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Are the Shannon entropy and Residual entropy synonyms?

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Abstract: The information theory and classical thermodynamics have at least one strong common point. Our analysis leads us to conclusion that the residual entropy (S_0 or R_0) of a closed thermodynamic system that contains N asymmetric particles (i.e. CO, H_2O, N_2O) aligned in nonmonotonic series in "imperfect" (non ideal) crystals is equal to Shannon entropy (H). The thermodynamic entropy S of "ideal" (perfect) crystals that contain symmetric particles (i.e. Cu, CO_2), or asymmetric particles aligned in a monotonic chain (monotonic string of CO molecules, i.e. CO..CO..CO..CO…) was found to be 0 at absolute zero. The information content (amount of information), Shannon entropy and residual entropy were also found to be 0 for such systems at absolute zero. The thermodynamic entropy S of imperfect crystals containing asymmetric molecules (CO, H_2O, N_2O, Nucleotides…) aligned in a nonmonotonic string (i.e. CO..CO..OC..CO…) was also found to be 0 at absolute zero. However, the information content was calculated to be some positive amount of bits at absolute 0. Thus the Shannon entropy is also a positive value (in J/K). The residual entropy of asymmetric molecules aligned in a nonmonotonic string (R_0 in J/K) found at absolute zero is also a positive value. It is equal to Shannon entropy (J/K). Shannon entropy is not just the expression for thermodynamic entropy as found in statistical mechanics (as suggested in literature), even though their equations have similar shapes. They have different probability distributions. Probability of thermodynamic entropy is given by Boltzmann distribution. Probability of Residual entropy and Shannon entropy is given by Gauss normal distribution or a delta distribution.

Keywords: Thermodynamic entropy; Shannon entropy; Residual entropy; symmetric/asymmetric particles; monotonic/non-monotonic series.

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1. Introduction

The total thermodynamic entropy of a closed thermodynamic system is proportional to the total number of (unaligned) particles it contains according to Boltzmann [1]

$$S = k_B \ln \Omega \qquad (1)$$

k_B is Boltzmann constant, and Ω is the number of microstates consistent with the given macrostate. Thermodynamic entropy is given in units of J/K. It represents a measure of disorder of a thermodynamic system. The thermodynamic entropy is proportional to the temperature of the closed system according to Nernst-Planck theorem/Third law of thermodynamics

$$\lim_{T \to 0} (\Delta S) = 0$$

Thus, according to Nernst, the thermodynamic entropy change for a reaction involving condensed substances is equal to zero at absolute zero. Thermodynamic entropy of condensed substances, containing aligned symmetrical molecules and asymmetrical molecules aligned in a monotonic chain, is zero at absolute zero. "*Although, some exceptions must be made with respect to the disordered solid and liquid solutions*[1] *and glassy substances*" [2]. Similarly, Sandler and Stanley claim "*Not all crystals are perfectly ordered*[2] *at T= 0K"* [3].A solid and liquid solution in disordered state „*retains*[3] *a certain amount of positive entropy*[4] *at absolute zero*" according to Lewis & Gibson [4]. However Pauling claims "*There are no exceptions to the third law; Entropy of a pure substance in the form of perfect crystal is zero at absolute zero*."[5], but "*There are some crystalline pure substances, however that retain*[5] *some entropy when they cooled to very low temperatures*" [5]. If the crystal is ideally ordered, and therefore "ideal", then the molecules are aligned in a monotonic chain.

Randomly organized molecules in a nonmonotonic chain lead to disorder in crystal. So it is concluded that such a crystal is imperfect and therefore it retains some entropy called the residual entropy. So it is predicted that residual entropy represents residuum of thermodynamic entropy. Such crystals may also possess information and Shannon entropy. „*Unlike the corresponding energy or enthalpy, entropy*[6] *is normally set equal to zero at 0 K in accord with the third law of thermodynamics thereby allowing for the calculation of its absolute values at any given temperature*"[6]. Informational or combinatoric method[7], derived using the coin tossing model[8], is traditionally used in textbooks to calculate residual entropy. It applies the Boltzmann–Planck formula:

$$\Delta S_{residual} = \lim_{T \to 0} \left[S_{Random\ Crystal} - S_{Perfect\ Crystal} \right] = k_B \ln \left[\frac{W_{2,random}}{W_{1,perfect}} \right]$$

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[1] In solutions at least two types of molecules must be present (also two characters in a terms of information theory).
[2] Perfectly ordered implies S=0, if not perfectly ordered then S≠0. Perfectly ordered=monotonic string. Not perfectly ordered=non-monotonic string.
[3] It means that it retains some of thermodynamic entropy.
[4] It is necessary to determine what kind of positive entropy is present at absolute zero (thermodynamic or Shannon entropy). In other words, is the residual entropy residuum of thermodynamic (Gibbs) entropy or does it represent nothing else but Shannon entropy?
[5] Again sentence suggests that system retains some thermodynamic entropy.
[6] Thermodynamic.
[7] Same method is used to calculate Shannon entropy.
[8] Also used to calculate Shannon entropy.

where W_2 and W_1 correspond to the numbers of microstates of the real and perfect crystals[9], respectively. This implies that residual entropy is a residuum of thermodynamic entropy. Thermodynamic entropy is derived from Boltzmann distribution, while normal distribution is used for describing residual entropy. The difference in entropy between randomly organized crystal and ideal crystal is in the arrangement of monomers/material carriers of information in a string. Randomly nonmonotonically organized crystal contains some information proportional to the number of material carriers of information /monomers because it is organized in nonmonotonic string (CO..CO..OC..CO..OC…= 11010…). It also contains some residual entropy. Therefore, hypothetically, Shannon information entropy (in information theory) may represent a property that is described as residual entropy in thermodynamics. So $H=R_0$.

Let us assume that CO molecule in crystal can exist in one of two configurations CO or OC, each corresponding to certain orientations of the CO molecules aligned in a string. CO molecule can change from one configuration to another by rotation in a string at low temperature above absolute zero. At absolute zero rotation is impossible, so the information in a string is locked. *"Pioneering work of the calorimetric measurement by Gibson and Giauque has shown that glycerol glass exhibited a sudden increase in heat capacity C_p"* [15] over a narrow temperature region, interpreted it as (thermodynamic) entropy[10] and suggested term: "*residual entropy S_o (or R_0 at 0 K)*"[11]. In that case it should represent the residuum of thermodynamic entropy at 0K. Residual entropy present in certain[12] crystals comprised of non-symmetric molecules, e.g., "*CO, is detected only by the difference between spectroscopic calculations of the absolute entropy of gaseous CO and calorimetric measurements of heat capacity and phase change from 0 K to the temperature of the gas*"[16]. This phenomenon results in the occurrence of a non-zero entropy at absolute zero [7]. For example, the observed entropy of crystalline hydrogen shows that even at very low temperatures the molecules of orthohydrogen in the crystal are rotating about as freely as in the gas [8]; subsequent to this discovery the phenomenon of rotation of molecules in crystals was found to be not uncommon. Shannon information entropy is the consequence of uncertainty of information stored in aligned asymmetric particles in a nonmonotonic string.

The aim of this paper is to find relations between two thermodynamic properties (thermodynamic entropy and residual entropy) and information theory properties (Shannon entropy and amount of information).

2. Theoretical analysis

Carbon monoxide (and other asymmetrical molecules) is found to crystallize with the CO molecules linearly oriented in its crystal lattice. But during crystallization, many CO molecules were found to align themselves in the direction exactly opposite to that for the other CO molecules making imperfect crystal containing residual entropy, information content and Shannon entropy. This string of linearly aligned CO molecules may contain some information content (CO:CO:OC:CO:OC =11010). *„Our knowledge of the structure of Crystals permits the prediction to be made that other crystals will be found to have residual entropy(R_0) at very low temperatures as a result of some randomness of atomic arrangement"(in chain)*[7]. Pauling underlined that the residual entropy is a consequence of

[9] Notice that molecules are aligned in a crystal. So the residual entropy is present only in nonmonotonically aligned crystals. In monotonically aligned (ideal, perfectly ordered) crystal the residual entropy is 0 at absolute 0.
[10] It may be also interpreted as increase in information.
[11] Notice that idea of residual entropy is a just an interpretation of experimentally obtained data of surprising C_p increase.
[12] But not all of them.

randomness of atomic arrangement (in a string containing information).The Shannon entropy is also a result of randomness of atomic arrangement. In that case we suggest that R_0 can be considered as Shannon entropy ($H=R_0$) because:

1. Both Shannon entropy and residual entropy are based on the same distribution – the normal distribution.
2. The same informational or combinatoric method, derived using the coin tossing model, is traditionally used in textbooks to calculate both residual and Shannon entropy.
3. The entropy values of carbon monoxide and nitrous oxide show that in imperfect crystals of these substances the molecules are not uniquely (not monotonically) oriented (in a string), but have a choice instead between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axis [7]. Nonmonotonic orientation in a string of asymmetrical particles causes R_0 according to Pauling. Nonmonotonic orientation in a string also causes existence of some information content (*I*). Randomness in a string causes Shannon entropy (*H*) in that string.
4. According to Boltzmann-Planck relation at 0 K:

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

Because $S_{perfect\ crystal} = 0$ at absolute zero according to III law. So

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

$S_{random\ crystal}$ appears as a consequence of nonmonotonically aligned asymmetrical particles in a string. Entropy of the randomly organized string is known as Shannon entropy in information theory. So

$$H = S_{random\ crystal}.$$

Therefore there are following indications

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

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

Darken and Gurry concluded that for any homogeneous substance that is in complete thermal equilibrium, the absolute thermodynamic entropy can be taken as zero at 0K [9]. This also predicts the Nernst theorem/III law of thermodynamics. Both perfect and imperfect crystals are in complete thermal equilibrium at absolute zero so for both the absolute thermodynamic entropy can be taken as zero at 0K.

For a classical closed system (i.e., a collection of classical particles) with a discrete set of microstates the (thermodynamic) entropy of the system is given as

$$S = - k_b \Sigma_i p_i \log_b(p_i) \qquad (2)$$

p_i is the probability for unaligned (solo) particles[13] that it occurs during the system's fluctuations, and k_B is Boltzmann constant. k_B has the same dimension (units) as entropy and heat capacity. The logarithm is dimensionless. Entropy is therefore given in J/K units.

It is believed that the above expression of the statistical entropy is "*a discretized version of Shannon entropy*, [10]. Shannon entropy therefore should have the same units (J/K). Shannon entropy is given as

[13] And aligned particles counted as 1 macromolecule.

$$H = - K \Sigma_i p_i * log_b(p_i^*) \qquad (3)$$

p_i^* is the probability for aligned particles (in a string that contains message) and K is a physical constant [11, 10]. So, p_i^* is the probability of character number i. *„Since this* (3) *is just the expression for entropy as found in statistical mechanics, it* (Shannon entropy) *will be called the entropy of the probability distribution p"* [14][10]. However in statistical thermodynamics probability p is related to all particles. Thermodynamic entropy is entropy of all molecules, including unaligned and aligned molecules. Particles assembled in an oligomer should be counted as one single particle. In Shannon equation, distribution p^* is related to aligned particles only (ATGCTGCATG…) [11]. In physical or more precisely thermodynamic sense, Shannon entropy is entropy of the nonmonotonically aligned asymmetrical molecules (such as a polymer that contains nonmonotonically aligned asymmetrical monomers i.e. CO.OC.CO.OC.OC…).

Shannon entropy represents the measure of disorder of information contained in a macromolecule[15], so it should have dimension of entropy (J/K). In that case for K in (3) the Boltzmann constant k_B (J/K) could be taken. Shannon himself suggested this [11].Therefore, (2) and (3) apparently have the same shape. However notice that $S \neq H$, because the probability in thermodynamic entropy equation (2) is for all particles (given by Boltzmann distribution) and probability in Shannon equation (3) is for non-monotonic aligned asymmetrical particles in a macromolecule only (given by Gauss distribution)[16]. There is a qualitative difference between thermodynamic and Shannon information entropy because $\Sigma_i p_i \, log_b(p_i) \neq \Sigma_i p_i * log_b(p_i^*)$. Let's mark probability in thermodynamic entropy equation p_i and probability of aligned particles in Shannon equation p_i^*.

Amount of information stored in the system (information content) is given as

$$I = - \Sigma_i p_i^* log_b(p_i^*) \qquad (4)$$

p_i^* is the probability for aligned particles (in a string that contains a message). Units of amount of information are bits, if number 2 is taken for the basis of the logarithm[17]. Notice that amount of information (4) is not equal to Shannon entropy (3). However, confusion between Shannon entropy (H) and amount of information (I) appears frequently in literature. For example in [12] at (p 197) I (information content) in equation (4) is replaced by H (Shannon information). However H and I are not the same property. On the other hand Garner [13] uses an appropriate equation (4) to calculate amount of information (p447). Amount of information is always positive. Shannon entropy (includes $\Sigma_i p_i^* log_b(p_i^*)$), residual entropy and thermodynamic entropy are non-negative quantities. Entropy can therefore have only a positive value, according to Popovic [14]. Amount of information is proportional to the number of symbols aligned in a string (p119) [12], Shannon entropy is the information entropy encoded in a string.

It is believed that information can be destroyed in real thermal processes. "The two fundamental laws in a manner which is common in classical axiomatic thermodynamics [17], namely:

(I) Energy is conserved in any real thermal process.

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[14]Notice that probability distribution is related to a molecules organized in a string. This is not the same distribution as in thermodynamic entropy (because this distribution is for unorganized molecules, so there is no chain in thermodynamic entropy).

[15]Macromolecule may appear as the result of polymerization, agglomeration, crystallization…

[16]Notice that the length of the chain (string) of macromolecule (so the amount of information also) depends on temperature according to Arrhenius equation, so k_B can be used in Shannon equation.

[17]Or nat, if e is taken as the basis of logarithm.

(II) Caloric (heat) cannot be annihilated in any real thermal process".

"*Theorem (II) can thus be reformulated in terms of information,* as *Information (I) is destroyed in any real thermal process*" [18]. Everyday experience that by "*burning of newspapers in a stove or combusting petrol these materials are lost forever, together with the information involved, is subject for discussion more than argument*"[18]. Popovic concluded that information cannot be destroyed, but only transited from its visible to potential form [14]. Unaligned particles of CO represent material carriers of information. They can be organized in a string and disorganized into single particles. The information contained in a string (visible form) is not destroyed but transformed in a potential form during change of temperature and restored in a reversible process. Both information and residual entropy change reversibly in thermal processes. *"A pure crystalline substance such as solid copper (symmetrical particle) at room temperatures is composed of copper atoms* (character 1)[18] *and crystal defects* (its opposition, character 0) *that are randomly distributed on face centered cubic lattice size has some positive residual entropy at room temperature"[2].* If copper atoms are marked as 1, and crystal defects as 0, then randomly organized crystal contains message (i.e. 1010101011111111111111111100) and Shannon entropy. It also contains the residual entropy. Crystalline copper can be considered as one macromolecule. *"If the temperature decreases the crystal defect diminishes progressively. At absolute zero in equilibrium conditions it approaches the unique low energy state, so the atoms will form perfectly ordered configuration without any defects[19]. Thus perfectly ordered crystalline is in complete internal equilibrium and hence free of defects"* [2].Thermodynamic, residual and Shannon entropy is 0 at absolute 0. Thermodynamic entropy of ideal crystal is taken to be zero at absolute zero according to the Nernst theorem. The same we can claim for the symmetrical diatomic gases (H_2, O_2, N_2, and CO_2, CH_4…).Typically, atoms and symmetrical molecules align themselves in perfectly ordered crystal lattice. Therefore their thermodynamic entropy (*S*) is 0 at absolute zero. Ω is equal to the number of possible ways in which the constituent particles of the system can be arranged. For the perfectly ordered crystal $\Omega=1$, so $S=0$ according to the Boltzmann equation (1).

2.1 System before polymerization

Let's consider thermodynamic, residual and Shannon entropies and amount of information for the following suggested closed systems. Nucleotides are the monomer constituents of nucleic acids (mRNA in this case). Suggested thermodynamic system consists 0.25 moles (which means $(6.022\times10^{23}) / 4$ particles) of nucleotides A, 0.25 moles of nucleotides U, 0.25 moles of nucleotides G and 0.25 moles nucleotides C, so the total amount of substances = 1 moles = unorganized Avogadro's number of particles. Entropy of a mixture of nucleotides, considered as ideal gasses, is given as

$$S=S_{comp,1}+S_{comp,2}+S_{comp,3}+S_{comp,4}+S_{mix}$$

where

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

[18] In information theory.

[19] In that case only one character is present, without opposite character.

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

where $S_{comp,i}$ is entropy of component i, N_i is the number of particles of component i, m_i is the mass of a particle of substance i, T is temperature, h is the Planck constant, V_{total} is the total volume of the container, S_{mix} is entropy of mixing, n_{total} the amount of all substances in the system, R the universal gas constant and x_i the mol fraction of component i. Because of the analogy with asymmetrical gas molecules an approximation of idealizing the mixture of substances was introduced (table 1.)

Table 1. Entropy of a mixture of nucleotides. The first column contains the entropy of all the components, the second has the entropy of mixing, while the third has the total entropy of the system.

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

The residual entropy (R_0) for this system is zero because the individual particles are not arranged in a chain.

Because there is no string, the information content is given as

$$I = - \Sigma_i p_i^* \log_b(p_i^*) = - \Sigma_i 1^* \log_b(1^*) = 0 bit$$

Because the particles are unorganized, so we take that1 particle is organized in a string. Consequently the Shannon entropy is given

$$H = - k \Sigma_i p_i * \log_b(p_i^*) = 0 J/K$$

Notice that $R_0 = H \neq S$. Shannon entropy and thermodynamic entropy are not equal for single monomers. So, Jaynes' [10] assumption should be reconsidered. Let's summarize, for this system $R_0 = 0$ *J/K*, $I = 0$ *bit*, $H = 0$ *J/K* and $S = 204.462$ *J/K*.

2.2. System after synthesis of iRNA

If self a assembly process (chemical reaction of polymerization) occurs in the system, and all of the particles randomly align in a chain (nonmonotonic string) of mRNA[20] containing information code, then we obtain one highly organized macro-molecule of mRNA, so there is only one possible state after the macro-molecule is synthesized and only one macromolecule, then $\Omega = (1)^N$ and consequently the thermodynamic entropy can be calculated as

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

This is because there is only one macromolecule of mRNA with one possible state after synthesis of mRNA. Nucleotides are fixed in the chain (string). Therefore thermodynamic entropy of a system containing one single highly organized molecule is zero at low temperatures.
There is no sense to calculate the statistical entropy for one single macro-molecule! However if the statistical entropy should be calculated for one macro-molecule it would be calculated as

$$S = - k_b \Sigma_i p_i \log_b(p_i) = - k_b \Sigma_i 1 \log_b(1) = 0 \text{J/K}$$

[20] An approximation is that mRNA is ideal. Only primary structure of the macromolecule for he sake of simplicity is considered in the analysis.

Because there is a string, the information content is given as

$$ATGCATGCATGCATGC\ldots = (\mathrm{ATGC}) \cdot N/4 = N = 1\mathrm{mol}$$

our string is: **ATGC x (6.022 x 10^{23})/4**
Alphabet of symbols in the string: **A, T, G, C**
Frequencies of alphabet symbols: **0.25 -> A, 0.25 -> T, 0.25 -> G, 0.25 -> C**
Information content can be calculated as follows:

$$I(X) = -[(0.25 \cdot \log_2 0.25)+(0.25 \cdot \log_2 0.25)+(0.25 \cdot \log_2 0.25)+(0.25 \cdot \log_2 0.25)]$$
$$I(X) = -[(-0.5)+(-0.5)+(-0.5)+(-0.5)]$$
$$I(X) = -[-2]$$
$$I(X) = 2\text{bits per character}$$

Given the above calculated amount of information per character rounded up, each symbol has to be encoded by 2 bits and we need to use ***$1.2044 \cdot 10^{24}$*** to encode our string (containing 0.25 moles of nucleotides A+ 0.25 moles of nucleotides T+ 0.25 moles of nucleotides G + 0.25 moles nucleotides U= 1 moles of substances) optimally. Amount of information carried by our string is I = 2 × 6.022 × 10^{23}

$$I = - \Sigma_i p_i^* \log_b(p_i^*) = 1.2044 \times 10^{24} \text{ bit}$$

Consequently Shannon entropy (because string is consisted from 4 different characters) is given

$$H = - k\, \Sigma_i p_i^* \log_b(p_i^*) = - k_b \cdot 1.2044 \cdot 10^{24} = 1.662 \cdot 10^1 = 16.62 \text{ J/K}$$

Notice that $H \neq S$. Shannon entropy and thermodynamic entropy are not equal.

The only entropy present after synthesis of mRNA molecule is Shannon information entropy of the string (H). Similarly, R_0 (defined as the entropy of nonmonotonic string) can be calculated

$$R_0 = - k_b \cdot 1.2044 \cdot 10^{24} = 1.662 \cdot 10^1 = 16.62 \text{ J/K}$$

Notice that $H=R_0$.

Thermodynamic entropy of such a highly ordered structure (mRNA) is 0 (in idealized case[21] at low temperature). Shannon entropy represents entropy of the chain (string). It is present only if the string is present in oligomer or polymer of asymmetrical nonmonotonically aligned molecules. Thermodynamic entropy is related to all molecules (nucleotides). Shannon entropy is related to the organized (aligned) molecules (mRNA). As the number of unorganized molecules (solo nucleotides) decreases during synthesis, proportionally increases the number of organized monomers (length of mRNA) because the system is closed and therefore the number of the particles is constant. Notice that thermodynamic (S) and Shannon (H) entropy are reciprocal.

2.3. Entropies of gaseous CO

Entropy of closed systems decreases from the state of „idealized" gas through real gas and liquid to the ideal crystal. Entropy correction for gas imperfection was found in three ways. The first way, which was described by Giauque [16], is based on the Berthelot equation of state. The entropy correction for gas imperfection ($\Delta S_{corr,Btl}$), based on the Berthelot equation of state, is given as

[21] Only primary structure is considered.

$$\Delta S_{corr,Btl} = R \cdot \frac{27}{32} \frac{(p/p_c)}{(T/T_c)^3}$$

where R is the universal gas constant, p and T are pressure and temperature, while p_c and T_c are the critical pressure and critical temperature of the substance of interest. Entropy corrections for gas imperfection based on the van der Waals and Redlich-Kwong equations of state were also found. They were found by expanding the corresponding equation of state into a virial equation of state in volume. After that the virial equation in volume was converted into a virial equation in pressure. In both cases the virial equation in pressure was truncated after the third term. After that the virial equation in pressure was multiplied by RT/pin order to make it yield molar volume instead of compressibility factor. Next a derivative with respect to T was made while holding p constant, yielding $(\partial V_m/\partial T)_p$, where V_m is molar volume. Then the following Maxwell relation was used

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

where V is volume. Entropy was expressed as

$$S = \int_0^p -\left(\frac{\partial V}{\partial T}\right)_p dp$$

Where integration is from zero to the pressure of the gas. By inserting the $(\partial V_m/\partial T)_p$ value found based on the van der Waals or Redlich-Kwong equation of state we get S_{real}, the entropy of a real gas described by the corresponding equation of state. The entropy correction for gas imperfection (ΔS_{cor}) is by definition

$$\Delta S_{cor}=S_{ideal}-S_{real}$$

Where S_{ideal} is the entropy of ideal gas. S_{real} was found by the method described above, while S_{ideal} was found by substituting the ideal gas value of $(\partial V_m/\partial T)_p= R \cdot p$ into the entropy integral. The difference of the ideal and real expressions is the entropy correction for gas imperfection. The entropy correction for gas imperfection (per mole of gas) for a gas described by the van der Waals equation of state ($\Delta S_{corr,vdW}$) was found to be

$$\Delta S_{corr,vdW} = R \cdot \left[\frac{27}{64}\frac{(p/p_c)}{(T/T_c)^2} - \frac{27}{256}\frac{(p/p_c)^2}{(T/T_c)^3} + \frac{2187}{8192}\frac{(p/p_c)^2}{(T/T_c)^4}\right]$$

While the entropy correction for gas imperfection (per mole of gas) for a gas described by the Redlich-Kwong equation of state ($\Delta S_{corr,RK}$) was found to be

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

The entropy corrections for the three equations of state are shown as a function of temperature at atmospheric pressure in figure 1.They were calculated from 81.6 K, the boiling point of CO, to 1000 K. The critical point properties of CO were taken from [19].

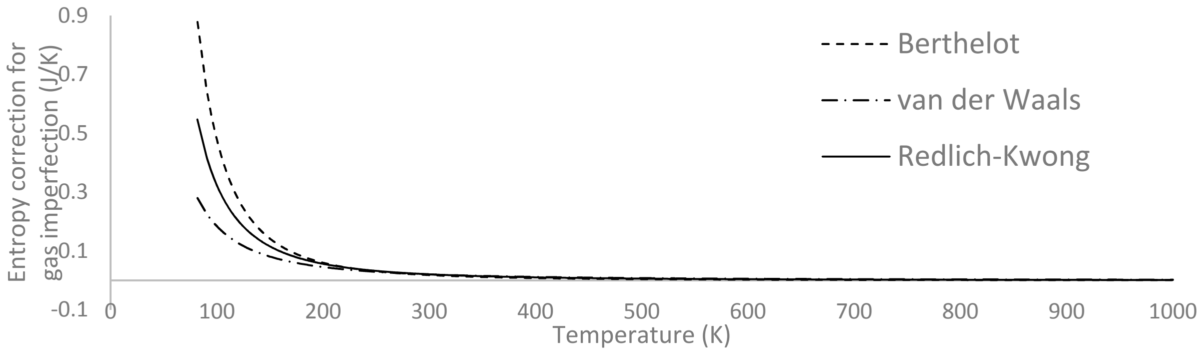

Figure 1. Entropy corrections for gas imperfection based on the Berthelot, van der Waals and Redlich-Kwong equations of state.

Analyzing figure 1 we conclude that increase in molecular interactions between CO molecules causes decrease in thermodynamic entropy (S) of the system. Therefore an ideal (or artificially idealized gas) gas has higher entropy then a real gas. By extrapolating, as the molecular interactions increase and assembly processes continue inside the system, the thermodynamic entropy decreases until system approaches absolute zero. At this point thermodynamic entropy reaches its minimum for system that contains symmetrical particles and asymmetrical particles aligned in monotonically series (ideal crystal). Molecular interactions in ideal crystal are maximized. The degree of freedom is minimized, so the thermodynamic entropy tends to zero.

However, asymmetrical particles aligned in a non-monotonic string at absolute zero also have thermodynamic entropy calculated to be zero, but such a system has some residual entropy (R_0) caused by non-monotonic arrangement of aligned particles [7]. The same calculation suggests that the system has a Shannon entropy (H) [10]. Arrangement of aligned molecules suggests that the system also contains some amount of information (information content) proportional to the number of non-monotonically aligned particles/material carriers of information [11].

Crystallized symmetrical and asymmetrical molecules aligned in a monotonic or non-monotonic string at absolute zero have thermodynamic entropy 0 (S=0), Residual entropy 0, information content 0, and Shannon entropy 0. However the asymmetrical molecules aligned in non-monotonic string have thermodynamic entropy 0, but residual entropy equal to Shannon entropy ($R_0=H\neq 0$) and some information content ($I\neq 0$) as the result of molecular arrangement in a string.

Entropy of gaseous CO was first calculated by treating it as an ideal gas. Rigid rotor-harmonic oscillator approximation was used. The ideal diatomic gas entropy (S_{IDG}) is given as

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

where m is the mass of a single CO molecule, V is volume, Θ_r is the compound rotational temperature, σ the symmetry number, Θ_v the compound vibrational temperature and ω_{el} is the degeneracy of the electronic ground state. The used values $\Theta_r=2.77\ K$, $\Theta_v=3103K$, $\sigma=1$ and $\omega_{el}=1$ were taken from [20].

Thermodynamic entropy of gaseous CO treated as an ideal gas was found to be 197.524 J/mol K at 298.15 K and atmospheric pressure.

$$S_{idealized\ CO} = 197.524\ J/mol\ K$$

After taking into account the correction for gas imperfection based on the Redlich-Kwong equation of state the thermodynamic entropy of CO treated as a real gas was found to be 197.504J/mol K.

$$S_{real\ CO} = 197.504\ J/mol\ K$$

The residual entropy (R_0=0) is 0 for gaseous CO.

There are no aligned molecules in gaseous CO, so there is no chain, and there is no string. In that case the information content of such a system is given as

$$I = -\ \Sigma_i\, p_i^*\ log_b(p_i^*) = -\ \Sigma_i\ 1\ log_b(1) = 0\ bit$$

because if

Alphabet of symbols in the string: CO

Frequencies of alphabet symbols: CO -> 1

Information content (amount of information) can be calculated as follows:

$I(X) = -[(1\cdot log_2 1)]$

$I(X) = -[(0)]$

$I(X) = -[0]$

$I(X) = \mathbf{0}\ bit$ per character

I = 0 · N = 0 bit of total information content

because the line contains one single molecule. Therefore, the Shannon entropy is given as

$$H = -\ k\ \Sigma_i\, p_i^*\ log_b(p_i^*) = -\ k\ \Sigma_i 1\ log_b(1) = 0$$

Notice that H≠S. Shannon entropy and thermodynamic entropy of CO at room temperature are not equal. Both residual entropy and Shannon entropy are 0 for gaseous CO, so R_0 = H.

2.4. Entropies of monotonically aligned CO

At absolute zero all of the particles are organized in a crystal, so it should be counted as one macro-molecule. The thermodynamic entropy is given according to the Boltzmann equation. Notice that for a perfectly ordered crystalline CO, Ω=1 and the entropy at absolute zero would be equal to 0. Perfectly ordered structure of crystalline CO is given

A: CO…CO…CO…CO…CO…CO…

Notice that the even asymmetrical molecules of CO can be aligned monotonically. In this case Ω=1, so S=0

$$S = k\ ln\ (1)^N = R\ ln\ 1 = 0\ J/K$$

Thermodynamic entropy of this chain is 0 at absolute zero as suggested above.

R_0 is also 0 because CO molecules are aligned monotonically in an ideal crystal.

This monotonic chain (string) caries no information code and therefore has no information content (amount of information is equal to zero, *I=0*) and has no Shannon entropy (*H=0*). Amount of information of string A can be calculated as

$$I = -\ \Sigma_i p_i^*\ log_b(p_i^*) = -\ \Sigma_i\ 1\ log_b(1) = 0\ bit$$

because if

Alphabet of symbols in the string: CO…CO…CO…CO…CO…CO…

Frequencies of alphabet symbols: CO…CO…CO…CO…CO…CO…**-> 1**

Information content (amount of information) can be calculated as follows:

$I(X) = -[(1 \cdot log_2 1)]$
$I(X) = -[(0)]$
$I(X) = -[0]$
$I(X) = 0\ bit$ per character

I = 0 · N = 0 bit of total information because there is no opposition (only one character is present)

Therefore, the Shannon entropy is given as

$$H = - k_B \Sigma_i p_i * log_b(p_i^*) = - k_B \Sigma_i 1\ log_b(1) = 0 J/K$$

Shannon entropy, residual entropy and thermodynamic entropy of CO aligned monotonically at absolute zero in an ideal crystal are 0.

2.5 Entropies of nonmonotonically aligned CO

Giauque reported the change in capacity of CO at absolute zero and interpreted it as residual entropy. Kozliak [6] calculated the residual entropy of CO near absolute zero as R_0 =5.8 J/K.

CO molecules can be aligned in nonmonotonic series at absolute zero. They contain some residual entropy, but also contain the information code and therefore contain some information content. Consequently such a system contains some Shannon entropy.

However the crystal made of aligned CO molecules is one highly ordered structure. It should be counted as one macro-molecule. Therefore its thermodynamic entropy at absolute 0 should be 0.

$$S = k\ ln\ (1)^N = R\ ln\ 1 = 0\ J/K$$

And, according to Kozliak [6],

$$R_0 = R\ ln\ 2 = 5.76\ J/mol\ K$$

Based on quantum mechanical calculations, Melhuish and Scott [21] concluded that the energy of intermolecular interactions is not high enough to make the CO molecules arrange monotonically in a crystal at the freezing point of CO. Therefore it has the residual entropy $R\ ln(2)$ [21].

CO is an asymmetrical molecule. Therefore it could be aligned as
B: CO…OC…CO…CO…OC…CO…CO… or
C: OC…OC…OC…CO…CO…CO…OC…or
D: OC…OC…CO…CO…OC…OC…CO…or...

In this case there are two characters (CO and OC that could be encoded as 0 for OC and 1 for CO), so in this case we have an information code and therefore some information content[22]. The linear alignment is random [7]. The random alignments, according to Hansen [22], carry information just as alignments copied from the matrices. Let's calculate
Alphabet of symbols in the string: 0 1 (CO OC)
Frequencies of alphabet symbols: 0.5 -> 0 and 0.5 -> 1

The information content can be calculated as follows:

$I(X) = -[(0.5 \cdot log_2 0.5)+(0.5 \cdot log_2 0.5)]$
$I(X) = -[(-0.5)+(-0.5)]$

22Assumption: N/2 is aligned as CO and N/2 as OC randomly.

$I(X) = -[-1]$
$I(X) = 1\ bit$ per character

Amount of information stored in 1 mole of nonmonotonically crystallized CO at absolute 0 is

$$I = 6.022 \times 10^{23}\ bit$$

Therefore the Shannon entropy of nonmonotonically aligned molecules of CO at absolute 0 is

$$H = -\ k_B \Sigma_i\, p_i * log_b(p_i^*) = 8.314\ J/K$$

Notice that $H \neq S$ at absolute zero for randomly nonmonotonically aligned CO in a crystal lattice[23]. All of the highly organized structures, such an ideal crystal at absolute zero and iRNA, have thermodynamic entropy calculated to be 0 at low energy state according to Nernst theorem/III law. Exceptionally asymmetrical molecules aligned nonmonotonically have some residual entropy, as reported by Giauque, which is equal to its Shannon entropy. „It is suggested that ice consists of water molecules arranged so that each is surrounded by four others, each molecule being oriented in such a way as to direct its two hydrogen atoms toward two of the four neighbors, forming hydrogen bonds. The orientations are further restricted by the requirement that only one hydrogen atom lie near each 0-0 axis. There are (3/2)N such configurations for N molecules, leading to a residual entropy of R ln 3/2 = 0.805 E. U., in good agreement with the experimental value 0.87 E. U. The structure and entropy of other crystals showing randomness of atom arrangement are discussed“[7]. Just as CO, water also aligns in a nonmonotonic string in a crystal lattice, having some information content. Because of randomness of orientation in a string water also carries some information content. This information is randomly organized, it is uncertain and therefore have some Shannon entropy=residual entropy.

2.6 Conservation of information

Amount of information is not destroyed in a thermal process, but is transformed from its visible form (information content) contained in a macromolecule to its potential form carried by single particles according to Popovic, because the material carriers of information are disorganized but not destroyed [14]. Moreover information can be rearranged in a reverse process. We may also conclude that information content is a thermodynamic property of any (isolated, closed or open) thermodynamic system that contains nonmonotonically aligned asymmetrical molecules.

There should be no exceptions to the third law of thermodynamics. All of highly organized substances in ideal crystals[24] should have thermodynamic entropy 0 at absolute zero. Some of the substances (if asymmetrical) can align at absolute zero in nonmonotonic chain (string) and have some information content. Therefore, at absolute zero they can have some Shannon entropy described by information theory that is also described as residual entropy (R_0) in classical thermodynamics.

3. Conclusions

We can conclude that the Shannon entropy is not equal to the thermodynamic entropy. Shannon entropy is equal to residual entropy at absolute zero. The residual entropy is present only in the systems containing asymmetric molecules if they are not aligned monotonically. The residual entropy

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23Notice that $H=R_0$ for 1 mole of nonmonotonically aligned asymmetrical particles of CO.

[24]I.e. symmetrical particles (elements and some molecules) and asymmetrical particles aligned in monotonic chain (CO…).

is not the residuum of thermodynamic entropy, but is actually equal to Shannon entropy. Shannon entropy is the property of a system that contains nonmonotonically aligned molecules in a string.

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