Thermodynamics:
- can the rxn go at all in a certain direction?
- would it be spontaneous under certain conditions?

Spontaneous process: can occur by itself without outside intervention once conditions have been established for its initiation.

Spontaneous does not mean fast!
Examples of spontaneous processes:

- combustion
- diffusion: ink in water
- dissolving: salt in soup
- gas expansion
- ice melting at room T
- rock going downhill
- heat flowing from hot to cold objects: hot cup of coffee cools down
- rusting of metals
What is a driving force for spontaneity???

Exotermicity?
- rock downhill
- combustion
- rusting
- cooling

But:
- melting of ice: endotermic
- dissolving of some salts is endotermic

Entropy increase <-> An increase of disorder in the Universe
Entropy: A measure of disorder

American artist, Jackson Pollock would literally stand back and hurl paint at his canvases. The result is certainly random, but occasionally quite fun. The painting below is in the Centre Georges Pompidou in Paris and is one of Pollock's slightly more normal, but still high entropy, paintings.

A somewhat more orderly, and perhaps lower entropy painting by Piet Mondrian.

Example from University of Idaho General Chemistry website
Example from University of Idaho General Chemistry website
Entropy: Quantitative probabilistic description

Probability of a molecule to be in one half of a container:

One molecule:

\[ P = \frac{1}{2} \]

Two molecules:

\[ P = \left( \frac{1}{2} \right)^2 \]

N molecules:

\[ P = \left( \frac{1}{2} \right)^N \]

If \( N = N_a = 6.02 \times 10^{23} \)

\[ P = \left( \frac{1}{2} \right)^{6 \cdot 10^{23}} = 10^{-2 \cdot 10^{23}} \]
Entropy is related to a number of arrangements available to a system in a given state of energy.

The larger is the number of ways a particular state of the system can be reached, the larger is the probability.
Different arrangements of 4 molecules

Arrangement I

Arrangement II

Arrangement III

Arrangement IV

Arrangement V

By how many ways each arrangement can be achieved?
Each of the possible arrangements is called *microstate*.
Ludwig Boltzmann defined an equation for the probability and entropy:

\[ S = k_b \ln \Omega \]

where

S is entropy

\( \Omega \) is the number of micro states available for a state of a system (both energy and position)

\( k_b \) is the Boltzmann constant:

\[ k_b = \frac{R}{N_a} \]
Entropy: Important properties

- positional - arrangements in space (e.g., right and left bulbs)
- energy of a molecule (more arrangements resulting in the same energy)
- state function: change depend only on the final and initial states
- additive: $S = S_1 + S_2$
Entropy is additive:

Consider two non-interacting subsystems: $A$ and $B$

Microstates for $A$: $\Omega_A$

Microstates for $B$: $\Omega_B$

Total # of microstates: $\Omega_A \cdot \Omega_B$

Entropy: $S_{AB} = k_b \ln \Omega = k_b \ln(\Omega_A \cdot \Omega_B) = k_b \ln \Omega_A + k_b \ln \Omega_B = S_A + S_B$
Positional entropy and volume

When volume increases - more positional arrangements are possible

Calculate change in entropy $\Delta S$ for gas expansion, $V_2=2V_1$ (T=const)

For one molecule $\Omega \sim V$

$$\Delta S = S_2 - S_1 = k_b \ln \Omega_2 - k_b \ln \Omega_1 =$$

$$k_b \ln \frac{\Omega_2}{\Omega_1} = k_b \ln \frac{V_2}{V_1} = k_b \ln 2$$

$\Delta S$ for 1 mole:

$$\Delta S = S_2 - S_1 = k_b \ln \Omega_2^{N_a} - k_b \ln \Omega_1^{N_a} =$$

$$k_b N_a \ln \Omega_2 - k_b N_a \ln \Omega_1 = \ldots = k_b N_a \ln 2 = R \ln(2)$$
For ideal gas changing volume from $V_1$ to $V_2$ at const $T$:

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

Examples of processes where positional entropy increases:
- gas expansion
- salt dissolving
- diffusion of gases/liquids
- ice melting
- evaporation
Energy and entropy

4 particles, each particle has average kinetic energy: \( E = \frac{3}{2}RT \)

Total \( E_t \) of 4 particles: \( E_t = 4 \cdot \frac{3}{2}RT = 6RT \)

Assume we have only quantized levels of energy for each particle:

- 45R
- 30R
- 15R
- 0

<table>
<thead>
<tr>
<th>T, K</th>
<th>( E_t )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2.5</td>
<td>15R</td>
</tr>
<tr>
<td>5.0</td>
<td>30R</td>
</tr>
</tbody>
</table>

How many different arrangements yield total \( E_t \)?

Link to **Entropy Model**