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Conceptual aspects of chemical thermodynamics

Juan Carlos Moreno[1,*], Liliana Giraldo[2], Rigoberto Quintana[3], Jean Rieumont[3], José Manuel Nieto-Villar[3]

[1]Deparment of Chemistry, Faculty of Chemistry, Andes University(Colombia), Carrrera 30 calle 45, Bogotá, Colombia, (USA)

[2]Department of Chemistry, Faculty of Chemistry, National University of Colombia, Colombia, (USA)

[3]Department of Physical Chemistry, Faculty of Chemistry, Ave. Zapata and G, Vedado & [3,4]*"H. Poincaré"* Complex Systems Division, University of Havana, Havana 10400, (CUBA)

E-mail : jumoreno@uniandes.edu.co

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ABSTRACT

Several features of the main concepts, and also some misinterpretations of chemical thermodynamics, are considered in the present paper. In particular, the following topics are discussed: 1. Relation between entropy and information; 2. Thermodynamic potentials. An evolutionary arrow of time of the natural systems 3. Gibbs free energy, ΔG, and chemical reaction spontaneity.

KEYWORDS

In the Classroom;
Chemical thermodynamics;
Second law of thermodynamics;
Entropy;
Information;
Thermodynamic potentials;
Gibbs free energy.

INTRODUCTION

Today Thermodynamics represent not only the theoretical framework but also the practical tool for studies in the field of theoretical biology and physical chemistry[1]. One of the problems present in the teaching of chemical thermodynamics at university level is related to some theoretical aspects of the Second Law of Thermodynamics and in particular with the entropy.

Entropy contrary to the heat and work does not have a direct meaning associated with the *praxis*. G. N. Alekseev commented[2] that a popular-science author of the early twentieth century wrote, "Entropy is the name of the Queen's shadow. Face to face with this phenomenon, Man cannot help feeling some vague fear: Entropy, like an evil spirit, tries to diminish or annihilate the best creations of that gracious spirit, Energy. We are all under the protection of Energy and all potential victims of the latent poison of Entropy ...". On the other hand, we can recall the sentence of the great Ludwig Boltzmann that *"Thus, the general struggle for life is neither a fight for basic material ... nor for energy ... but for entropy becoming available by the transition from the hot sun to the cold earth"*[3].

Another important aspect under discussion refers to the spontaneity of the chemical reaction using the Gibbs free energy ΔG. The main purpose of the present paper is to discuss some[1] conceptual aspects of chemical thermodynamics as a typical course in chemical curriculum (see reference[4]).

Therefore, in order to get a better insight into these concepts, some features will be discussed in detail:

Entropy and information

Thermodynamic potentials. An evolutionary arrow of time of the natural systems

The link between Gibbs free energy ΔG and chemical reaction spontaneity

The link between these topics is using in a concrete way the thermodynamic function "entropy", in fields such as information, direction of processes and chemical reaction.

DISCUSSION

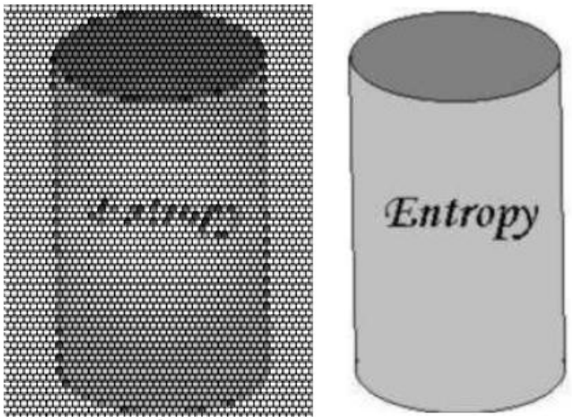
Entropy and information

Entropy, generally related to "disorder", is perhaps one of the most polemical, mysterious and controversial thermodynamic magnitudes. The increase of entropy is then described as an increase of disorder, as the destruction of any coherence that may be present in an initial state. This has unfortunately led to the view that the consequences of the Second Law are obvious or trivial. Anyway, there also exist some misinterpretations (see, for example, reference[5]) that have arisen from the unawareness of the essence of the Second Law[6].

The goal of this item is to show how the use of the information theory makes it better and easier to understand the entropy meaning, and at the same time gives a formal definition of it. Recently Hynne[7] suggests an interpretation of entropy via the Boltzmann formula.

In order to illustrate our ideas, let us begin with the following experiment (Figure 1a). We have a body at rest, so that its energy is constant, but we cannot see its features because an opaque glass is in front of it.

It creates some uncertainties about it. Later the glass is taken away (Figure 1b), and uncertainty about it disappears, thus, we can say that in relation to this body we have obtained more information. It is to be noted that in any moment its energy has not changed.



A B

Figure 1 : Experiment with a body at rest: A. An opaque glass is between the observer and the body. B. The glass was drawn out

Thus, according to Shannon (1948), average information, "I", can be quantified through this relation:

$$I = -k\sum p_i \ln p_i \qquad (1)$$

Where p_i represents the probability of any event, for example, in the previous experiment, of the can being of juice, beer, soda, etc., or of what type of juice, soda, etc. It can be observed that the greater the uncertainty, i.e., the events are less probable, the greater the average information is. The units of I are given by the value of constant k.

If $k = \frac{1}{\ln 2}$, the unit is the bit (binary digit); on the contrary, if we take $k = k_B = 1.38066x10^{-23}\,JK^{-1}$ where k_B is the Boltzmann's constant, the units are the JK^{-1}

Thus, if constant k in equation 1 is Boltzmann's constant, instead of speaking of information, we are talking about entropy, S. The previous experiment allowed us to arrive intuitively at the concept of entropy through the information.

Entropy, unfortunately, has been generally related to "disorder", and maybe it is the most polemical, mysterious and controversial magnitude in thermodynamics.

Thus, the increase of entropy would result in an increase of disorder or the destruction of the coherence present in an initial state, and because of this view, the Second Law would appear to be obvious or trivial.

Thus, the introduction of the formalism of the information theory into thermodynamics, through Shannon's equation, allows us to understand the concept of entropy as a synonym of information.

Then, we can formulate the fundamental postulate of the Second Law, as: "Natural systems create information during their evolution". From this postulate, the following corollaries derive:

a. Entropy, i.e., information, is different from energy, and it is created during the evolution of a system.
b. The same has a probabilistic nature.
c. It gives time a physical meaning.
d. It confers an irreversible nature upon natural pro-

cesses, since entropy is created, but it is not destroyed.

e. It measures the complexity of a system.

There are three levels of Information:

Syntactical: It gives the extent to which the signs that express the meaning for the receiver remove the uncertainty.

Semantic: It designates the meaning of the information.

Pragmatic: The purpose or usefulness of the information for the receiver.

Equation 1 only makes it possible to quantify the information at the syntactical level.

If all the events have the same probability *a priori*, $p_i = \Omega^{-1}$, equation 1 turns into

$$S = k\ln\Omega \quad (2)$$

Equation 2 is known as Boltzmann's equation, and was sculptured on his tomb in Vienna in 1906. The variable ? is known as complexions, or thermodynamic probability, and represents the number of microstates compatible with a given macrostate of the system. By applying the conditional extreme condition, and taking into account that $\sum p_i = 1$, it can be demonstrated that 2 is maximum at equilibrium. That is to say, the formalism of statistical thermodynamics rests on equation 2.

T. De Donder (1872-1957) established that during the evolution of a system, the entropy of the same might vary for two causes, one due to the exchange of the entropy of the system with the surroundings, δSe, or entropy flow, and the other due to the creation during the evolution thereof, δSi. Therefore, we have that the quantitative formulation of the Second Law according to De Donder is

$$dS_s = \delta S_e + \delta S_i \quad (3)$$

Hence, the entropy flow is given by

$$\delta S_e = \frac{\delta Q}{T} \quad (4)$$

Thus, the entropy flow may be positive, if it receives entropy from the surroundings, negative if it "gives away" entropy, and zero when the system is isolated. Therefore, the fundamental postulate of the Second Law can be formulated as δSi≥0.

Thermodynamic potentials. An evolutionary arrow of time of the natural systems

Thermodynamic potentials like other potential functions let us give a criterion of equilibrium and stability. The role of the thermodynamic potential in chemical thermodynamic is not too understandable. What is the difference between thermodynamic potentials and other potential functions of Physics?

Different from the common physical potentials, the thermodynamic potentials offer an evolutionary arrow of time[9] for the system under study depending on the constraints of it. This is in fact its main feature.

Thus, in order to develop the formalism to obtain a suitable potential to describe the system, the following steps should be considered:

a. To obtain the canonical equations
b. To identify the constraints
c. To develop a formal method (Legendre transformation) in order to obtain the thermodynamic potential
d. Formulation of an extremum Principle

Canonical equations

Canonical equations can be obtained from the "first principles", that is to say, from the joint expressions of the first and second laws of thermodynamics respectively. Thus, we have:

For the First Law: $\mathbf{dE = \delta Q - pdV}$ (5)

For the Second Law: $\mathbf{dS = \frac{\delta Q}{T} + \delta S_i}$ (6)

and we obtain the *canonical equations*

$$\mathbf{dE = TdS - pdV - T\delta\delta_i} \quad (7)$$

$$\mathbf{dS_s = \frac{1}{T}dE + \frac{p}{T}dV + \delta S_i} \quad (8)$$

Terms *E, T, S, V, p* represent the internal energy, temperature, entropy, volume, and pressure, and S_i is the entropy production due to irreversible processes. The first equation is known as the energetic representation of the system and the second one as the entropic representation.

Constraints

The conditions of the surroundings are constituted by those variables that identify the system under study. They allow us to choose the adequate potential function that provides an evolutive criterion of equilibrium and stability for a system. In the specific case of the above expressions, 7 and 8, we see that if the system is characterized by the variables S and V, the adequate function to describe the system is the inner energy, while if the variables are E and B, then the potential is the entropy of the system.

In order to define new potential functions, we will use a formal method, which will allow us, from the external conditions of the system, to define the thermodynamic potential.

Formal method. Legendre transformation.

We can apply the Legendre transformation either to canonical equations 7 and 8 respectively. The application thereof to the entropic representation, equality 8, generates functions that are of special interest in statistical thermodynamics.

In our case, we will use as a starting point for the development of the formalism, the energetic representation, equality 7. Thus, we have the following possibilities:

1. We add to both sides of equality 7 the term d(pV), and we obtain:

$$\mathbf{d(E+pV)=TdS_s-pdV-T\delta\delta_i+d(pV)}$$
$$\mathbf{d(E+pV)=TdS_s-pdV-T\delta\delta_i+pdV+Vdp} \qquad \mathbf{(9)}$$
$$\mathbf{d(E+pV)=TdS_s+Vdp-T\delta\delta_i}$$

Formally, we can identify the left side of equality 9 as *(E+pV)=H*. Thus, by making a substitution at 9, we have that:

$$\mathbf{dH=TdS_s+Vdp-T\delta\delta_i} \qquad \mathbf{(10)}$$

We realize as in this case that if the variables that represent the system are S and p, enthalpy is the adequate thermodynamic potential to describe it.

2. We subtract the term d(TS) from both sides of equality 7, and we obtain:

$$\mathbf{d(E-TS_s)=TdS_s-pdV-T\delta\delta_i-d(TS_s)}$$
$$\mathbf{d(E-TS_s)=TdS_s-pdV-T\delta\delta_i-S_sdT-TdS_s} \qquad \mathbf{(11)}$$
$$\mathbf{d(E-TS_s)=-S_sdT-pdV-T\delta\delta_i}$$

We can identify the left side of equality 11 as: *(E-TS$_s$)=F*, which we will name work function; thus, by making a substitution at 11, we get:

$$\mathbf{dF=-SdT-pdV-T\delta\delta_i} \qquad \mathbf{(12)}$$

In this case, if the variables representing the system, i.e., the constraints are T and V, the work function is the adequate thermodynamic potential to describe it.

3. Finally, we add d(pV) and subtract (TS) on both sides of equality 7 and the following is obtained:

$$\mathbf{d(E+pV-TS_S)=TdS_S-pdV-T\delta\delta_i+}$$
$$\mathbf{d(pV)-d(TS_S)} \qquad \mathbf{(13)}$$
$$\mathbf{d(E+pV+TS_s)=-SdT+Vdp-T\delta\delta_i}$$

Formally, we can identify the left side of equality 13 as $(E+pV-TS_S)\equiv G$, which we will call Gibbs free energy, thus, by making a substitution at 13, we get:

$$\mathbf{dG=-S_SdT+Vdp-T\delta\delta_i} \qquad \mathbf{(14)}$$

In this case, if the variables that represent the system, i.e., the constraints, are T and p, Gibbs free energy is the adequate thermodynamic potential to describe it.

Extremum Principle

It is formulated from the fundamental postulate of the Second Law[1]. Thus, by applying the extremum principle, for example in the case of *G* (see formula 4), we have that for *T* and *p* constants:

$dG_{Tp}=-T\delta S_i<0$, ***evolution***
$dG_{Tp}=0$, ***thermodynamic equilibrium***
$d^2G_{Tp}>0$, ***stability (minimum)***

Often, the criterion of evolution is confused with the spontaneity[10]. For this reason, it is suitable to clarify this misinterpretation.

ΔG AND REACTION SPONTANEITY

The use of Δ*G* to decide about the spontaneity or not of a reaction is a criterion generally accepted[10]. In fact, it is used to decide the direction of the process[11], for example, for the reaction $A=B$ if $\Delta G<0$ it means that the reaction goes from *A* to *B*, on the contrary if $\Delta G>0$ it occurs from *B* to *A*.

In order to illustrate our ideas, we will resort to Gibbs free energy, which is general, and independent of the potential chosen. Thus, we have to identify, in addition to the constraints, variables associated with the nature characteristic of system under study. For instance, in the case of a chemical reaction, besides the temperature and pressure, we must specify the amount of substance, $n_{k,\,of}$ each of the species involved in the reaction.

Thus, the functional relation of Gibbs free energy is sought, with these variables of the form:

$$G = G(T,p,n_1,n_2,\cdots,n_k)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{pn_k} dT + \left(\frac{\partial G}{\partial p}\right)_{Tn_k} dp + \qquad (15)$$

$$\sum_{i=1}^{k}\left(\frac{\partial G}{\partial n_k}\right)_{Tpn\neq n_k} dn_k$$

If we compare 15 with 14, we can identify the coefficients of 16, so we have that

$$\left(\frac{\partial G}{\partial T}\right)_{pn_k} = -S \text{ and } \left(\frac{\partial G}{\partial p}\right)_{pn_k} = V \qquad (16)$$

In the case of the third coefficient, $\left(\frac{\partial G}{\partial n_k}\right)_{Tpn\neq n_k}$ we know that it is a partial molar magnitude that we symbolize by the Greek letter μ_k and call chemical potential. The chemical potential represents physically what is capable of changing Gibbs free energy for the amount of substance involved in the chemical reaction, in other words, it represents the “motive power” of the reaction. Therefore, we have that

$$\left(\frac{\partial G}{\partial n_k}\right)_{Tpn\neq n_k} \equiv \mu_k \qquad (17)$$

By replacing 17 and 16 at 15, we get:

$$dG = -SdT + Vdp + \sum_{i=1}^{k}\mu_k dn_k \qquad (18)$$

If we compare 18 with 14, we see that:

$$-T\delta\delta_i = \sum_{i=1}^{k}\mu_k dn_k$$

$$\delta S_i = -\frac{1}{T}\sum_{i=1}^{k}\mu_k dn_k \qquad (19)$$

Thus, we arrive at a significant result; we can see how, for a chemical reaction, we can evaluate the creation of entropy during the process through the chemical potentials, thus, the problem comes down to knowing how to calculate the chemical potential of each of the species that are involved in the reaction.

Alternatively, for a chemical reaction we can introduce in the place of n_k, the degree of progress of the reaction ξ. In a way analogous to the procedure followed in 15, and considering 16, we obtain:

$$G = G(T,p,n_1,\xi)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{p\xi} dT + \left(\frac{\partial G}{\partial p}\right)_{T\xi} dp + \left(\frac{\partial G}{\partial \xi}\right)_{Tp} d\xi \qquad (20)$$

$$dG = -SdT + Vdp + \left(\frac{\partial G}{\partial \xi}\right)_{Tp} d\xi$$

The coefficient $\left(\frac{\partial G}{\partial \xi}\right)_{Tp}$ was identified by T. De Donder as

$$A = -\left(\frac{\partial G}{\partial \xi}\right)_{Tp} \qquad (21)$$

that he called Affinity. Affinity measures physically the change in Gibbs free energy by unit of degree of progress of the reaction. By replacing 21 at 20, we get

$$dG = -SdT + Vdp - Ad\xi$$

$$-T\delta\delta_i = -Ad\xi$$

$$\delta S_i = \frac{1}{T}Ad\xi \geq 0 \qquad (22)$$

$$A = T\frac{\delta S_i}{d\xi} \geq 0$$

Again, we have a significant result. We can see that the affinity of a reaction measures the creation of entropy of the process by unit of degree of progress of the reaction. Thus, we can see that through the affinity we can both calculate the creation of entropy for a chemical reaction and decide how far it will go, in other words, if affinity is positive, that means that the reaction goes up to that degree of progress, and in fact a higher yield can be achieved; if affinity is zero, it implies that the degree of progress corresponds with equilibrium and is in fact maximum, and finally, if affinity is negative, it means that the reaction cannot obtain that yield, since for such a degree of progress, the creation of entropy is negative, but it does not mean that the reaction does not occur.

Thus, the problem comes down to evaluating the affinity of a reaction. Thus, taking into account 19, and making a substitution at 22, we obtain that

$$A = -\sum_{i=1}^{k}\mu_K\frac{dn_k}{d\xi} = -\sum_{i=1}^{k}\mu_K\nu_k \qquad (23)$$

We can see how through equality 23 we can calculate the affinity of a reaction[9]. In general, we can represent the chemical reaction as an equality

$$\nu_A A_{(g)} + \nu_B B_{(g)} = \nu_C C_{(g)} + \nu_D D_{(g)}$$

where on the left are the reactants A, B, and on the right the products C, D. ν_k is the stoichiometric coefficient of species k. Physically, equality should not be interpreted as a symmetrical algebraic equality, since with the chemical equation such as we wrote it we are indicating that the process under study is the conversion of the reactants into products until reaching equilibrium.

Thus, the first step is the characterization of the chemical equilibrium. Considering that the constants T and p are the ideal behavior for the species involved in the reaction and the general condition of chemical equilibrium, it is established that

$$\sum_{i=1}^{k} \mu_K \nu_k = 0 \qquad (24)$$

By doing the algebraic sum and replacing explicitly the chemical potential expression, for each of the species, we obtain

$$\begin{aligned} &-\nu_A\left(\mu_A^{\theta}(T) + RT\ln p_A\right) - \nu_B\left(\mu_B^{\theta}(T) + RT\ln p_B\right) + \\ &\nu_C\left(\mu_C^{\theta}(T) + RT\ln p_C\right) + \nu_D\left(\mu_D^{\theta}(T) + RT\ln p_D\right) = 0 \end{aligned} \qquad (25)$$

Regrouping similar terms, we can rewrite equation 25 as

$$\nu_k \sum_{i=1}^{k} \ln p_k = \frac{-\sum_{i=1}^{k} \nu_k \mu_k^{\theta}(T)}{RT} \qquad (26)$$

In equality 26, we observe that the right term is a constant that only depends on the temperature of the system, by analogy with the left side, we will symbolize it as the logarithm of a constant K, thus, we can rewrite 26 of the form.

$$\nu_k \sum_{i=1}^{k} \ln p_k = \ln K_p(T) \qquad (27)$$

The relation 27 constitutes the quantitative expression of the Law of mass action. The same allows us to determine quantitatively the equilibrium constant of the system, the subindex p symbolizes that said relation is determined from the partial pressures evaluated at equilibrium.

Following the same line of thought, once the equilibrium is defined, as a particular case of attractor of the system, we use affinity to describe the evolution of a chemical reaction; thus, considering equality 23 and replacing the chemical potential expression, we have

$$A = -\sum_{i=1}^{k} \mu_K \nu_k = -\left\{ \sum_{i=1}^{k} \nu_k \mu_k^{\theta}(T) + RT \sum_{i=1}^{k} \nu_k \ln p_k \right\} \qquad (28)$$

By replacing 26 and 27 at 28, it is obtained that

$$A = RT\ln K_p - RT \sum_{i=1}^{k} \nu_k \ln p_k \geq 0 \qquad (29)$$

Equality 29 is known as a reaction isotherm. The same constitutes a general expression to evaluate the affinity of a chemical reaction. It can be observed how the right side of the equality has two terms, one in which the equilibrium constant appears, which is strictly related to equilibrium, and the other that is structurally similar to the equilibrium term, but it is connected with the partial pressures outside the equilibrium. It can be observed that when both terms become equal, affinity is zero, as expected, since we are in the presence of equilibrium.

In the same way, Lewis and Randall[12] identify the term $\left(\frac{\partial G}{\partial \xi}\right)_{Tp}$ as

$$\left(\frac{\partial G}{\partial \xi}\right)_{Tp} \equiv \Delta G \qquad (30)$$

Thus, the reaction isotherm can be rewritten as

$$\Delta G = -RT\ln K_p + RT\sum \nu_i \ln p_i \qquad (31)$$

That is to say, $\Delta G = -A$. We can see that the equilibrium constant K_p appears in the first term of the right side of the equation. It means that independently of the value of A or its equivalent ΔG, the reaction will take place because K_p is a positive constant and only depends on temperature. But the reaction will occur to a given extent of reaction according to the reaction conditions.

In this way, if we postulate that the reaction occurs spontaneously[10] if $\Delta G < 0$, it is a tautology and has nothing to do with spontaneity.

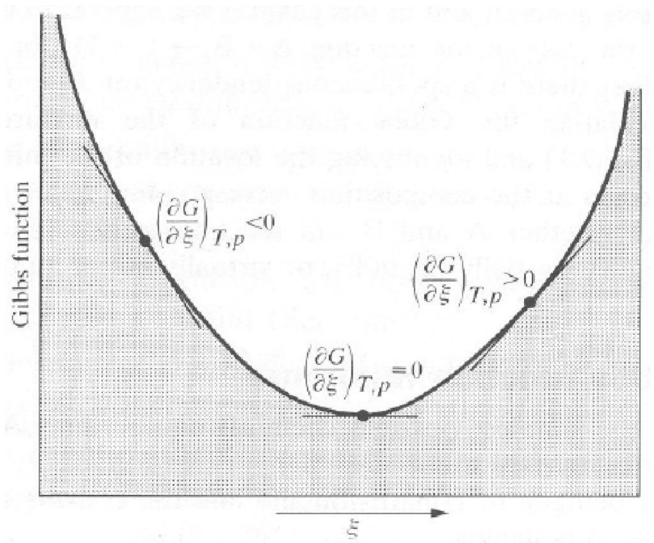


Figure 2 : Dependence of Gibbs free energy on the extent of reaction ξ

In order to clear up our ideas and as an example, the functional dependence of *G versus* ξt is shown in Figure 2.

Three main regions appear in Figure 2: the region where a minimum is attained on the curve corresponding to chemical equilibrium $A = 0$ ($\Delta G=0$), before the equilibrium is reached $\Delta G< 0$, and after that, $\Delta G> 0$. Then, evidently, the question that arises is: Could the system reach a certain extent of reaction for certain reaction conditions? In other words, will be possible to obtain a certain yield?

If for these reaction conditions, $\Delta G< 0$, then the answer is positive and is indicating that a higher yield is yet possible to obtain; if $\Delta G = 0$, the answer is positive too, but the maximum yield attainable is just at equilibrium. If $\Delta G> 0$, then the answer is negative; it is not possible to obtain such yield for these rate conditions; it does not mean that the reaction will not occur, but it will go to the contrary side[11].

Finally, we show an example, i.e., the formation of iodine acid in gas phase at 730,6 *K*. Figures 3 and 4 show the dependence of Gibbs free energy and affinity on the extent of reaction ξ. As it can be seen, the maximum yield corresponds possibly with ξ = 0.776 just at equilibrium. TABLE 1 shows the value of the affinity of reaction for different extents of reaction.

TABLE 1 : The value of affinity of the reaction for different extents of reaction.

Affinity [cal]	10073	7703	6128	4837	3652	2467	1175	0	-399	-2769
Reaction extent ξ [mole]	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.776	0.8	0.9

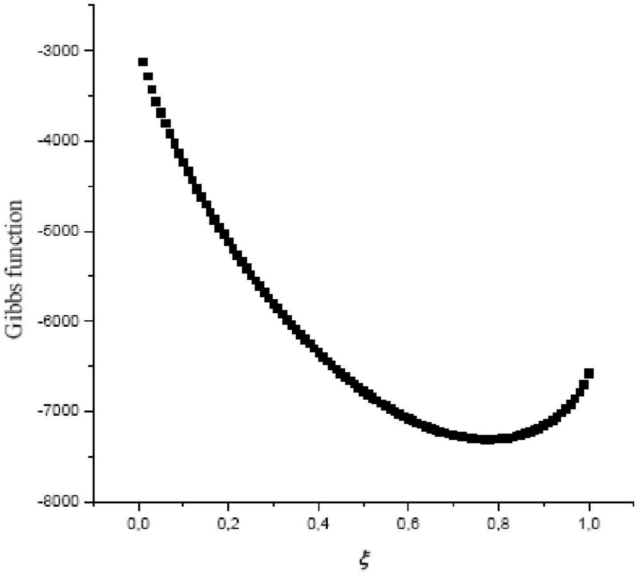


Figure 3 : Dependence of Gibbs free energy on the extent of reaction ξ for formation of iodine acid in gas phase at 730, 6 *K*

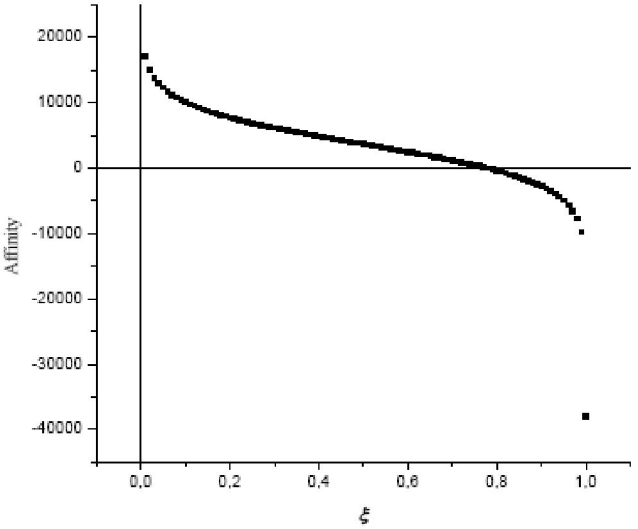


Figure 4 : Dependence of affinity *A* on the extent of reaction ξ for formation of iodine acid in gas phase at 730, 6 *K*

CONCLUSIONS

1. Entropy and information are equivalent ways of probabilistic quantification of the degree of uncertainty of a system.
2. Thermodynamic potentials contrary to other potential functions, offer an evolutionary arrow of time of the natural systems.

3. ΔG for a chemical reaction or its equivalent, the affinity gives a criterion about the extent of reaction that can be attained and the yield to be obtained.

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