ARE THE SHANNON ENTROPY AND RESIDUAL ENTROPY SYNONYMS? $H = R_0$?

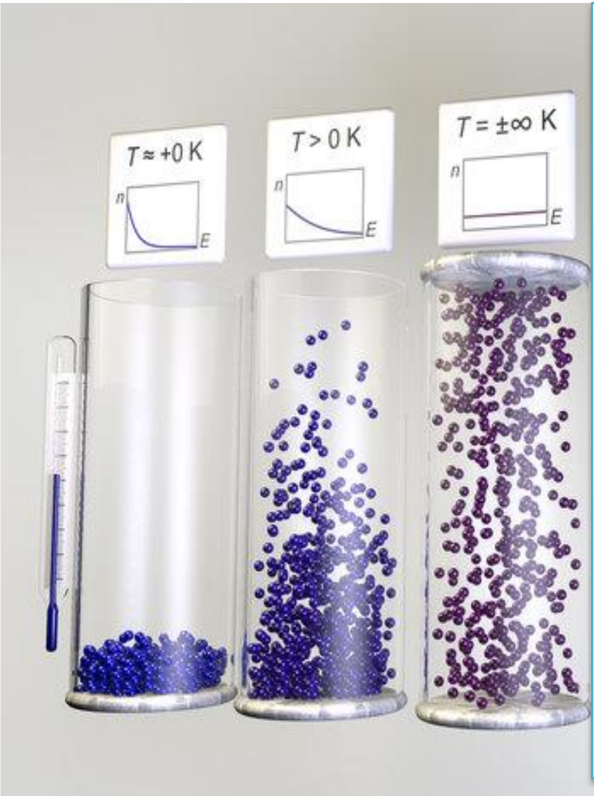
MARKO POPOVIC

DEPARTMENT OF CHEMISTRY AND BIOCHEMISTRY, BYU, PROVO, UT 84602, POPOVIC.PASA@GMAIL.COM

Thermodynamic entropy - S (J/K)

Boltzmann equation:

$$S = k \ln W$$



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 I>0 bit

At T> 0K →

S>0J/K

Ro=0J/K

H=0 J/K

I =0 bit

Nernst theorem:

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

Residual entropy

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

$$R_0 = S_{random\ crystal} - S_{perfect\ crystal}$$

$$S_{perfect\ crystal} = 0$$

$$R_0 = S_{random\ crystal}$$

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

$$R_0 = k_B \ln\left[\frac{W_{2,random}}{W_{1,perfect}}\right]$$

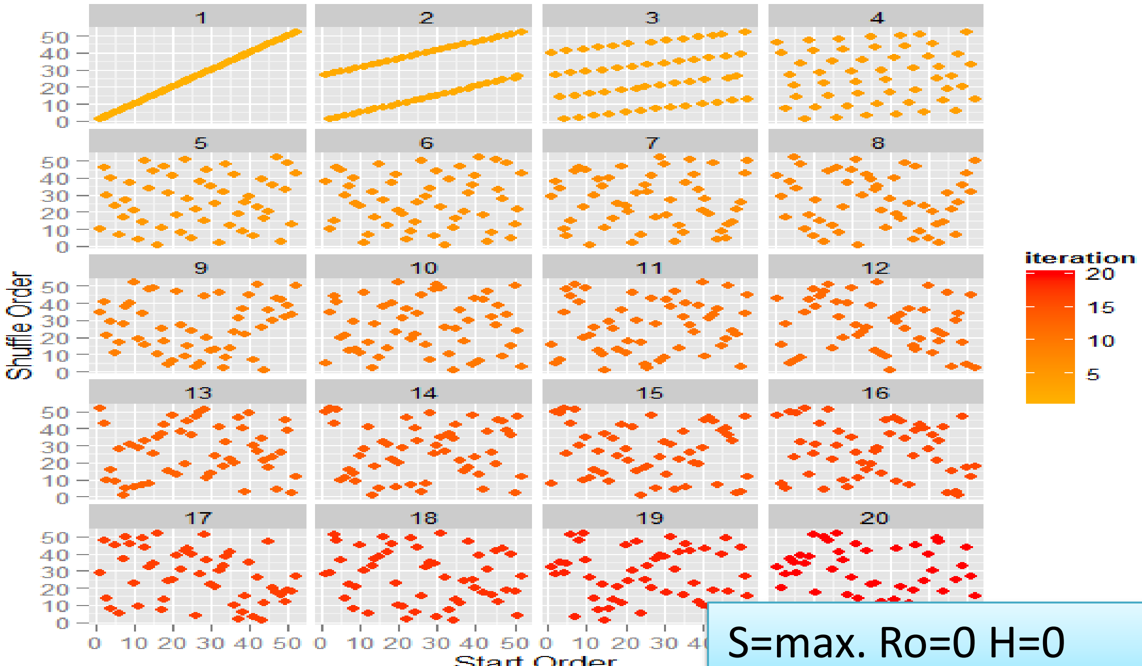
Shannon entropy

- 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=max. 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

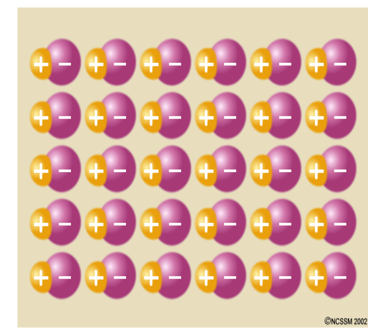
Ideal crystal
S=0; Ro=0,
H=0, I=0

Symetric molecules (CO_2)

Monotonic series
OCO··OCO··OCO··OCO

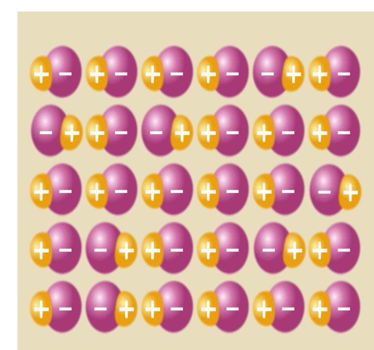
Asymetric molecules (CO)

Monotonic series
CO··CO··CO··CO··CO



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

Nonmonotonic series
CO··CO··**OC**··CO··**OC**



Perfect and imperfect crystal/bit string

- Nonmonotonic string of particles aligned in an lattice (imperfect crystal):

  CO … CO … OC … CO … OC …

  Nonmonotonic string of material carriers of information (bit string):

  11010…

- Monotonic string of particles in a lattice (perfect crystal):

  CO … CO … CO … CO … CO …

- Monotonic string of material carriers of information: 11111111111111…

  or

  00000000000000…

  (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

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

$$S_{mix} = -n_{total} R \sum_i x_i \ln(x_i)$$

S_{comp} (J/K)	S_{mix} (J/K)	S (J/K)
192.936	11.526	204.462

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

Nucleotides after polymerization

- **String:**

  p(A)=0.25 p(T)=0.25

  p(G)=0.25 p(C)=0.25

- **Thermodynamic Entropy** at *0 K*:

  $S = k \ln W = k \ln 1 = 0\ J/K$

- **Information:**

  $I = 2$ *bits per character*

  $H = 16.62\ J/K$ *per mol*

Carbon monoxide: Gas

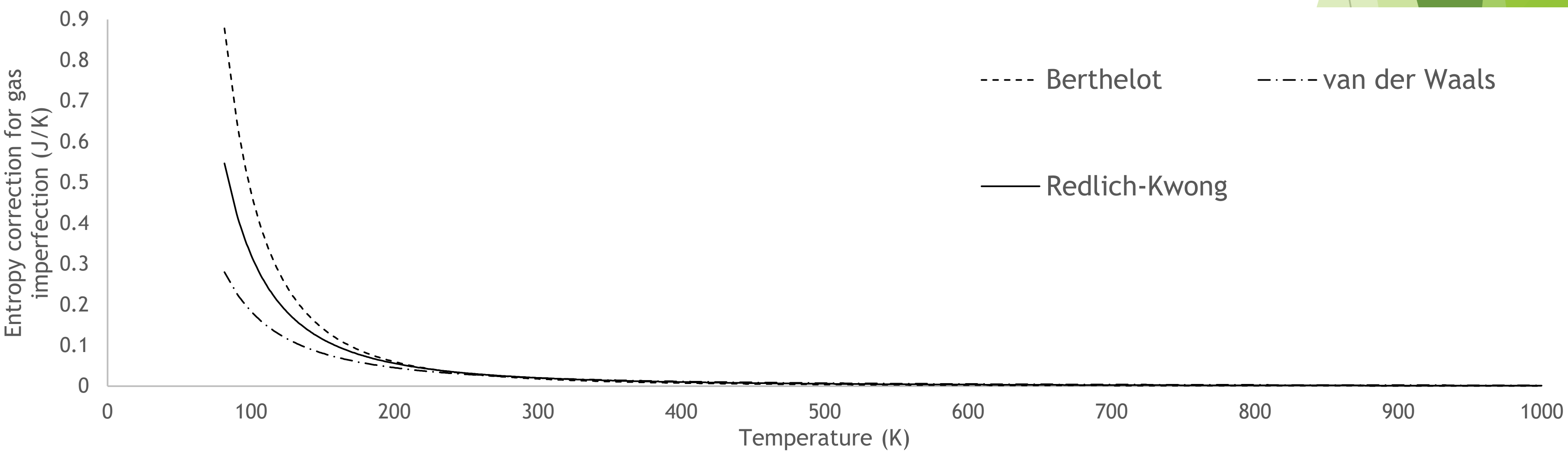
- Entropy:

$$S_{IDG} = N\ k\ \left\{ \ln\left[\left(\frac{2\ \pi\ m\ k\ T}{h^2} \right)^{3/2} \frac{V\ e^{5/2}}{N} \right] + \ln\left(\frac{T\ e}{\sigma\ \Theta_r} \right) + \frac{\Theta_v\ /\ T}{e^{\Theta_v\ /\ T} - 1} - \ln\left(1 - e^{-\Theta_v\ /\ T}\right) + \ln\left(\omega_{e1}\right) \right\}$$

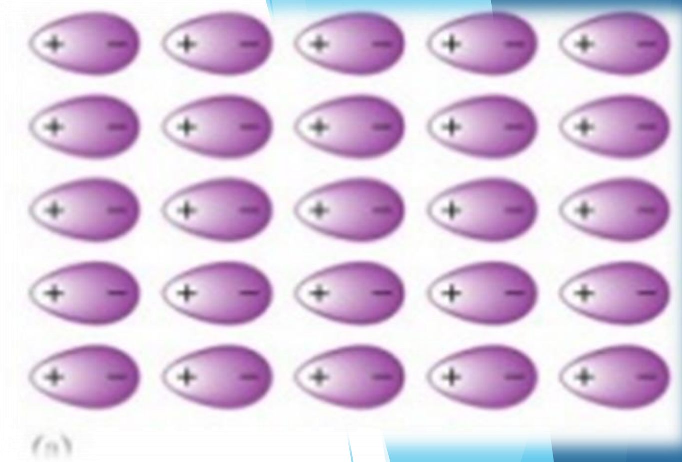
$$\Delta S_{corr,RK} = R \cdot \left[\frac{3}{2} \cdot 0.42748 \cdot \frac{(p/p_c)}{(T/T_c)^{5/2}} - \frac{15}{4} \cdot 0.42748 \cdot 0.08662 \cdot \frac{(p/p_c)^2}{(T/T_c)^{7/2}} + 2 \cdot (0.42748)^2 \frac{(p/p_c)^2}{(T/T_c)^5} \right]$$

S = 197.504 J/mol K

- Information: I=0 H=0



CO: Monotonic array



- **Perfectly ordered crystal**
  CO···CO···CO···CO···CO···CO ···

- **Entropy**
  $S = k \ln (1)^N$
  $S = 0\ J/K$

- **Information**
  $I = - \Sigma_i\, p_i^* \log (p_i^*) = - \Sigma_i\ 1 \log (1) = 0\ bit$
  $H = - k_B \Sigma_i\, p_i^* \ln (p_i^*) = - k_B\, \Sigma_i 1 \ln (1) = 0\ J/K$

CO: Nonmonotonic array

- **Disorder in arrangement exists**

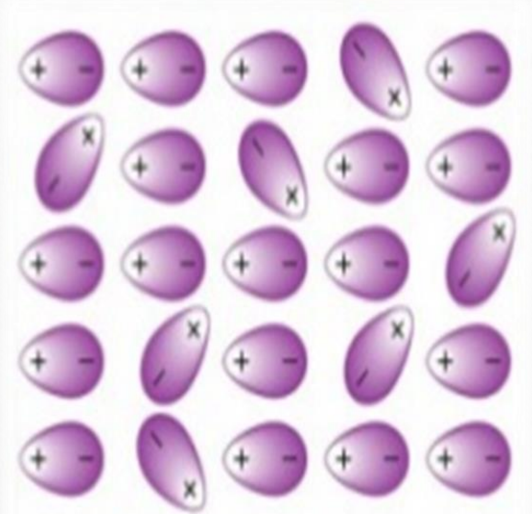
  CO···**OC**···**OC**···CO···**OC**···CO···CO···CO···**OC**···CO

  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.**



(b)

PROPERTIES OF A NONMONOTONIC ARRAY

- **Entropy**
  $S = k \ln (1)^N$
  $S = 0$
- **Residual entropy**
  $R_0 = R \ln (2) = 5.76\ J/K$
- **Shannon entropy**
  $H = 5.76\ J/mol\ K$
- **Information**
  $p(CO) = 0.5$ $p(OC) = 0.5$
  $I(X) = -[(0.5 \cdot \log_2 0.5) + (0.5 \cdot \log_2 0.5)]$
  $I(X) = 1$ *bit* per character or 6 $\cdot 10^{23}$ *bits per mole*

Analysis of the models

iRNA	S (J/K)	R_0 (J/K)	H (J/K)	I (bit)
Before polymerization	204.4	0	0	0
After polymerization	0	11.5	11.5	$1.2 \cdot 10^{24}$

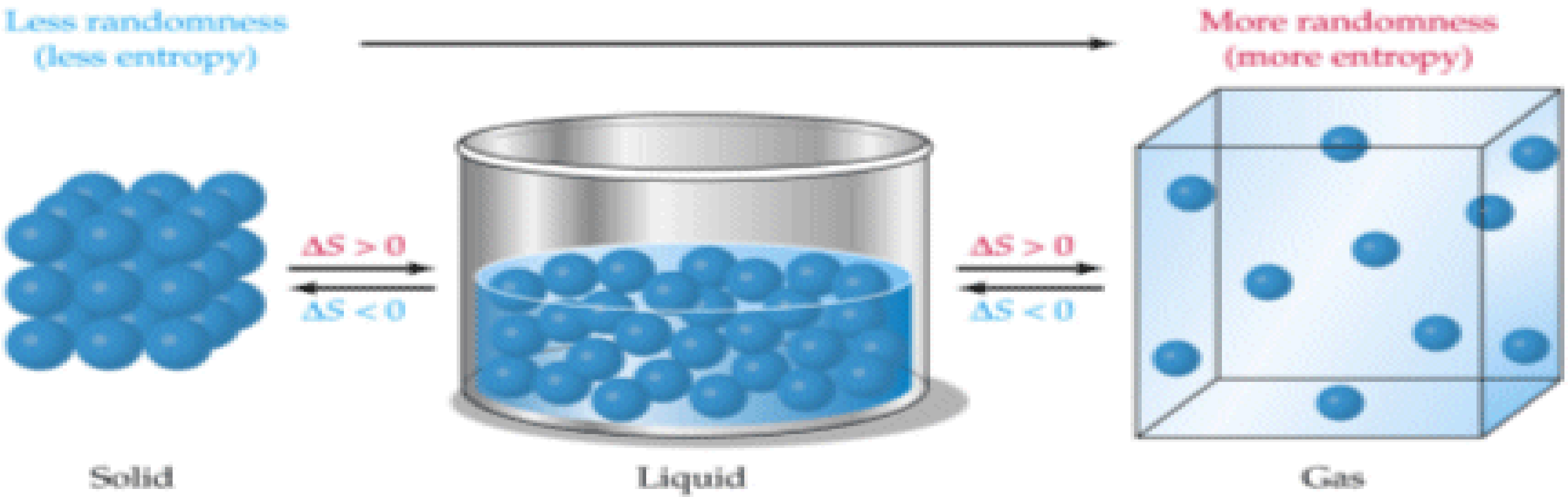
CARBON MONOXIDE	S (J/K)	R_0 (J/K)	H (J/K)	I (bit)
Gas	197.504	0	0	0
Ideal crystal	0	0	0	0
Unideal crystal	0	5.76	5.76	$6.02 \cdot 10^{23}$

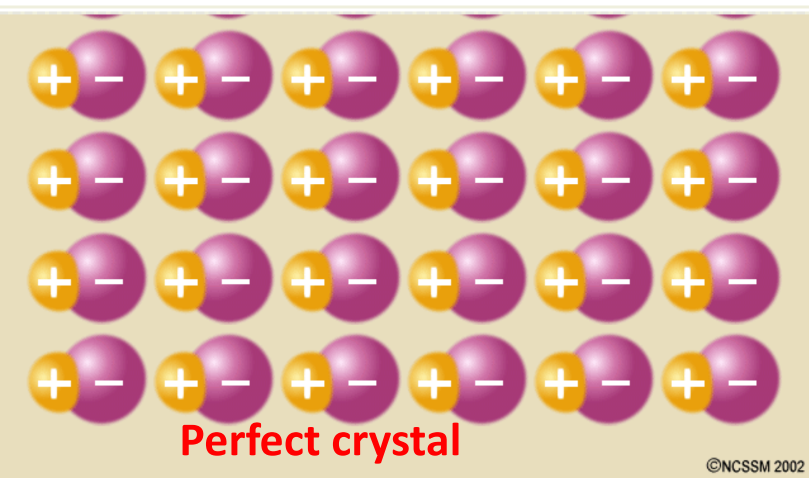
In both cases residual entropy (R_0) and Shannon entropy (H) behave in the same way, different from thermodynamic entropy (S).

Three reasons for H=Ro

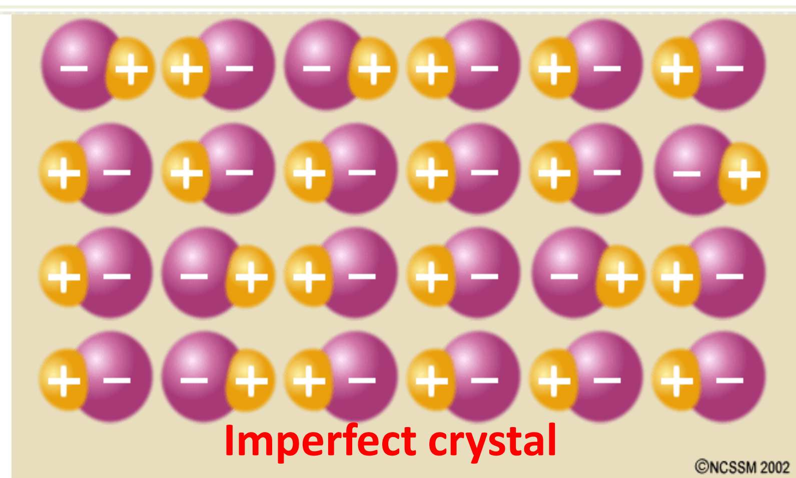
- Both Residual entropy and Shannon entropy are the consequence of **the same randomness of atomic arrangement** (CO:OC:CO:CO:CO… and 10111).
- Both Shannon entropy and residual entropy are based on the **same distribution** – the normal distribution.
- The **same** informational or combinatoric **method**, 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





S =0	S=0
Ro= 0	Ro≠0
H=0	H≠0
I=0	I≠0



*What does this mean?

* 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.

Literature

- Boltzmann L.Theoretical Physics and Philosophical Problems: Selected Writings (Vienna Circle Collection). New York: Springer-Verlag; 1974.
- Rao Y. Stoichiometry and Thermodynamics of Metallurgical Processes. Cambridge: Cambridge university press; 1985.
- Sandler IS, An introduction to applied statistical thermodynamics, chapter: a comment to the third law of thermodynamics. Hoboken: Wiley; 2011.
- Lewis GN, Gibson GE. The third law of thermodynamics and the entropy of solutions and of liquids.J Am ChemSoc 1920; 41: 1529-1533.
- Pauling L. General Chemistry. New York: Dover Publications Inc; 1988.
- Kozliak E. Consistent Application of the Boltzmann Distribution to Residual Entropy in Crystals. J Chem Edu 2007; 84: 493-498.
- Pauling L. The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement. J AmChemSoc 1935; 57: 2680-2684.
- Pauling L. The Rotational Motion of Molecules in Crystals. Phys Rev 1930; 36: 430-443.
- Darken LS, Gurry RW. Physical chemistry of metals.New York: McGraw-Hill; 1953.
- Jaynes E. Information theory and statistical mechanics.PhysRev 1957; 106: 620-630.
- Shannon CE. A mathematical Theory of Communication. The Bell System Technical Journal 1948; 27: 379-423.
- Hisdal E. Quantitative measure of the amount of information acquired in a learning process. BIT Numerical Mathematics 1979; 19: 196-203.
- Garner WR,Hake HW. The amount of information in absolute judgements. Psychological Review 1951; 58: 445-459.
- Popovic M. Comparative study of entropy and information change in closed and open thermodynamic systems. Thermochimica Acta 2014; 598: 77-81.
- Simon J, Sestak J, Mares JJ, Hubik P, editors. Glassy, Amorphous and Nano-Crystalline Materials: Thermal Physics, Analysis, Structure and Properties. Berlin: Springer; 2011.
- Clayton JO, Giauque WF. The Heat Capacity and Entropy of Carbon Monoxide. J Am ChemSoc 1932; 54: 2610-2626.
- Truesdell C. Rational Thermodynamics. 1sted.New York: McGraw-Hill; 1969.
- Sestak J. Science of Heat and Thermophysical Studies: A Generalized Approach to Thermal Analysis. Amsterdam: Elsevier; 2005.
- Goodwin RD. Carbon monoxide thermophysical properties from 68 to 1000 K at pressures to 100 MPa. J PhysChem Ref Data 1985; 14: 849-932.
- McQuarrie DA. Statistical Mechanics. Sausalito: University Science Books; 2000.
- Melhuish MW, Scott RL. Energies of disorientation in solid carbon monoxide and nitrous oxide. J PhysChem 1964; 68: 2301-2304.
- Hansen L, Creedle R, Battley E. Biological calorimetry and the thermodynamics of the origination and evolution of life. Thermochimica Acta 2009; 81: 1843-1855.