dQ_{rev}}{T}$$

- Q_{rev} = the heat that is transferred when the process is carried out *reversibly* at a constant temperature.
- T = temperature in Kelvin.

For *irreversible* processes in a non-isolated system.



For thermally isolated systems $\Delta S \ge 0$.

Entropy is an extensive property $\Delta S_{total} = (\Delta S_{system}) x$ (moles reacted)

$$\Delta S = \int_{1}^{2} \frac{dQ_{rev}}{T} = S(2) - S(1)$$



Thermodynamics and atomic hypothesis

- Ludwig BOLTZMAN
- 1872: *Kinetic theory*
- 1880: Statistical interpretation of entropy: disorder in energy space

The Boltzmann (physical) Entropy. It is a thermodynamic state function that measure how the dispersal of energy alters when a system changes from one state to another.

There are W(U) states available to a physical system with energy U. Once the system has come to equilibrium, its entropy is defined as: $S(U) = k_B \ln[W(U)]$

 $k_B = 1.380662 \cdot 10^{-23} \, J/K$

Entropy is a state function describes the direction of a process due to changes in heat input or output and the associated molecular rearrangements.

PROBABILITY suggests that a spontaneous reaction will result in entropy created by the dispersal

* of energy $(\Delta S_{surround})$ * of matter (ΔS_{system})

Higher entropy is often associated with greater disorder, but really measures how energy is spread out in a system.



Global States vs. Microstates





For 4 trials, $P_{HHHH} = P_{HTHH} = (0.5)^4$,	HHHH	THHH
All sequences are equally probable		HTHH
Dut not all compositions		HHTH
But not all compositions		HHHT
$W(n,N) = \frac{N!}{n! * (N-n)!}$	0T4H	1T3H

W is the *Wahrscheinlichkeit*, the frequency of occurrence of a macrostate or the number of possible microstates corresponding to the macroscopic state of a system

Multiplicity

W(n,	$N) = \frac{N!}{n! * (N - N)}$	- <i>n</i>)!
n	W	InW
4	$\frac{4!}{0!4!} = 1$	0
3	$\frac{4!}{1!3!} = 4$	1.386
2	$\frac{4!}{2!2!} = 6$	1.792
1	$\frac{4!}{3!1!} = 4$	1.386
0	$\frac{4!}{4!0!} = 1$	0
Total <i>W</i> = 16		







Multiplicity



In any number of trials the composition has a tendency to 50%H50%T

For any system, if W(n) is known, n* where dW(n)/dn = 0 is the most likely number to observe

The same applies to lnW(n)

Barometric formula

a particle above the ground



potential energy = mgh = work against the gravity

A column of compressible gas in the gravity field: *T* is constant, but density depends on height



Barometric formula

$$\frac{p}{p_o} = e^{-mgh/kT}$$

$$p_o$$

because pressure is proportional to the number of particles $p \sim n$

$$\frac{n}{n_o} = e^{-mgh/kT}$$

n = number of particles per unit volume

$$\frac{C}{C_o} = e^{-E_{pot}/kT}$$

normalizing to the volume
$$c = n/V$$

C = concentration (which is probability)

$$\frac{C}{C_o} = e^{-\Delta H/kT}$$

$$H = U + E_{pot}$$

in our case U is constant because T is constant

Boltzmann equation uses probabilities

i=

the relative populations of particles in states *i* and *j* separated by an energy gap

$$\frac{p_i}{p_j} = e^{-(E_i - E_j)/kT}$$
the fraction of particles in each state:

$$p_j = \frac{e^{-E_j/kT}}{\sum_{j=1}^{t} e^{-E_j/kT}}$$

$$\frac{1}{\sqrt{2}} = \frac{\Delta E_{3-2}}{\Delta E_{2-1}}$$

The energy difference here represents enthalpy $S = k \ln W$ H = U + W(internal energy +work) W - the number of micro-states p_i p_j ΔH ΔH Free energy difference $\Delta G = \Delta H - T\Delta S$ p_i / p_j $e^{-1} = 0.37$ entropic advantage $e^{-2} = 0.135$ For two global states which can be $\frac{p_i}{dt} = e^{-\Delta H/kT}$ $e^{-3} = 0.05$ ensembles of microstates: p_{i} $e^{-4} = 0.018$ $\frac{P_i}{dt} = e^{-\Delta G/kT}$ $e^{-5} = 0.007$ p_i

Multiplicity can be connected to the macroscopic world through definition of Entropy



 $\Delta S = \int \frac{dQ}{dT}$

There are W(U) states available to a physical system with energy U.



Once the system has come to equilibrium, its entropy is defined as:

 $S(U) = k_B \ln[W(U)]$ $k_{\rm R} = 1.380662 \cdot 10^{-23} \, J/K$

flow of the heat into the system allows this system to occupy more states



Example of enthropy estimation

An isothermal (dU = 0) expansion.



Initial state of a **reversible** expansion through absorption of heat, **dQ**. $dW = -dQ \neq 0$, and $dS_{rev} = dQ/T$;



Initial state for **irreversible** expansion caused by removal of a partition dividing the chamber

 $\mathbf{dW} = \mathbf{dQ} = \mathbf{dU} = \mathbf{0}$, and $\mathbf{dS}_{irr} > \mathbf{0}$;



The identical final state that is reached, with the final volume = twice initial volume.

The first experiment - reversible



The change in piston position and molecular distribution is a result of the absorption of a heat at constant temperature.

 $S = -\frac{dQ}{T} = \frac{dW}{T} = \frac{pdV}{T}$

For 1 mole of a dilute molecular population, pV=RT

For constant temperature
$$(dU(T) = 0)$$

$$dQ = -dW$$

$$dS = \frac{RT}{T} \frac{dV}{V} = R \frac{dV}{V}$$

and

$$\Delta S = R \int_{1}^{2} \frac{dV}{V} = R \ln \frac{V_{0}}{V_{1}} = R \ln 2$$

 $V_2 = 2V_1$



The second experiment irreversible

↓ For a large number of particles (1 mole), this redistribution is irreversable.

4 If there are N identical molecules, and N_j and N_k in each compartment.

4 The relative probability of having a given number N_j and N_k on each side of the partition is proportional to the number of different ways, $W_{j,k}$, in which this may occur.



♣ The initial state – all N particles on one side.

$$W_{j,k} = W_{N,0} = \frac{N!}{N!0!} = W_1 \equiv 1$$

After the partition is removed, there are N/2 particles on each side.

From the Boltzmann expression for S, since $W_1 = 1$

$$W_{j,k} = W_{N/2,N/2} = \frac{N!}{\left(\frac{N}{2}!\right)^2}$$
$$\Delta S = k \ln \frac{W_1}{W_2} = k \ln \frac{N!}{\left(\frac{N}{2}!\right)^2}$$

 $\ln N! = N \ln N - N$

"Stirling's approximation" (large N) Substituting in the expression for ΔS

$$\Delta S = k \left[N \ln N - N - 2 \left(\frac{N}{2} \ln \frac{N}{2} - \frac{N}{2} \right) \right] = k N \ln \frac{N}{N/2} = k N \ln 2$$

the gas constant $\mathbf{R} = \mathbf{k} \mathbf{N}_{\mathbf{A}}$

The entropy change is the same when calculated from "particle in the box" experiments based on the view of Clausius or that of Boltzmann (entropy is a state function).

Entropy changes in the surroundings are determined by the heat flow.

The size of ΔS_{surr} depends on temperature.

An exothermic process is favored because by giving up heat, the entropy of the surroundings increases.



The number of microstates and, therefore, the entropy tends to increase with increases in

- ✤ Temperature.
- Volume (gases)
- ✤ The number of independently moving molecules.
- ✤ The freedom of motion of molecules.

✤ The more atoms in its molecules, the greater is the entropy of a substance.

Microstates and Macrostates

Example 1: Gas in a Box



- Described by **microstate** $\{p_i, q_i\}$. The position and momentum of all particles.
- 3 positions, q_i and 3 momentums, p_i per particle. So in all (3+3) x10²³ microvariables.
- Macrostate described by 3 quantities T, V, N.

Microstates and Macrostates

Example 2: Polymer Chain



- The **microstate** described a particular configuration of the chain on the lattice.
- If there are N links on the chain, there are N variables.
- Macrostate described by just the thermodynamic radius R of the chain.

Microstates and Macrostates

Example 3: Gas Adsorption



- The gas binds on the binding sites on the substrate with favorable energy.
- The **microstate** described by a particular binding configuration of the gas on the substrate.
- Macrostate described by just the average number <N> of particles bound to the substrate.

Boltzmann Distribution Law Predicts How the System Be Distributed Among Available Microstates





Boltzmann distribution law defines probability to find a particle in microstate i

Exponential distribution law defines relative occupancy of microstates i and j



Standard Molar Entropy Change for the System

Standard molar entropy, *S*°, is the entropy of one mole of a substance at standard state (usually at 25°C).

Standard State

solids or liquids: pure element or compound at 1 atm and temperature of interest. *gases*: pure gas behaving as an ideal gas at 1 atm and temperature of interest.

Standard entropy changes for chemical reactions:

 $\Delta S^{\circ} = \sum n \cdot S^{\circ}(products) - \sum m \cdot S^{\circ}(reactants)$

n,m - stoichiometric coefficients

Standard entropies tend to increase with increasing molar mass.

Standard molar entropies of selected substances at 298 K.

Substance	S°, J/mol-K
Gases	
$H_2(g)$	130.6
$N_2(g)$	191.5
$O_2(g)$	205.0
$H_2O(g)$	188.8
$NH_3(g)$	192.5
$CH_3OH(g)$	237.6
$C_6H_6(g)$	269.2
Liquids	
$H_2O(l)$	69.9
$CH_3OH(l)$	126.8
$C_6H_6(l)$	172.8
Solids	
Li(s)	29.1
Na(s)	51.4
K(s)	64.7
Fe(s)	27.23
$FeCl_3(s)$	142.3
NaCl(s)	72.3

Entropy of a substance increases with temperature.





 $\Delta H_{transition}$ ΔS $\overline{T}_{transition}$

The Second Law of Thermodynamics Once disorder is created, it cannot be destroyed. Universe = System + Surroundings $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} \ge 0$

An *irreversible* (spontaneous) process, in the absence of external forces, a system moves toward a state of greater probability or greater disorder. The entropy of the Universe must increase.

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

In reversible processes, the system remains in, or very close to, a state of maximum probability (at equilibrium). The entropy of the Universe does not change. $\Delta S_{sys} + \Delta S_{surr} = 0$

$$\Delta S_{sys} = \Delta S_{created} + \Delta S_{transferred}$$

The meaning of 2nd law

Energy is conserved in all processes, but not all energy conserving processes can happen!

100% heat → work (process A) cannot occur, but

100% work \rightarrow heat (time reversal of A) can occur

2nd law refers to macroscopic processes only.

Some macroscopic processes are not reversible!

ENTROPY & INFORMATION

Second Law of Thermodynamics

The entropy can only

increase

Over time, the information contained in an isolated system can only be

destroyed

A physical system of particle reaches *equilibrium* when all information but the one that must be conserved (mass, momentum, energy) have vanished.

A living system may be characterized as an ordered and information processing macroscopic system.

A system can pass to the state with smaller entropy, $\Delta S_{syst} < 0$, if $\Delta S_{surr} > 0$.

The existence of all living beings is based on entropy export.

- The evolution is a process of such successive selforganizational steps.

- Each step is driven by interactions, self-reproduction, mutation and selection.

Transmitting information

Coding theory uses *redundancy* to transmit binary bits of information



A cell is a big factory designed to duplicate the information contained in the DNA

• The cell divides before the information contained in the DNA fades away

• In this way, cell division and DNA duplication at fast pace, conserve the genetic information for millions of years.



Entropy & Information summary

- The Second Law of Thermodynamics leads to global loss of information.
- Systems out of equilibrium produce information... to the cost of the environment.
- Information can be coded, transmitted, memorized, hidden, treated.
- Life is a way of producing information: genetic code, proteins, chemical signals, pattern formation, neurons, brain.