ARE THE SHANNON ENTROPY AND RESIDUAL ENTROPY SYNONYMS?

\[ H = R_0 ? \]

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Thermodynamic entropy - $S$ (J/K)

Boltzmann equation:

$$ S = k \ln W $$

Nernst theorem:

Thermodynamic entropy of a “perfect (ideal) crystal” (monotonic series of aligned asymmetric molecules) at absolute zero is exactly equal to zero.

At $T=0K$ →
ideal crystal imperfect c.
$S=0$ J/K $S=0$ J/K
$Ro=0$ J/K or $Ro>0$ J/K
$H=0$ J/K or $H>0$ J/K
$I=0$ bit or $I>0$ bit

At $T>0K$ →
$S>0$ J/K
$Ro=0$ J/K
$H=0$ J/K
$I=0$ bit
Residual entropy

- $S_0$ or $R_0$ also known as $S_{\text{random crystal}}$. Units: J/K.

- Boltzmann-Planck formula

\[ R_0 = S_{\text{random crystal}} - S_{\text{perfect crystal}} \]

\[ S_{\text{perfect crystal}} = 0 \]

\[ R_0 = S_{\text{random crystal}} \]

- Appears as a consequence of nonmonotonically aligned asymmetrical particles in a string.

\[ R_0 = k_B \ln \left( \frac{W_{2,\text{random}}}{W_{1,\text{perfect}}} \right) \]
Shannon entropy

- Shannon equation

\[ H = K \sum_i p_i \ln p_i \]

- Konstant \( K = k_B \)

S=0  H>0  Ro>0 or H=0 Ro=0

S=\text{max.}  \text{ Ro}=0  H=0
AMOUNT OF INFORMATION (BIT, NAT)

Defined by Shannon as

\[ I = N \sum_{i} p_i \log_b p_i \]
Near absolute zero

Ideal crystal
S=0; Ro=0, H=0, I=0

Symmetric molecules (CO₂)
- Monotonic series: OCO⋅OCO⋅OCO⋅OCO

Asymmetric molecules (CO)
- Monotonic series: CO⋅CO⋅CO⋅CO⋅CO

Imperfect crystal
S=0; Ro=X; H=X; I=Y

Symmetric molecules (CO₂)
- Nonmonotonic series: CO⋅CO⋅OC⋅CO⋅OC

Asymmetric molecules (CO)
- Nonmonotonic series: CO⋅CO⋅OC⋅CO⋅OC
Perfect and imperfect crystal/bit string

- Nonmonotonic string of particles aligned in an lattice (imperfect crystal):
  \[ \text{CO} \ldots \text{CO} \ldots \text{OC} \ldots \text{CO} \ldots \text{OC} \ldots \]
  Nonmonotonic string of material carriers of information (bit string):
  \[ 11010\ldots \]

- Monotonic string of particles in a lattice (perfect crystal):
  \[ \text{CO} \ldots \text{CO} \ldots \text{CO} \ldots \text{CO} \ldots \text{CO} \ldots \]

- Monotonic string of material carriers of information: \[ 11111111111111\ldots \]
  or
  \[ 00000000000000\ldots \]
  (bit string containing no information)
TO BE CLEAR AND AVOID THE HIGH ENTROPY AREA!

- THERMODYNAMIC ENTROPY (S): MEASURE OF DISORDER OF UNALIGNED PARTICLES
- RESIDUAL ENTROPY (RO OR SO): MEASURE OF DISORDER OF ASYMETRICAL PARTICLES ALIGNED IN NONMONOTONIC CHAIN
- SHANNON ENTROPY (H): MEASURE OF DISORDER OF AN INFORMATION SYSTEM CONTAINING ASYMETRICAL PARTICLES ALIGNED IN NONMONOTONIC STRING
- AMOUNT OF INFORMATION: MEASURE FOR QUANTIFICATION OF INFORMATION
Relationships

• Relationships between the 4 quantities are not clearly defined.
• Two models were analyzed in order to determine the relationships:
  1. iRNA polymerization.
  2. Carbon monoxide gas, ideal crystal and imperfect crystal.
Nucleotides before iRNA polymerization

- Mixture: 0.25mol A 0.25mol T
  0.25mol G 0.25mol C

- Entropy estimate can be found through

\[
S_{\text{comp},i} = N_i k_B \ln \left( \frac{2\pi n_i k_B T}{\hbar^2} \right)^{3/2} \frac{V_{\text{total}} e^{5/2}}{N_i}
\]

\[
S_{\text{mix}} = -n_{\text{total}} R \sum_i x_i \ln(x_i)
\]

- Information content:
  No string to contain information, so I=0.

<table>
<thead>
<tr>
<th>$S_{\text{comp}}$ (J/K)</th>
<th>$S_{\text{mix}}$ (J/K)</th>
<th>$S$ (J/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>192.936</td>
<td>11.526</td>
<td>204.462</td>
</tr>
</tbody>
</table>
Nucleotides after polymerization

- **String:**
  
  \[ p(A) = 0.25 \quad p(T) = 0.25 \]
  \[ p(G) = 0.25 \quad p(C) = 0.25 \]

- **Thermodynamic Entropy** at 0 K:
  
  \[ S = k \ln W = k \ln 1 = 0 \text{ J/K} \]

- **Information:**
  
  \[ I = 2 \text{ bits per character} \]
  \[ H = 16.62 \text{ J/K per mol} \]
Carbon monoxide: Gas

Entropy:

\[
S_{\text{IDG}} = N \, k \left\{ \ln \left( \frac{2 \, \pi \, m \, k \, T}{h^2} \right)^{3/2} \frac{V \, e^{5/2}}{N} \right\} + \ln \left( \frac{T \, e}{\sigma \, \Theta_r} \right) + \frac{\Theta_v / T}{e^{\Theta_v / T} - 1} - \ln \left( 1 - e^{-\Theta_v / T} \right) + \ln \left( \omega_e \right) \}
\]

\[
\Delta S_{\text{corr, RK}} = R \left[ \frac{3}{2} \cdot 0.42748 \cdot \frac{(p / p_c)}{(T / T_c)^{5/2}} - \frac{15}{4} \cdot 0.42748 \cdot 0.08662 \cdot \left( \frac{p / p_c}{(T / T_c)} \right)^{7/2} + 2 \cdot (0.42748)^2 \left( \frac{p / p_c}{(T / T_c)^5} \right) \right]
\]

\[
S = 197.504 \text{ J/mol K}
\]

Information: \( I=0 \) \( H=0 \)
CO: Monotonic array

Perfectly ordered crystal

CO⋯CO⋯CO⋯CO⋯CO⋯CO⋯CO⋯ ◦⋯

Entropy

\[ S = k \ln (1)^N \]
\[ S = 0 \text{ J/K} \]

Information

\[ I = - \sum_i p_i^* \log (p_i^*) = - \sum_i 1 \log (1) = 0 \text{ bit} \]
\[ H = - k_B \sum_i p_i^* \ln (p_i^*) = - k_B \sum_i 1 \ln (1) = 0 \text{ J/K} \]
**CO: Nonmonotonic array**

- Disorder in arrangement exists
  \[ \text{CO} \cdots \text{OC} \cdots \text{OC} \cdots \text{CO} \cdots \text{OC} \cdots \text{CO} \cdots \text{OC} \cdots \text{CO} \]

Or alternatively: 1001011101

**Giauque:** Experiments show that CO has an entropy of 4.6 J/mol K at absolute zero.

- The origin of **residual entropy** is disorder in **molecular arrangement**.
- The origin of **Shannon entropy** is disorder in **molecular arrangement**.
PROPERTIES OF A NONMONOTONIC ARRAY

- **Entropy**
  \[ S = k \ln (1)^N \]
  \[ S = 0 \]

- **Residual entropy**
  \[ R_0 = R \ln (2) = 5.76 \text{ J/K} \]

- **Shannon entropy**
  \[ H=5.76 \text{ J/mol K} \]

- **Information**
  \[ p(CO)=0.5 \quad p(OC)=0.5 \]
  \[ I(X) = -[(0.5 \cdot \log_2 0.5) + (0.5 \cdot \log_2 0.5)] \]
  \[ I(X) = 1 \text{ bit per character or } 6 \cdot 10^{23} \text{ bits per mole} \]
## Analysis of the models

<table>
<thead>
<tr>
<th>iRNA</th>
<th>$S$ (J/K)</th>
<th>$R_0$ (J/K)</th>
<th>$H$ (J/K)</th>
<th>$I$ (bit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before polymerization</td>
<td>204.4</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>After polymerization</td>
<td>0</td>
<td>11.5</td>
<td>11.5</td>
<td>$1.2 \cdot 10^{24}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CARBON MONOXIDE</th>
<th>$S$ (J/K)</th>
<th>$R_0$ (J/K)</th>
<th>$H$ (J/K)</th>
<th>$I$ (bit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>197.504</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ideal crystal</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Unideal crystal</td>
<td>0</td>
<td>5.76</td>
<td>5.76</td>
<td>$6.02 \cdot 10^{23}$</td>
</tr>
</tbody>
</table>

In both cases residual entropy ($R_0$) and Shannon entropy ($H$) behave in the same way, different from thermodynamic entropy ($S$).
Three reasons for $H=Ro$

• Both Residual entropy and Shannon entropy are the consequence of the same randomness of atomic arrangement (CO:OC:CO:CO:CO... and 10111).

• Both Shannon entropy and residual entropy are based on the same distribution – the normal distribution.

• The same informational or combinatoric method, derived using the coin tossing model, is traditionally used in textbooks to calculate both residual and Shannon entropy.
Apples and oranges, Thermodynamic and Residual/Shannon entropy

Less randomness (less entropy)

Solid

Less $\Delta S$ > 0
Less $\Delta S$ < 0

Less randomness (less entropy)

Liquid

More $\Delta S$ > 0
More $\Delta S$ < 0

More randomness (more entropy)

Gas

$S = 0$  $S = 0$
$R_0 = 0$  $R_0 \neq 0$
$H = 0$  $H = 0$
$I = 0$  $I \neq 0$

Perfect crystal

Imperfect crystal
Both perfect and imperfect crystals can be considered as a single macromolecule (polymer).

Imperfect crystals consist of asymmetrical molecules aligned in a nonmonotonic string.

Nonmonotonic string of asymmetrical molecules has an information content.

Both Crystals are highly organized systems. Thermodynamic entropy for both crystals is 0 at absolute zero.

Residual and Shannon entropy of imperfect crystals are equal and nonzero. Both are a consequence of molecular arrangement in a string.
Conclusions

- Residual entropy is present only in the systems containing asymmetric molecules if they are not aligned monotonically. Shannon entropy also.

- Residual entropy is not just a remnant of thermodynamic entropy at absolute zero.

- Shannon entropy and Residual entropy are properties of a system that contains nonmonotonically aligned molecules in a string.

- Shannon entropy is equal to Residual entropy at absolute zero.
• Hisdal E. Quantitative measure of the amount of information acquired in a learning process. BIT Numerical Mathematics 1979; 19: 196-203.
• Popovic M. Comparative study of entropy and information change in closed and open thermodynamic systems. Thermochimica Acta 2014; 598: 77-81.