

Utilisation du modèle IdEP-IdLA pour l'étude des processus agrégatifs en systèmes fermés

Use of the IdEP-IdLA model for the study of aggregative processes in closed systems

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ABSTRACT. As a consequence of the results obtained in a previous work, the study of aggregative reactions in closed gas systems is here addressed. Using the IdEP-IdLA mathematical model, the fundamental formulas that describe both autopoietic and heteropoietic aggregative processes are expounded. Particular emphasis is placed on the different roles that chance and necessity play according to the coding level of the processes themselves. The model responds coherently with the physical chemistry of reactions in a wide range of conditions, thus being accredited as a promising tool of theoretical investigation. In particular, in heteropoietic processes, the need to extend the entropic balance to coding agents (not only as order promoters but also as producers of compensatory entropy) is demonstrated.

RÉSUMÉ. En conséquence des résultats obtenus dans un article précédent, l'étude des réactions agrégatives dans les systèmes de gaz fermés est ici abordée. En utilisant le modèle mathématique IdEP-IdLA, les formules fondamentales qui décrivent à la fois les processus d'agrégation autopoïétique et hétéropoïétique sont exposées. Un accent particulier est mis sur les différents rôles que jouent le hasard et la nécessité selon le niveau de codage des processus eux-mêmes. Le modèle répond de manière cohérente avec la chimie physique des réactions dans un large éventail de conditions, étant ainsi accrédité comme un outil prometteur d'investigation théorique: en particulier, dans les processus hétéropoïétiques, la nécessité d'étendre l'équilibre entropique aux agents codants (comme promoteurs d'ordre mais aussi comme producteurs d'entropie compensatrice) est démontré.

KEYWORDS. Entropy, Mathematical modeling, Aggregative processes, Markov sources, Chance and necessity, Closed systems.

MOTS-CLÉS. Entropie, Modélisation mathématique, Processus agrégatifs, Sources de Markov, Hasard et nécessité, Systèmes fermés.

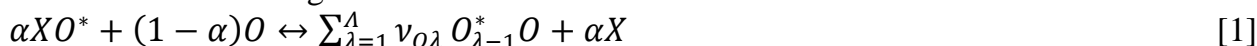
Foreword

The present study aims to use the IdEP-IdLA model [Ref.1] to simulate aggregative processes of heterogeneous gaseous systems when energy, but not matter, is exchanged toward the environment. For the benefit of an easier reading of the text, the fundamental hypotheses underlying the IdEP-IdLA model are summarized below:

- the ideal gas equation is accepted as valid
- ideal elementary particles (IdEP) and related aggregates (IdLA) have a linear frame, free of internal vibrations: consequently energy is iso-distributed on 5 degrees of freedom.

The formulas obtained in Ref.1 are also repropounded.

a) The reference exchange reaction is:



where

- α is the molar fraction of the *giver compounds*

- XO^* are the giver compounds consisting of one IdEP X , called the *grey particle*, and one IdEP O^* of ζ_{O^*} different colours, called the *active primary particle*
- O are the free IdEPs, called *passive primary particles*, of ζ_O different colours
- $O_{\lambda-1}^*O$ represents the generic IdLA of length λ (with Λ = maximum value of λ) variously composed of $\lambda - 1$ active primary particles and a single passive primary particle at the end of the sequence
- $\nu_{O\lambda}$ is the molar fraction of IdLAs of length λ .

b) E_b is the energy that must be supplied to a mole of giver compounds to break the internal bonds and E_f is the energy released by a mole of aggregates as a result of the formation of new bonds, both in [KJoule/mole] (ε_j^b , energy stored in each of the ζ_{O^*} different types of $X - O^*$ bonds in the giver compounds; ε_{jk}^f , energy stored in each of the $(\zeta_{O^*}^2 + \zeta_{O^*}\zeta_O)$ different types of $O^* - O^*$ and $O^* - O$ bonds within the IdLAs; l_j^b , the number of j -type bonds between ζ_{O^*} types of $X - O^*$ bonds globally present in the initial system; l_{jk}^f , the number of jk -type bonds between the $(\zeta_{O^*}^2 + \zeta_{O^*}\zeta_O)$ types of $O^* - O^*$ and $O^* - O$ bonds globally present in the IdLAs produced by a mole of giver compounds):

$$E_b = \frac{1}{\alpha} \sum_{j=1}^{\zeta_{O^*}} l_j^b \varepsilon_j^b \quad [2/a]$$

$$E_f = \frac{1}{\alpha} \sum_{j=1}^{\zeta_{O^*}} \sum_{k=1}^{(\zeta_{O^*} + \zeta_O)} l_{jk}^f \varepsilon_{jk}^f \quad [2/b]$$

c) h_O is the entropy of the *descriptor* $[p_i]$ of the population of passive primary IdEPs; h_{XO^*} is the entropy of the *descriptor* $[p_j]$ of giver compounds; h_X is the entropy of the *descriptor* of grey particles; h_{IdLA} is the entropy of the IdLA *descriptor*:

$$h_O = \sum_{i=1}^{\zeta_O} p_i \ln \frac{1}{p_i} = \gamma_O \ln \zeta_O \quad (\gamma_O, \text{ disequilibrium factor of } [p_i]) \quad [3/a]$$

$$h_{XO^*} = \sum_{j=1}^{\zeta_{O^*}} p_j \ln \frac{1}{p_j} = \gamma_{O^*} \ln \zeta_{O^*} \quad (\gamma_{O^*}, \text{ disequilibrium factor of } [p_j]) \quad [3/b]$$

$$h_X = 0 \quad (\text{as grey particles are all of the same colour}) \quad [3/c]$$

$$h_{IdLA} = (1 - \eta) \left[h_O + \frac{\alpha}{1 - \alpha} h_{XO^*} + \frac{1}{1 - \alpha} h_\alpha \right] \quad [3/d]$$

$$(\eta, \text{ coding factor ranging from 0 to 1 and } h_\alpha = \alpha \ln \frac{1}{\alpha} + (1 - \alpha) \ln \frac{1}{1 - \alpha})$$

d) ρ is the *allocation inertia* in $[\text{m}^2 \text{Kg}^{5/2}]$ where μ and δ respectively are the mass in [Kg] and linear dimension in [m] of the IdEP:

$$\rho = \delta^2 \sqrt{\mu^5} \quad [4/a]$$

e) ν_O is the volume of the *allocation cell* of the primary passive particles; ν_{XO^*} is the volume of the *allocation cell* of the giver compounds; ν_{IdLA} is the volume of the *allocation cell* of IdLAs, where p_λ is the probability that the generic IdLA has length λ ; all of them in $[\text{m}^3]$:

$$\nu_O = \nu_X = \nu_{IdEP} = \frac{2,85685 \cdot 10^{-112}}{\rho} \quad [4/b]$$

$$\nu_{XO^*} = 2^{-\frac{9}{2}} \nu_{IdEP} \quad \ln \nu_{XO^*} = \ln \nu_{IdEP} - \frac{9}{2} \ln 2 \quad [4/c]$$

$$\nu_{IdLA} = \prod_{\lambda=1}^{\Lambda} (\nu_{IdEP} \lambda^{-\frac{9}{2}})^{p_\lambda} \quad \ln \nu_{IdLA} = \ln \nu_{IdEP} - \frac{9}{2} \sum (\alpha) \quad [4/d]$$

$$(\text{where } \sum (\alpha) = \sum_{\lambda=1}^{\Lambda} p_\lambda \ln \lambda)$$

- f) S_O , S_{XO^*} , S_X , S_{IdLA} and S are the entropies of the reactants, of the products and of the mixture respectively in [Joule/°Kmole]. All of them, as a function of the extent of reaction ξ ($R = 8,314463$ Joule/°Kmole is the gas constant; $n_A = 6,0221409 \cdot 10^{23}$ is the number of Avogadro; T is the absolute temperature, in [°K]; V is the molar volume in [m^3]):

$$S_O(\xi) = \frac{5}{2}R(1-\xi)(1-\alpha)\ln T + R(1-\xi)(1-\alpha) \left[\ln \frac{V}{(1-\xi)(1-\alpha)n_A} - \ln(v_O) + 1 + h_O \right] \quad [5/a]$$

$$S_{XO^*}(\xi) = \frac{5}{2}R(1-\xi)\alpha\ln T + R(1-\xi)\alpha \left[\ln \frac{V}{(1-\xi)\alpha n_A} - \ln(v_{XO^*}) + 1 + h_{XO^*} \right] \quad [5/b]$$

$$S_X(\xi) = \frac{5}{2}R\xi\alpha\ln T + R\xi\alpha \left[\ln \frac{V}{\xi\alpha n_A} - \ln(v_X) + 1 + h_X \right] \quad [5/c]$$

$$S_{IdLA}(\xi) = \frac{5}{2}R\xi(1-\alpha)\ln T + R\xi(1-\alpha) \left[\ln \frac{V}{\xi(1-\alpha)n_A} - \ln(v_{IdLA}) + 1 + h_{IdLA} \right] \quad [5/d]$$

$$S(\xi) = S_O(\xi) + S_{XO^*}(\xi) + S_X(\xi) + S_{IdLA}(\xi) \quad [5]$$

- g) ΔS_R is the reaction entropy in [Joule/°Kmole] (ξ_0 , extent of reaction at the equilibrium):

$$\begin{aligned} \Delta S_R = R \left[\xi_0 \ln \frac{1}{\xi_0} + (1-\xi_0) \ln \frac{1}{(1-\xi_0)} \right] + R\xi_0(1-\eta)h_\alpha + \\ + R\xi_0(1-\alpha) \left[\frac{9}{2} \sum_{\lambda=1}^A p_\lambda \ln \lambda - \eta \gamma_O \ln \zeta_O \right] - R\xi_0\alpha \left[\frac{9}{2} \ln 2 + \eta \gamma_{O^*} \ln \zeta_{O^*} \right] \end{aligned} \quad [6]$$

- h) H_O , H_{XO^*} , H_X , H_{IdLA} and H are the enthalpies of the reactants, of the products and of the mixture respectively in [KJoule/mole]. All of them as a function of the extent of reaction ξ ($\Delta E = E_b - E_f$, molar energy balance)

$$H_O(\xi) = \frac{7}{2}(1-\alpha)(1-\xi)RT \quad [7/a]$$

$$H_{XO^*}(\xi) = \frac{7}{2}\alpha(1-\xi)RT + \alpha\xi E_b \quad [7/b]$$

$$H_X(\xi) = \frac{7}{2}\alpha\xi RT \quad [7/c]$$

$$H_{IdLA}(\xi) = \frac{7}{2}\xi(1-\alpha)RT - \alpha\xi E_f \quad [7/d]$$

$$H(\xi) = \frac{7}{2}RT + \alpha\xi \Delta E \quad [7]$$

- i) ΔH_R is the reaction enthalpy in [KJoule/mole]:

$$\Delta H_R = H(\xi_0) - H(0) = \alpha\xi_0 \Delta E \quad [8]$$

- j) Derivatives of entropies in [Joule/°Kmole] with respect to the extent of reaction are:

$$\frac{dS_O}{d\xi} = -R(1-\alpha) \left[\frac{5}{2} \ln T + \ln \frac{V}{(1-\xi)(1-\alpha)n_A} - \ln(v_O) + h_O \right] \quad [9/a]$$

$$\frac{dS_{XO^*}}{d\xi} = -R\alpha \left[\frac{5}{2} \ln T + \ln \frac{V}{(1-\xi)\alpha n_A} - \ln(v_{XO^*}) + h_{XO^*} \right] \quad [9/b]$$

$$\frac{dS_X}{d\xi} = R\alpha \left[\frac{5}{2} \ln T + \ln \frac{V}{\xi\alpha n_A} - \ln(v_X) + h_X \right] \quad [9/c]$$

$$\frac{dS_{IdLA}}{d\xi} = R(1-\alpha) \left[\frac{5}{2} \ln T + \ln \frac{V}{\xi(1-\alpha)n_A} - \ln(v_{IdLA}) + h_{IdLA} \right] \quad [9/d]$$

$$\frac{dS}{d\xi} = \frac{dS_O}{d\xi} + \frac{dS_{XO^*}}{d\xi} + \frac{dS_X}{d\xi} + \frac{dS_{IdLA}}{d\xi} = \quad [9]$$

$$= R \left[\left(\ln \frac{1}{\xi} - \ln \frac{1}{1-\xi} \right) + (1-\alpha) \left(\frac{9}{2} \Sigma(\alpha) - \eta h_O \right) - \alpha \left(\frac{9}{2} \ln 2 + \eta h_{XO^*} \right) + (1-\eta)h_\alpha \right]$$

- k) $A(\xi)$ is the affinity:

$$A(\xi) = T \frac{dS}{d\xi} - \alpha \Delta E \quad [10]$$

1) λ^* is the *weighted average* of the IdLAs *length*, regardless of the aggregation rule:

$$\lambda^* = \frac{1}{1-\alpha} \quad [11]$$

1. Random autopoietic aggregations

Let the system of reactants and products described by [1] be a closed one. This means that exchanges toward the environment (which is supposed to be maintained at constant pressure and temperature) involve energy but not matter. Let us also suppose that the binding energies in the given compounds are equal to each other ($\varepsilon_j^b = \varepsilon^b$) and the same for the binding energies in IdLAs ($\varepsilon_{jk}^f = \varepsilon^f$). Then, in this case [2/a] and [2/b] take the following forms:

$$E_b = \frac{\varepsilon^b}{\alpha} \sum_{j=1}^{\zeta_{O^*}} l_j^b = \frac{\varepsilon^b}{\alpha} \alpha n_A = \varepsilon^b n_A \quad [12/a]$$

$$E_f = \frac{\varepsilon^f}{\alpha} \sum_{j=1}^{\zeta_{O^*}} \sum_{k=1}^{(\zeta_{O^*} + \zeta_O)} l_{jk}^f = \frac{\varepsilon^f}{\alpha} \alpha n_A = \varepsilon^f n_A \quad [12/b]$$

so that the molar energy balance of the reaction is:

$$\Delta E = E_b - E_f = n_A(\varepsilon^b - \varepsilon^f) \quad [13]$$

In autopoietic mode the coupling between particles can then take place only in a random way¹ such that the sequencer of the IdEP-IdLA model, providing particles assembly, operates without memory and draws at random from the primary particle tank: therefore in [3/d] we have $\eta = 0$. Then, due to the total randomness in coupling, the probability p_λ that a generic aggregate is of length λ (independently of the colour sequence) can be easily calculated. In fact, the probability that the sequencer forms an aggregate with length λ , is that it proposes $\lambda - 1$ active particles (with a presentation probability that, regardless of colours, is equal to α) and a single inactive closing particle (with a presentation probability that, regardless of colours, is equal to $1 - \alpha$). Therefore

$$p_\lambda = \alpha^{\lambda-1}(1 - \alpha) \quad [14]$$

which leads to the populations indicatively represented in Fig.1. The table shows also the average lengths $\lambda^*(\alpha)$ of each population, weighted according to the probabilities p_λ ²:

$$\lambda^* = \sum_{\lambda=1}^A p_\lambda \lambda = (1 - \alpha) \sum_{\lambda=1}^A \alpha^{\lambda-1} \lambda = \frac{1}{1-\alpha} \quad [15]$$

which in this specific case confirms [11], obtained through a more general reasoning. Consequently, the volume of the allocation cell of the IdLA mixture (whose percentage composition is supposed to be constant when ξ varies) and its logarithm assume, on the basis of [4/d], the forms numerically calculable:

$$v_{IdLA} = \prod_{\lambda=1}^A (v_{IdEP} \lambda^{-\frac{9}{2}})^{(1-\alpha)\alpha^{\lambda-1}} \quad [16/a]$$

¹ This is a purely theoretical hypothesis, not very close to the reality of ordinary chemical reactions but far from being inadequate, as will be seen later, to constitute a useful starting point for the study of codified aggregations.

² The series $\sum_{i=1}^{\infty} i\alpha^i = \alpha/(1 - \alpha)^2$ is recalled here.

$$\ln v_{IdLA} = \ln v_{IdEP} - \frac{9}{2}(1 - \alpha) \sum_{\lambda=1}^{\Lambda} \alpha^{\lambda-1} \ln \lambda \quad [16/b]$$

α	λ					λ^*
	1	2	3	4	>4	
0,00	100,00%	0,00%	0,00%	0,00%	0,00%	1,000
0,05	95,00%	4,75%	0,24%	0,01%	0,00%	1,053
0,10	90,00%	9,00%	0,90%	0,09%	0,01%	1,111
0,15	85,00%	12,75%	1,91%	0,29%	0,05%	1,176
0,20	80,00%	16,00%	3,20%	0,64%	0,16%	1,250
0,25	75,00%	18,75%	4,69%	1,17%	0,39%	1,333
0,30	70,00%	21,00%	6,30%	1,89%	0,81%	1,429
0,35	65,00%	22,75%	7,96%	2,79%	1,50%	1,538
0,40	60,00%	24,00%	9,60%	3,84%	2,56%	1,667
0,45	55,00%	24,75%	11,14%	5,01%	4,10%	1,818
0,50	50,00%	25,00%	12,50%	6,25%	6,25%	2,000
0,55	45,00%	24,75%	13,61%	7,49%	9,15%	2,222
0,60	40,00%	24,00%	14,40%	8,64%	12,96%	2,500
0,65	35,00%	22,75%	14,79%	9,61%	17,85%	2,857
0,70	30,00%	21,00%	14,70%	10,29%	24,01%	3,333
0,75	25,00%	18,75%	14,06%	10,55%	31,64%	4,000
0,80	20,00%	16,00%	12,80%	10,24%	40,96%	5,000
0,85	15,00%	12,75%	10,84%	9,21%	52,20%	6,667
0,90	10,00%	9,00%	8,10%	7,29%	65,61%	10,000
0,95	5,00%	4,75%	4,51%	4,29%	81,45%	20,000

Figure 1. Random aggregation: IdLA populations as a function of α

In other terms, $\Sigma(\alpha)$ in [4/d] takes the form

$$\Sigma_0(\alpha) = (1 - \alpha) \sum_{\lambda=1}^{\Lambda} \alpha^{\lambda-1} \ln \lambda \quad [17]$$

which converges³ on the values shown in Fig.2.

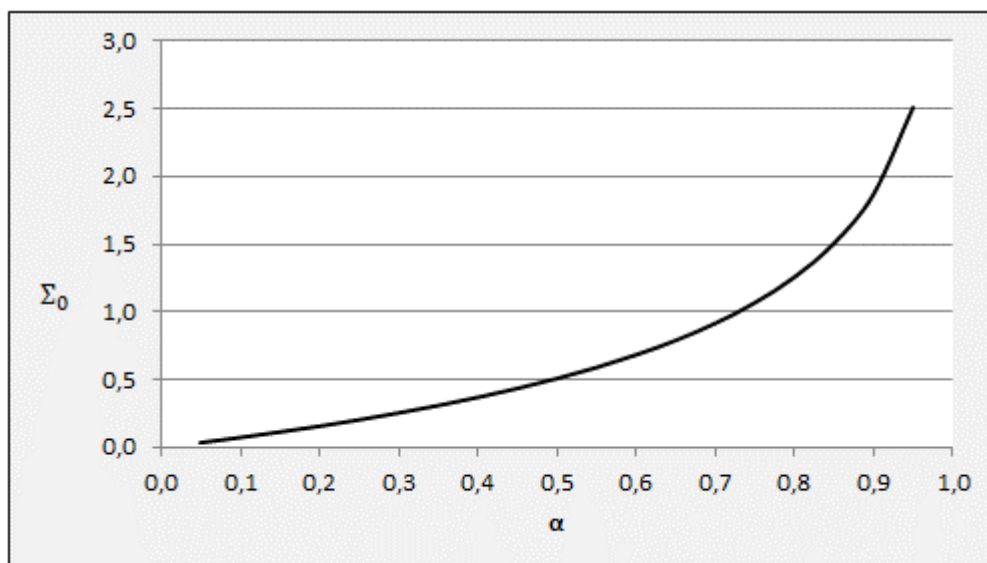


Figure 2. Random aggregation: $\sum_{\lambda=1}^{\Lambda} p_{\lambda} \ln \lambda$ as a function of α

³ The value of Λ increases significantly with α : for $\alpha = 0,05$ the sum converges on a stable value of the fourth significant digit already with $\Lambda = 5$ while for $\alpha = 0,95$ the same degree of precision is obtained with $\Lambda = 160$.

We have now all the elements needed to carry out the calculations with the formulas recalled in the foreword. It is sufficient to define:

- temperature T and pressure p
- allocation inertia ρ of the reference IdEP, combining mass μ and dimension δ
- entropy h_o of the descriptor $[p_i]$, combining the number of colours ζ_o and the disequilibrium factor γ_o of passive primary particles
- entropy h_{o^*} of the descriptor $[p_j]$, combining the number of colours ζ_{o^*} and the disequilibrium factor γ_{o^*} of active primary particles
- molar fraction α of the giver compounds
- molar energy balance ΔE .

It is therefore a matter of choosing appropriate numerical values for each of these parameters. First of all, as the main purpose of this work is the study of aggregative processes of biological interest, we can assume that temperature and pressure vary very little: indeed we can certainly adopt the standard values of these quantities ($T=298,15$ °K and $p=101.325$ Pa; consequently $V=0,024465$ m³/mole)⁴ as constant and invariable.

Secondly, for the same reason stated above we can limit the investigation to values of the allocation inertia ρ ranging between 10^{-81} and 10^{-83} [m²Kg^{5/2}]. As clearly shown in Fig.3, such values largely cover ranges of δ and μ that can be considered pertaining to elementary components of biological interest. However, it is appropriate to consider that the allocation inertia is a relatively unimportant parameter since, although it affects the absolute entropy (through the volumes of the allocation cells as clearly shown by [5]) it does not influence the derivative of the entropy (as shown in [9]), neither affinity (as shown in [10]), nor reaction entropy (as shown in [6]).

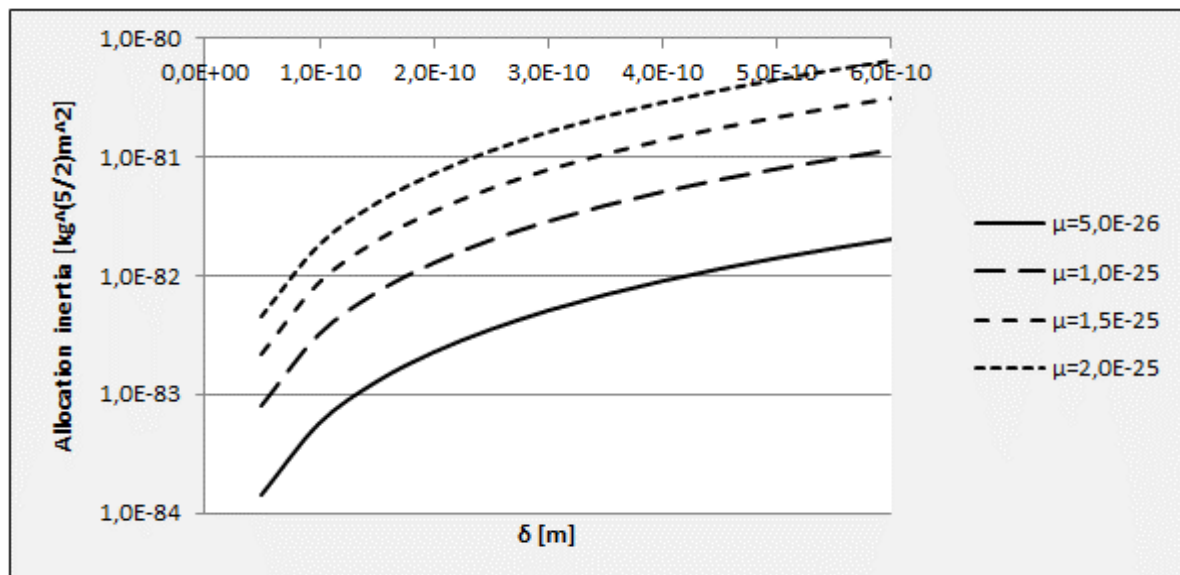


Figure 3. Trend of $\rho(\delta)$ for different values of μ

⁴ It is worth remembering that a temperature close to the environmental conditions is a necessary condition for the validity of the absolute entropy expression used in the calculations. Only at these thermal levels can the vibrational contribution to entropy be considered negligible and therefore the Markovian expression obtained in [Ref.1] (on which construction of the whole model is based) is valid.

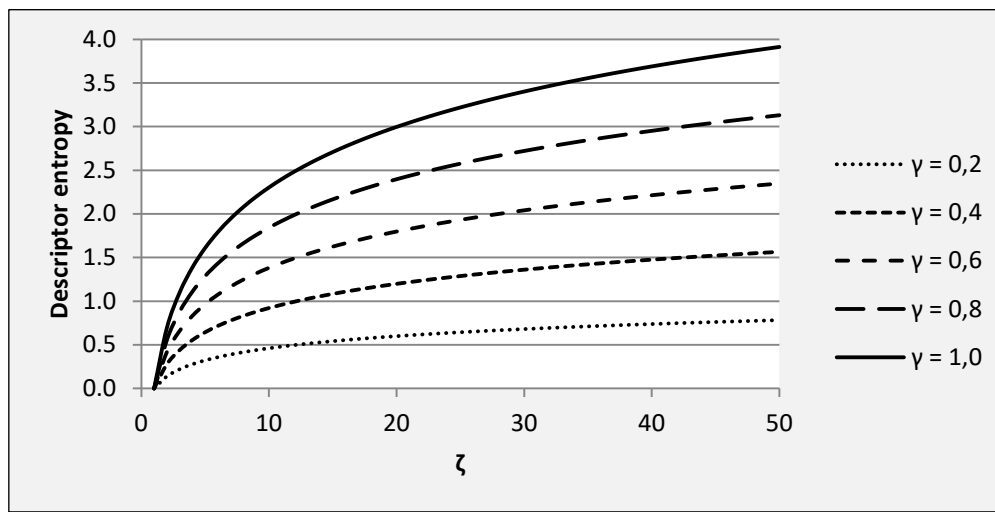


Figure 4. Trends of entropy $h(\zeta)$ of a generic descriptor for different values of γ

Thirdly, as far as entropy h of a generic descriptor is involved, the number of colours ζ and the disequilibrium factors γ play⁵ as shown in Fig.4. But even these parameters are relatively unimportant in the case of random aggregation since, once again, if on the one hand they influence the absolute entropy, on the other they do not affect either its derivative or affinity. Anyway, most entropy calculations are carried out with $h_0 = h_{x0^*} = 1,5$, a value which, in any case, covers a rather wide range of μ and δ combinations: this choice is also justified in the light of the sensitivity analysis that will be carried out in the following paragraph when the coded aggregations will be examined (see Fig.17).

⁵ Note that entropy is annulled both for $\gamma = 0$ (whatever the value of ζ) and for $\zeta = 1$ whatever the value of γ : these are in fact two different ways to translate the same information into mathematical terms, namely that the system is made up of indistinguishable particles.

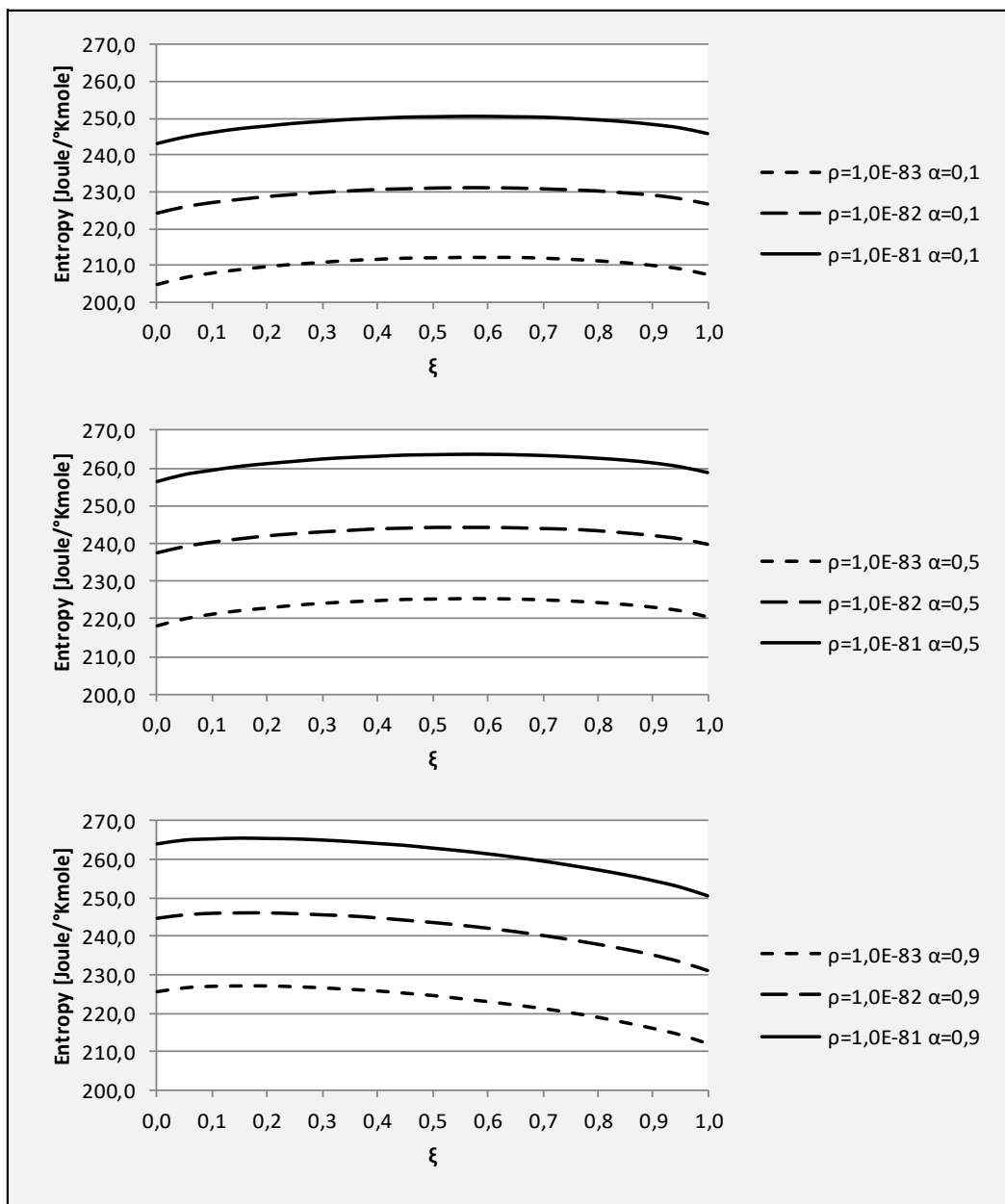


Figure 5. Random aggregation: trends of $S(\xi)$ for different values of ρ and α ($h_o = h_{xo^*} = 1,5$)

Given the above, the table of Fig.5 shows the trend of $S(\xi)$ when α and ρ vary, while $\zeta_o, \gamma_o, \zeta_o^*$ and γ_o^* are such that $h_o = h_{xo^*} = 1,5$. They give the following indications:

- in all the cases explored, entropy initially increases to reach a maximum and then decreases: $S(\xi)$ has a stable maximum around $\xi = 0,6$ for $\alpha \leq 0,5$ while for $\alpha > 0,5$ the maximum moves towards decreasing values of ξ . The aggregative process, therefore, implies an initial increase of the disorder and a subsequent recovery of more ordered internal structures. In particular for high concentrations of giver compounds the phase of the initial disorder is short while the subsequent construction of the order is consistent
- all other conditions being equal, the allocation inertia ρ of the reference IdEP has a significant influence on the initial entropy value and therefore on the value of $S(\xi)$. In particular, the greater the inertial characteristics of the IdEP, the greater is the system's entropy in all phases of the aggregative process. This is because, as already pointed out in Ref.1, heavier particles can access a greater number of energy levels, determining an increase in the number of microstates that are physically possible, as provided by statistical mechanics

- conversely, the allocation inertia ρ does not affect the shape of $S(\xi)$, determining only vertical translations of the graphs. In particular it does not affect the maximum which depends exclusively on α . And, in fact, ΔS_R does not depend on ρ , as already highlighted above.

Although not evident from the graphs, it should finally be noted that, according to [9], it is always:

$$\text{a) } \lim_{\xi \rightarrow 0} \frac{dS}{d\xi} = +\infty \quad \text{b) } \lim_{\xi \rightarrow 1} \frac{dS}{d\xi} = -\infty \quad [18]$$

Enthalpy $H(\xi)$ depends only on α and on the molar energy balance ΔE according to [7]. Its graphic representation (see Fig.6 in the particular case of $\alpha = 0,5$) is a rectilinear segment with its origin in $H(0) = (7/2)RT$ and angular coefficient $\alpha\Delta E$. In the case of exothermic reactions, particularly of our interest, the slope is negative.

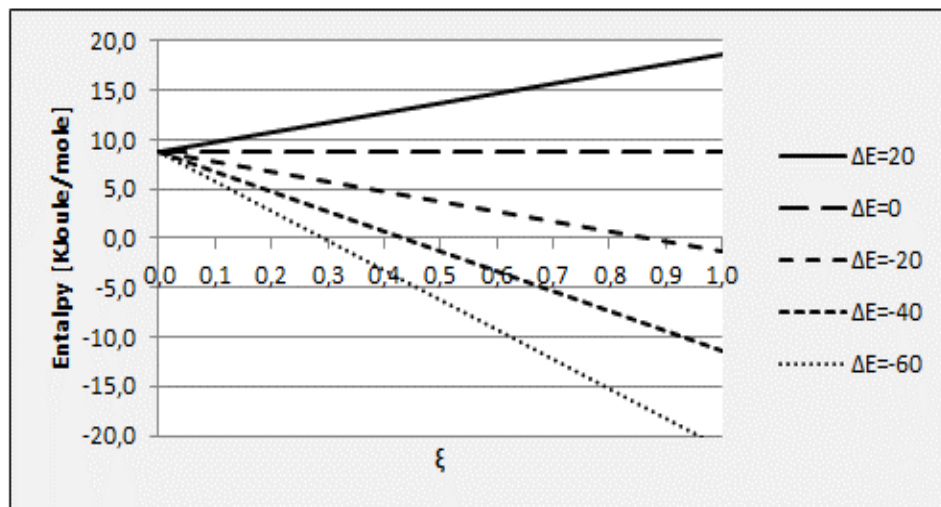


Figure 6. Random aggregation: trends of $H(\xi)$ for different values of ΔE with $\alpha = 0,5$

As a consequence of the trends of $S(\xi)$ and $H(\xi)$ just highlighted, the free energy $G(\xi) = H(\xi) - TS(\xi)$ can only have a shape with the convexity facing upwards in the whole range $0 \leq \xi \leq 1$. Moreover, due to the presence of a maximum in $S(\xi)$, $G(\xi)$ has a minimum in correspondence with the extent of reaction ξ_0 for which affinity expressed by [10] is zero. This happens when

$$\frac{dS}{d\xi} = \frac{\alpha\Delta E}{T} \quad [19]$$

The graphs in Fig.7 show the results of the calculations in the case of exothermic reactions (for $\rho = 10^{-82}$ and $h_o = h_{xo^*} = 1,5$ as previously specified).

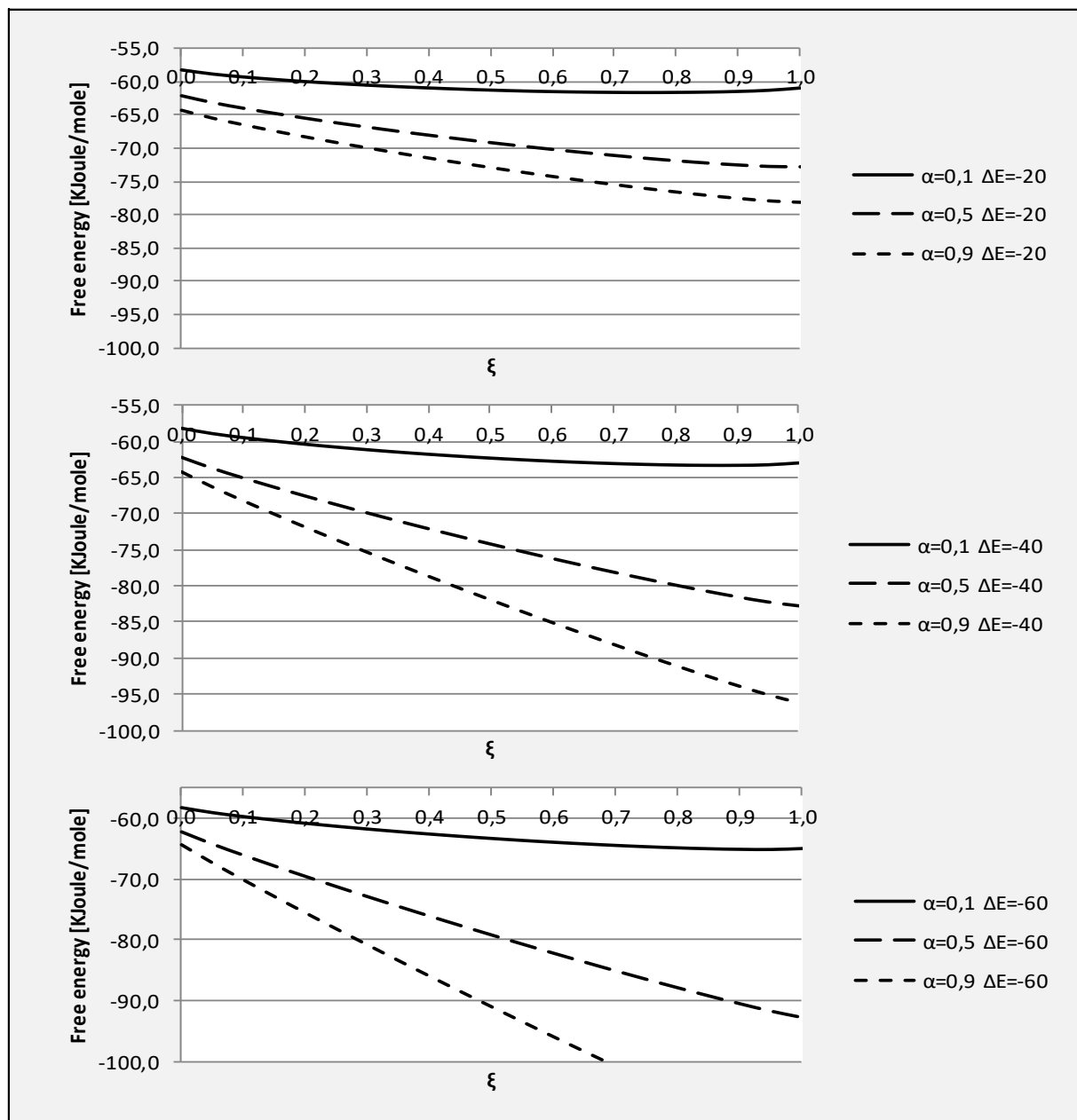


Figure 7. Random aggregation: trends of $G(\xi)$ for different values of α and ΔE
 $(\rho = 10^{-82}$ and $h_o = h_{XO^*} = 1,5)$

They give rise to the following considerations:

- with the same energy balance ΔE , the higher the α concentration of the given compounds, the lower the free energy $G(\xi)$; similarly, with the same α the free energy reduces as ΔE increases
- for relatively small values of the $\alpha\Delta E$ product ($|\alpha\Delta E| < 5$) the free energy $G(\xi)$ reaches the minimum in correspondence to the values of the extent of reaction quite far from 1. As the $\alpha\Delta E$ product increases, the minimum of $G(\xi)$ is pushed more and more toward the right: in this regard it is worth specifying that, for the [18/b], there is always a $\xi_0 < 1$ such as to satisfy [19], whatever the value of $\alpha\Delta E$.

And now we come to the calculation of the reaction functions ΔS_R , ΔH_R and ΔG_R to determine which the extent of reaction at equilibrium ξ_0 must be known. This is obtained by solving numerically the equation $A(\xi) = 0$ where the expression of affinity is given by [10]. In this case, as already mentioned, both the allocation inertia ρ and the entropies h_o and h_{XO^*} of the reagent descriptors are irrelevant. Basically, only two parameters contribute: α and ΔE . The results of the calculations are summarized in the table of Fig. 8 where for each combination of α (ranging between

0,1 and 0,9) and of ΔE (ranging between -60 and +20 KJoule/mole) the values of ξ_0 , ΔS_R , ΔH_R and ΔG_R are displayed. Examination of the results, together with the analysis of graphs in Fig.9 and in Fig.10, reveals the following:

- in the case of endothermic reaction the aggregative process is largely incomplete: it starts and runs for a while only if the α concentration of the giver compounds is low. As α grows, ξ_0 decreases until, for higher α values the reaction hardly even starts. Consequently, with the growth of α the reaction entropy, the reaction enthalpy and the reaction free energy tend asymptotically to zero: ΔS_R always remaining positive and ΔG_R always remaining negative
- also for $\Delta E = 0$ the reaction proceeds at a slower rate the higher is the value of α and even in this case any level of aggregation always implies an increase of the overall disorder in the final system. The maximum reaction development is recorded for a value of α just under 0,3 with an extent of reaction to equilibrium equal to about 0,62
- in the case of exothermic reactions, the higher the dissipation of thermal energy in the environment, the more the process tends to develop completely. However, the reaction entropy becomes negative only for relatively high values of α : in particular, only when $\alpha > 0,6$ is the final system more ordered than the initial system. The free energy of reaction, always negative, has a minimum that moves to the right (towards high values of α) the more energetic the reaction is.

It therefore appears evident that both a high exothermicity of the reaction [1] and a high concentration of giver compounds play in favour of a complete development of the aggregation process. From the analysis of the data shown in Fig.8, those processes for which $\Delta E \leq -30$ KJoule/mole and $\alpha \geq 0,7$ can be considered complete over 99.9%. It may be useful to observe that, in these cases, the expressions of the reaction functions for a random aggregation take the following simplified forms:

$$\Delta S_R = R \left[\frac{9}{2} (1 - \alpha) \Sigma_0(\alpha) - \frac{9}{2} \alpha \ln 2 + h_\alpha \right] \quad [20]$$

$$\Delta H_R = \alpha \Delta E \quad [21]$$

$$\Delta G_R = \Delta H_R - T \Delta S_R = \Delta H_R - RT \left[\frac{9}{2} (1 - \alpha) \Sigma_0(\alpha) - \frac{9}{2} \alpha \ln 2 + h_\alpha \right] \quad [22]$$

α	Reaction function	ΔE								
		20	10	0	-10	-20	-30	-40	-50	-60
0,1	$\xi_0 =$	0,379	0,477	0,577	0,671	0,754	0,821	0,873	0,911	0,939
	$\Delta S_R =$	6,499	6,990	7,159	7,005	6,592	6,033	5,426	4,856	4,342
	$\Delta H_R =$	0,758	0,477	0,000	-0,671	-1,508	-2,463	-3,492	-4,555	-5,634
	$\Delta G_R =$	-1,180	-1,607	-2,134	-2,759	-3,473	-4,262	-5,110	-6,003	-6,929
0,2	$\xi_0 =$	0,236	0,410	0,609	0,777	0,887	0,946	0,975	0,989	0,995
	$\Delta S_R =$	5,411	7,135	7,804	7,270	6,195	5,227	4,558	4,141	3,922
	$\Delta H_R =$	0,944	0,820	0,000	-1,554	-3,548	-5,676	-7,800	-9,890	-11,940
	$\Delta G_R =$	-0,669	-1,307	-2,327	-3,722	-5,395	-7,234	-9,159	-11,125	-13,109
0,3	$\xi_0 =$	0,125	0,324	0,617	0,844	0,948	0,984	0,995	0,998	$\rightarrow 1$
	$\Delta S_R =$	3,628	6,522	7,981	6,948	5,460	4,585	4,209	4,060	4,029
	$\Delta H_R =$	0,750	0,972	0,000	-2,532	-5,688	-8,856	-11,940	-14,976	-17,982
	$\Delta G_R =$	-0,332	-0,972	-2,379	-4,604	-7,316	-10,223	-13,195	-16,186	-19,183
0,4	$\xi_0 =$	0,057	0,266	0,604	0,901	0,979	0,996	0,999	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	2,018	6,142	7,700	7,175	5,735	5,197	5,045	4,999	4,986
	$\Delta H_R =$	0,456	1,064	0,000	-3,604	-7,830	-11,947	-15,984	-19,996	-23,999
	$\Delta G_R =$	-0,146	-0,767	-2,296	-5,743	-9,539	-13,497	-17,488	-21,486	-25,486
0,5	$\xi_0 =$	0,023	0,149	0,569	0,908	0,987	0,998	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	0,963	3,842	6,990	4,639	2,843	2,412	2,314	2,299	2,325
	$\Delta H_R =$	0,230	0,745	0,000	-4,540	-9,870	-14,970	-19,995	-24,999	-29,988
	$\Delta G_R =$	-0,057	-0,401	-2,084	-5,923	-10,718	-15,689	-20,685	-25,685	-30,681
0,6	$\xi_0 =$	0,008	0,084	0,507	0,921	0,992	0,999	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	0,389	2,419	5,887	2,525	0,633	0,295	0,253	0,248	0,247
	$\Delta H_R =$	0,096	0,504	0,000	-5,526	-11,904	-17,987	-23,999	-30,000	-36,000
	$\Delta G_R =$	-0,020	-0,217	-1,755	-6,279	-12,093	-18,075	-24,074	-30,074	-36,074
0,7	$\xi_0 =$	0,003	0,041	0,416	0,923	0,995	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	0,138	1,307	4,476	-0,337	-2,533	-2,786	-2,807	-2,809	-2,809
	$\Delta H_R =$	0,035	0,287	0,000	-6,461	-13,930	-20,994	-27,999	-35,000	-42,000
	$\Delta G_R =$	-0,006	-0,103	-1,335	-6,361	-13,175	-20,163	-27,162	-34,162	-41,162
0,8	$\xi_0 =$	0,000	0,016	0,296	0,914	0,996	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	0,000	0,567	2,919	-4,142	-6,953	-7,182	-7,198	-7,199	-7,199
	$\Delta H_R =$	0,000	0,128	0,000	-7,312	-15,936	-23,995	-32,000	-40,000	-48,000
	$\Delta G_R =$	0,000	-0,041	-0,870	-6,077	-13,863	-21,854	-29,854	-37,854	-45,854
0,9	$\xi_0 =$	0,000	0,005	0,162	0,879	0,996	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$	$\rightarrow 1$
	$\Delta S_R =$	0,000	0,193	1,470	-8,940	-13,389	-13,651	-13,660	-13,660	-13,660
	$\Delta H_R =$	0,000	0,045	0,000	-7,911	-17,928	-26,997	-36,000	-45,000	-54,000
	$\Delta G_R =$	0,000	-0,013	-0,438	-5,245	-13,936	-22,927	-31,927	-40,927	-49,927

Figure 8. Random aggregation: values of ξ_0 , ΔS_R , ΔH_R and ΔG_R as a function of α and ΔE

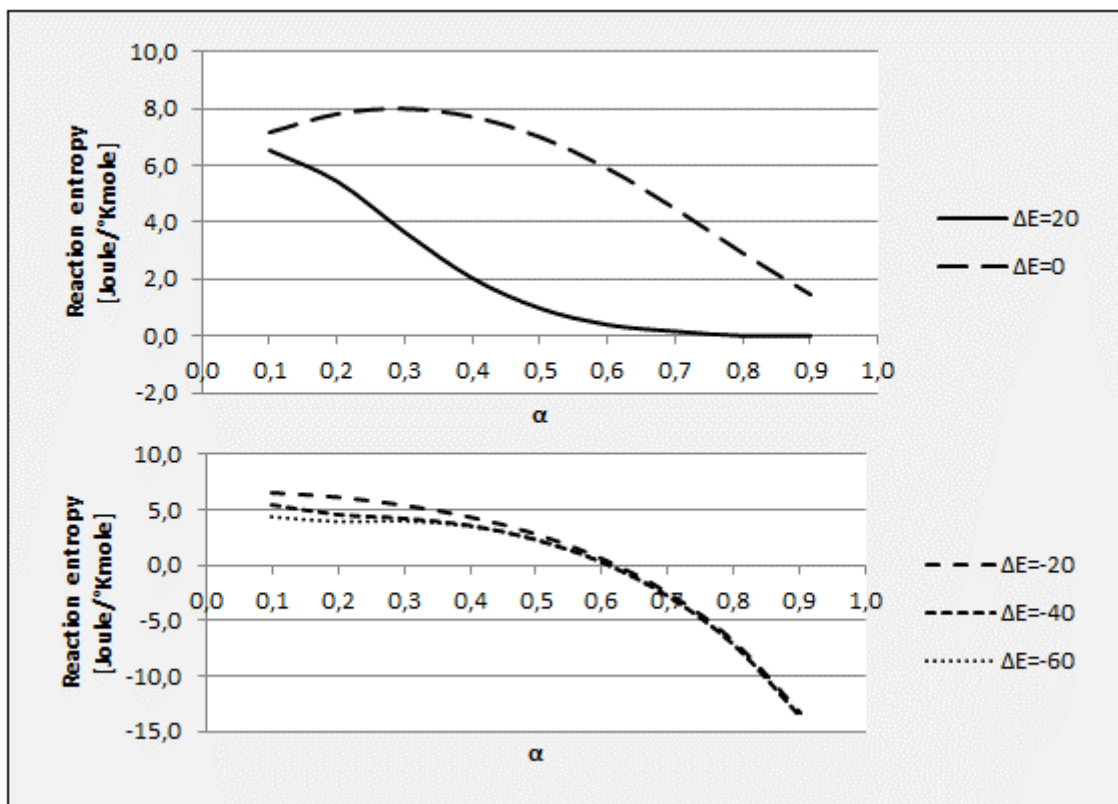


Figure 9. Random aggregation: trends of ΔS_R as a function of α and ΔE

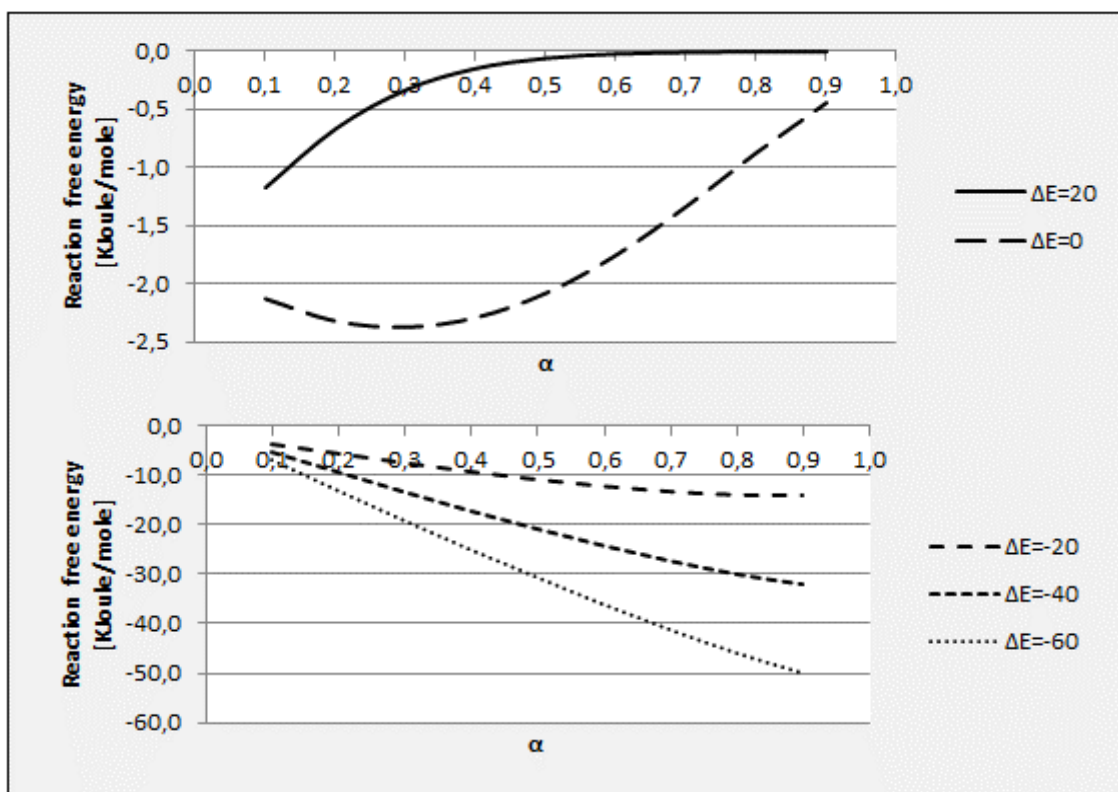


Figure 10. Random aggregation: trends of ΔG_R as a function of α and ΔE

2. Codified autopoietic reactions

Let us now suppose that the binding energies ε_i^b , holding the particles of the giver compounds together, are different from each other depending on the colours of the primary particles and that the

same is true for the binding energies ε_{jk}^f among primary particles in IdLAs. In this case, the energy E_b that must be supplied to a mole of giver compounds to break the internal bonds, and the energy E_f released into the environment by a mole of aggregates for the formation of new bonds, remain expressed in their general form by [2/a] and [2/b]. This time the autopoietic formation of the aggregates follows a preferential path, guided by the differences between the elementary energies involved in each single coupling. It is assumed that such a way of evolving can be simulated in our mathematical model by imposing a memory on the primary particles sequencer. It does not matter, for our study, that an analytical relation between the chemical kinetics determined by the differentiation of bonds and the probabilistic structure of the sequencer, is identified. It is enough to admit that such a relationship exists and that there is an appropriate value of the coding factor η (between 0 and 1) such as to represent mathematically the effect on entropy of the driving force implicit in the system.

Due to the fact (as already highlighted in Ref.1) that the relationship between the sequencer mode of operation and the coding factor is not biunivocal, different IdLA populations may correspond to the same value of η . We must then also make hypotheses on the aggregates population, i.e. an expression must be given to $\Sigma(\alpha)$, as was done in the previous paragraph in the case of random aggregation. In fact, if the IdLA's average length λ^* depends only on α according to [11], the probabilistic distribution of lengths, affecting $\Sigma(\alpha) = \sum_{\lambda=1}^A p_{\lambda} \ln \lambda$, depends on the way the sequencer works. We then wonder within what limits the sequencer can make the summation value vary.

To start, let's assume that the sequencer produces aggregates all of the same length λ^* (even if not having the same colour sequence). In this case we can then place:

$$\Sigma_1 = \sum_{\lambda=1}^A p_{\lambda} \ln \lambda = \ln \lambda^* = \ln \frac{1}{1-\alpha} \quad [23]$$

Now, if the single type of aggregate of length λ^* is replaced by two aggregates with lengths λ_a and λ_b and with probability p_a and p_b , then compliance with [11] requires that

$$p_a \lambda_a + p_b \lambda_b = \frac{1}{1-\alpha} = \lambda^*$$

so that [23] can also be written as follows

$$\Sigma_1 = \ln \lambda^* = \ln [p_a \lambda_a + (1 - p_a) \lambda_b]$$

At the same time summation $\sum_{\lambda=1}^A p_{\lambda} \ln \lambda$ takes the form

$$\Sigma_2 = p_a \ln \lambda_a + p_b \ln \lambda_b = \ln [\lambda_a^{p_a} \lambda_b^{(1-p_a)}]$$

and, as for $\lambda_a \geq 1$, $\lambda_b \geq 1$, $p_a < 1$, is always

$$p_a \lambda_a + (1 - p_a) \lambda_b > \lambda_a^{p_a} \lambda_b^{(1-p_a)}$$

then necessarily:

$$\Sigma_2 < \Sigma_1$$

This means that the passage from a single type of IdLA to two types of IdLAs (α being equal and therefore λ^*) implies a decrease in the value of the summation $\sum_{\lambda=1}^A p_{\lambda} \ln \lambda$. Since the procedure just

proposed can be repeated many times, in general we can say that the more differentiated is the population of aggregates produced by the sequencer, the lower is the summation value. In other words, the less strict are the conditions dictated by the sequencer, the more articulated and various is the aggregates population and the lower is the value of $\sum_{\lambda=1}^A p_{\lambda} \ln \lambda$. At the limit, when the sequencer loses any ability to manage particle coupling, the codified aggregation degenerates into random aggregation and the summation value reaches the minimum. The domain within which $\sum_{\lambda=1}^A p_{\lambda} \ln \lambda$ can vary according to the code of the sequencer is therefore limited by two calculable values: downwards by the value that the parameter assumes in case of random (autopoietic) aggregation according to [17]

$$\Sigma_{min}(\alpha) = \Sigma_0(\alpha) = (1 - \alpha) \sum_{\lambda=1}^A \alpha^{\lambda-1} \ln \lambda \quad [24/a]$$

and upwards by the value assumed in the case of production of aggregates all of the same length according to the [22]

$$\Sigma_{max}(\alpha) = \ln \frac{1}{1-\alpha} \quad [24/b]$$

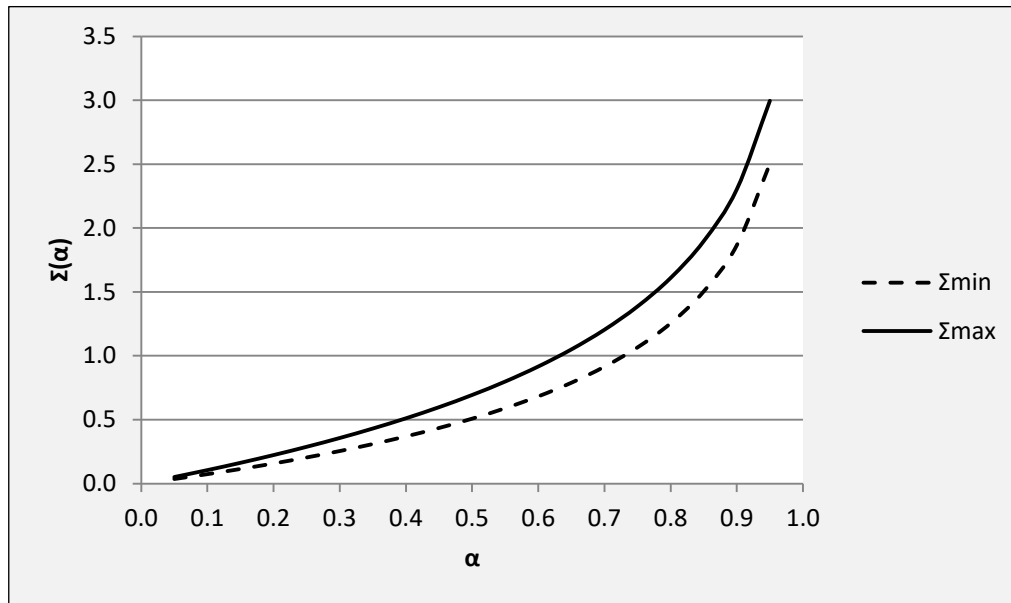


Figure 11. Trends of Σ_{min} and Σ_{max} as a function of α

The graphs in Fig.11 show the trends of $\Sigma_{min}(\alpha)$ and $\Sigma_{max}(\alpha)$ and consequently identifies the area of the possible values for $\Sigma(\alpha) = \sum_{\lambda=1}^A p_{\lambda} \ln \lambda$.

Even though, as already said, there is no two-way relationship between this summation and η , in order to limit the number of independent variables in calculations, the following *matching rule* between these two parameters has been adopted:

$$\eta \rightarrow \Sigma(\alpha) = \Sigma_{min}(\alpha) + \eta[\Sigma_{max}(\alpha) - \Sigma_{min}(\alpha)] \quad [25]$$

The matching is correct and exclusive for $\eta = 0$ and for $\eta = 1$ since it reposes [24/a] and [24/b] respectively. It is correct but not exclusive for the values of η quite far from the extremes. Once the matching rule [25] has been established, the entropy trend can be calculated by means of [5].

We now propose to compare the behaviour of $S(\xi)$ in the case of coded autopoietic aggregation ($\eta \neq 0$) with the behavior of the same thermodynamic function in the case of random aggregation ($\eta = 0$) discussed in the previous paragraph. Beyond the fact that the calculations can be carried out in a very wide range of cases, by varying as desired the many parameters involved, in order to appreciate the salient differences between the two scenarios, the examination of a limited number of situations is sufficient. By way of example, the graphs of Fig.12 show the trend of the entropy $S(\xi)$ for different values of α and η , in the case of a weakly exothermic reaction ($\Delta E = -20$ KJoule/mole), with $\rho = 10^{-82} \text{ m}^2\text{Kg}^{5/2}$ and $h_o = h_{xo^*} = 1,5$. This is an emblematic case, sufficient to highlight the most significant effects of the coding.

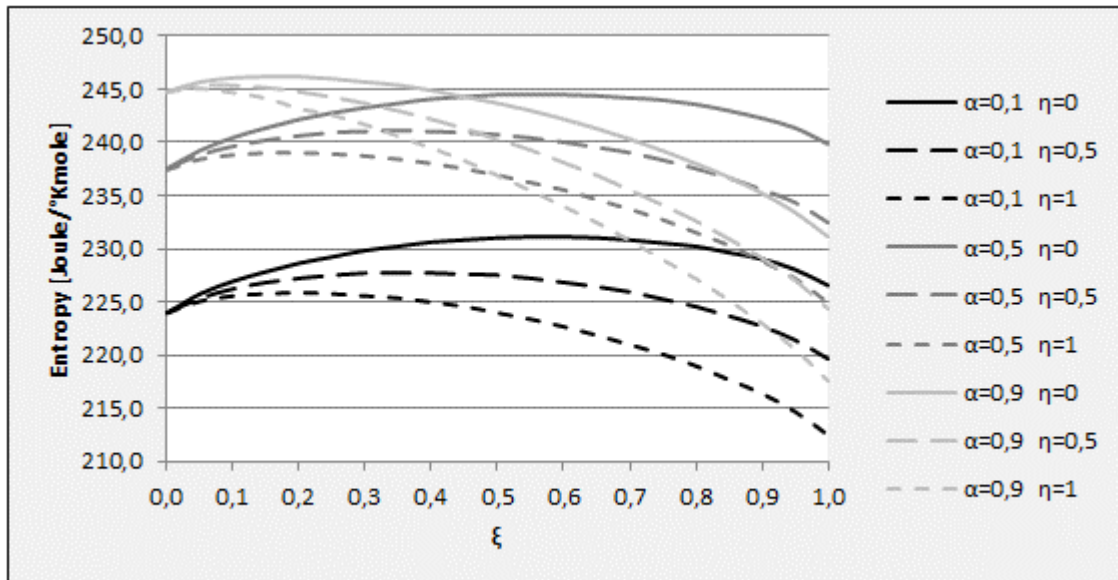


Figure 12. Autopoietic coded aggregation: trends of $S(\xi)$ depending on α and η
($\Delta E = -20$, $h_o = h_{xo^*} = 1,5$, $\rho = 10^{-82}$)

It seems evident that the presence of a code guiding the particles coupling always implies a reduction in entropy with respect to the random aggregation process. This is all the more consistent the higher the coding factor is and the more the reaction proceeds. Also in this case all curves have a maximum point, but it tends to move to the left as η increases. This shift towards lower values of ξ has a considerable impact on free energy and affinity and therefore on the extent of reaction at equilibrium. In fact, given that the enthalpy $H(\xi)$ is not conditioned by η so that even in the case of coded autopoietic aggregation the graphs of Fig.6 continue to apply, the calculation of $G(\xi)$ is immediate. The graphs of Fig.13 show its trend for different values of η and α and for the values of ΔE , ρ , h_o and h_{xo^*} specified above. It is evident that, all other conditions being invariant, the higher is the value of η , (i.e. the more stringent the sequencer encoding),

- the more incomplete is the reaction (the minimum moves more and more to the left)
- the higher is the value that the free energy maintains throughout the aggregative process until its conclusion.

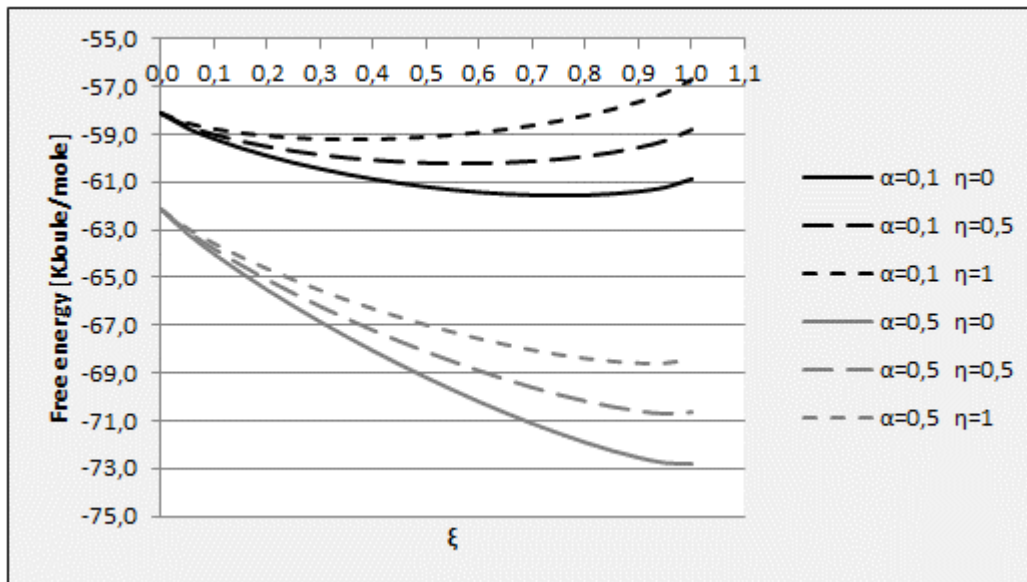


Figure 13. Autopoietic coded aggregation: trends of $G(\xi)$ depending on α and η
 $(\Delta E = -20, h_o = h_{xo^*} = 1,5, \rho = 10^{-82})$

It is therefore appropriate to examine more carefully where the extent of reaction to equilibrium ξ_0 is positioned as η varies. This knowledge is in fact essential, as already highlighted for random aggregations, to calculate the reaction functions. Given that, this time too, the equation $A(\xi) = 0$ must be numerically solved, the table in Fig.14 illustrates on a wide range of α and η , the marked tendency of the reaction to find the equilibrium for ever lower values of ξ_0 as the coding factor η increases, all other conditions being equal. This effect is all the more pronounced the lower the α concentration of the giver compounds. The data presented refer to a value of the energy balance ΔE (-20 KJoule/mole) specifically chosen to make the phenomenon evident (the reaction is significantly incomplete), but it can be said that the trend is general.

As we know ξ_0 , then ΔS_R , ΔH_R and ΔG_R can finally be calculated.

α	$\eta=0,00$	$\eta=0,25$	$\eta=0,50$	$\eta=0,75$	$\eta=1,00$
0,1	0,754	0,667	0,567	0,462	0,359
0,2	0,887	0,834	0,764	0,676	0,573
0,3	0,948	0,921	0,881	0,826	0,752
0,4	0,975	0,961	0,940	0,909	0,865
0,5	0,987	0,979	0,968	0,952	0,926
0,6	0,992	0,988	0,982	0,972	0,958
0,7	0,995	0,992	0,988	0,982	0,973
0,8	0,996	0,994	0,991	0,987	0,980
0,9	0,996	0,995	0,992	0,988	0,982

Figure 14. Autopoietic coded aggregation: values of ξ_0 as dependent on α and η
 $(\Delta E = -20, h_o = h_{xo^*} = 1,5, \rho = 10^{-82})$

The table in Fig.15 shows the results of the calculations when α and η vary, still for $\Delta E = -20$ and $h_o = h_{xo^*} = 1,5$.⁶ Moreover in Fig.16 the trends of the reaction free energy as dependent on the explored parameters are reposed in graphic form.

α	$\eta=0$			$\eta=0,5$			$\eta=1$		
	ΔS_R	ΔH_R	ΔG_R	ΔS_R	ΔH_R	ΔG_R	ΔS_R	ΔH_R	ΔG_R
0,1	6,592	-1,508	-3,473	3,158	-1,134	-2,076	1,294	-0,718	-1,104
0,2	6,195	-3,548	-5,395	1,755	-3,056	-3,579	-0,616	-2,292	-2,108
0,3	5,460	-5,688	-7,316	-0,023	-5,286	-5,279	-3,545	-4,512	-3,455
0,4	4,392	-7,800	-9,109	-1,810	-7,520	-6,980	-6,549	-6,920	-4,967
0,5	2,843	-9,870	-10,718	-3,746	-9,680	-8,563	-9,352	-9,260	-6,472
0,6	0,592	-11,916	-12,093	-6,158	-11,784	-9,948	-12,266	-11,496	-7,839
0,7	-2,533	-13,930	-13,175	-9,299	-13,832	-11,060	-15,614	-13,622	-8,967
0,8	-6,953	-15,936	-13,863	-13,631	-15,856	-11,792	-19,933	-15,680	-9,737
0,9	-13,450	-17,946	-13,936	-19,876	-17,856	-11,930	-25,954	-17,676	-9,938

Figure 15. Autopoietic coded aggregation: values of ΔS_R , ΔH_R e ΔG_R as dependent on α and η ($\Delta E = -20$ e $h_o = h_{xo^*} = 1,5$)

It is evident that, all other conditions being equal (and specially with the same energy balance ΔE),

- the value of $|\Delta S_R|$ is lower when the coding factor is higher
- reaction enthalpy is significantly affected by the coding factor for small values of α . In fact, when the concentration of giver compounds is low, ξ_o decreases rapidly with the increase of η ; for the opposite reason, the closer α approaches 1, the less ΔH_R is affected by η
- as the coding factor increases, the final system finds the equilibrium for gradually higher values of free energy.

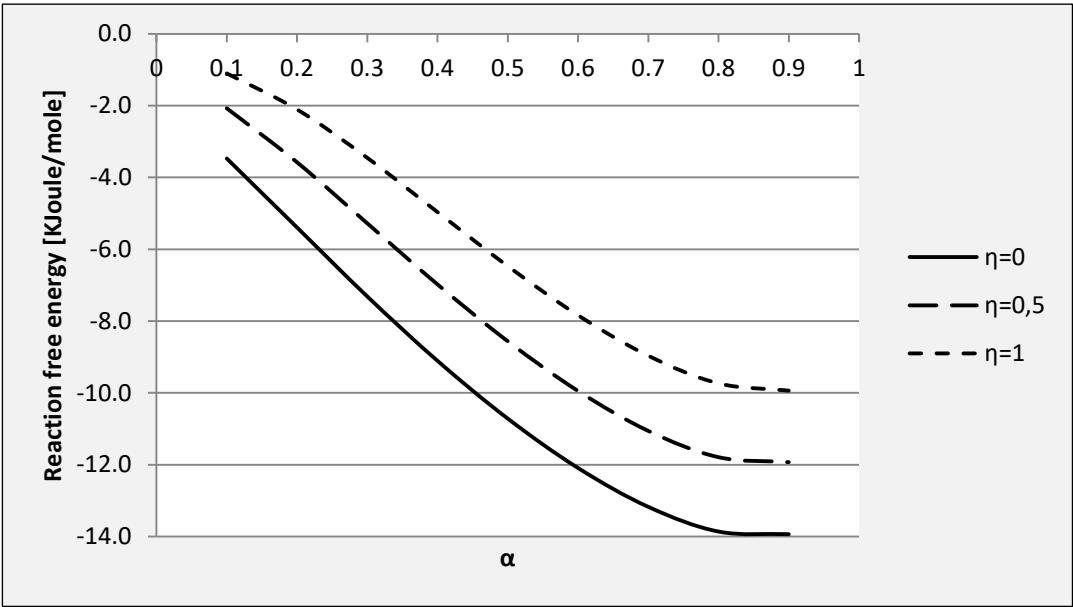


Figure 16. Autopoietic coded aggregation: trends of ΔG_R as dependent on α and η ($\Delta E = -20$ and $h_o = h_{xo^*} = 1,5$)

⁶ This time, unlike in the case of random aggregation, the entropies of the descriptors matter as it is $\eta \neq 0$. On the other hand, the inertial characteristics of the reference IdEP continue to be irrelevant.

However, it would be inaccurate to conclude that a codified autopoietic process leads a system to a higher final free energy than a random one, for there is no system that can spontaneously (in an autopoietic way) evolve in both a random and a codified way, dissipating the same molar energy. An autopoietic aggregative reaction (random or codified as it may be) always develops out of necessity, driven by the matrices of the binding energies (and by the matrices of the bonds). The results are necessarily implicit in the premises. The molar energy balance ΔE is therefore the result of a very precise set of initial conditions, which characterize the system and make it evolve in a unique way. This does not mean that the same value of ΔE cannot be produced by different binding energy matrices, but they will always be different systems.⁷ The condition “with the same energy balance ΔE ” specified in the premise of the previous observations must therefore be strictly framed in a logic of comparison between different systems.

Finally, full reactions deserve special attention ($\xi_0 = 1$). As far as complete aggregative processes are concerned, relation [6] takes the form:

$$\Delta S_R = R \left[\frac{9}{2} (1 - \alpha) \Sigma(\alpha) - \frac{9}{2} \alpha \ln 2 + (1 - \eta) h_\alpha - (1 - \alpha) \eta \gamma_O \ln \zeta_O - \eta \alpha \gamma_{O^*} \ln \zeta_{O^*} \right] \quad [26]$$

This differs from [20] by the non-zero value of η . The graphs in Fig.17 show the results obtained: in this case the opportunity is also taken to verify how different entropies of the reactant descriptors affect the results. The following considerations apply:

- as a rule, the higher the coding factor η , the lower (higher in absolute value) is the reaction entropy. Coding always implies the achievement of a higher degree of order
- for any value of η , when the descriptors of the primary particles have higher entropies, the final entropy of the system is always lower. In other words, at parity of any other condition, between two systems with different degrees of initial disorder, the more disordered of the two gains more from the aggregation process in terms of final order, than the other.

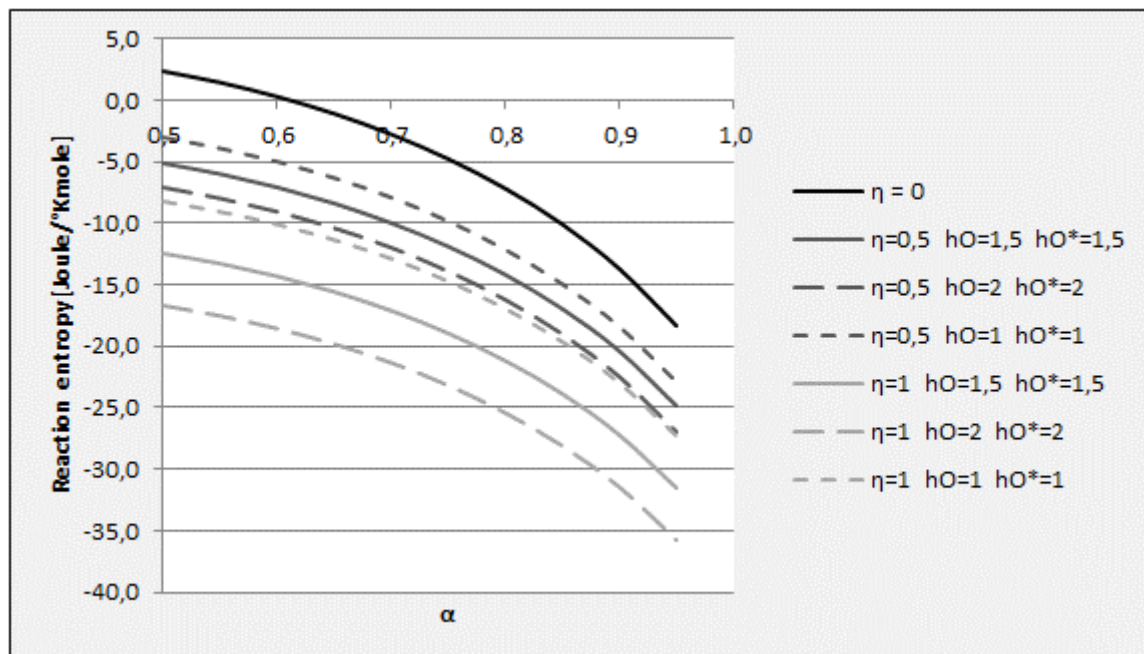


Figure 17. Complete codified autopoietic aggregation: $\Delta S_R(\alpha)$ trend for different values of η , h_O and h_{O^*}

⁷All other conditions being equal, it is possible to hypothesize matrices of bonds that generate higher ΔE values with lower η coding factors and vice versa.

The reaction free energy ΔG_R is therefore a function of α , η , h_O and h_{O^*} (as depending on ΔS_R) and of ΔE (as depending on ΔH_R). Then, posited that $h_O = h_{O^*} = 1,5$, the results of the calculations performed are shown in the graphs of Fig.18. The following considerations apply:

- normally, with the same energy balance ΔE , the higher the coding factor η the higher (lower in absolute value) is the reaction free energy. The coding always pushes in the direction of a final state of the system characterized by a higher residual free energy
- all other conditions being equal, when the negative energy balance ΔE increases, the system of aggregates reaches lower and lower energy states
- with the same energy balance ΔE , the variation of η substantially implies a vertical translation of the curve $\Delta G_R(\alpha)$ that keeps the minimum point unchanged. The minimum point moves more to the right (towards higher values of α), the higher is the negative energy balance.

Also in this case, for a correct interpretation of these remarks it is important to remember once more that autopoietic aggregations are not in competition with each other. Each system has its own code, written in the chemical-physical characteristics of the particles: a code that determines by necessity the evolution of that particular system. Any comparison between different processes must therefore be made with this basic reservation. In an autopoietic process it is not possible to act freely on η and ΔE that are inherent to the system itself. In substance, it would be inappropriate and even misleading to look at the groups of curves of fig.18, at parity of ΔE , as possible alternatives for the same system.

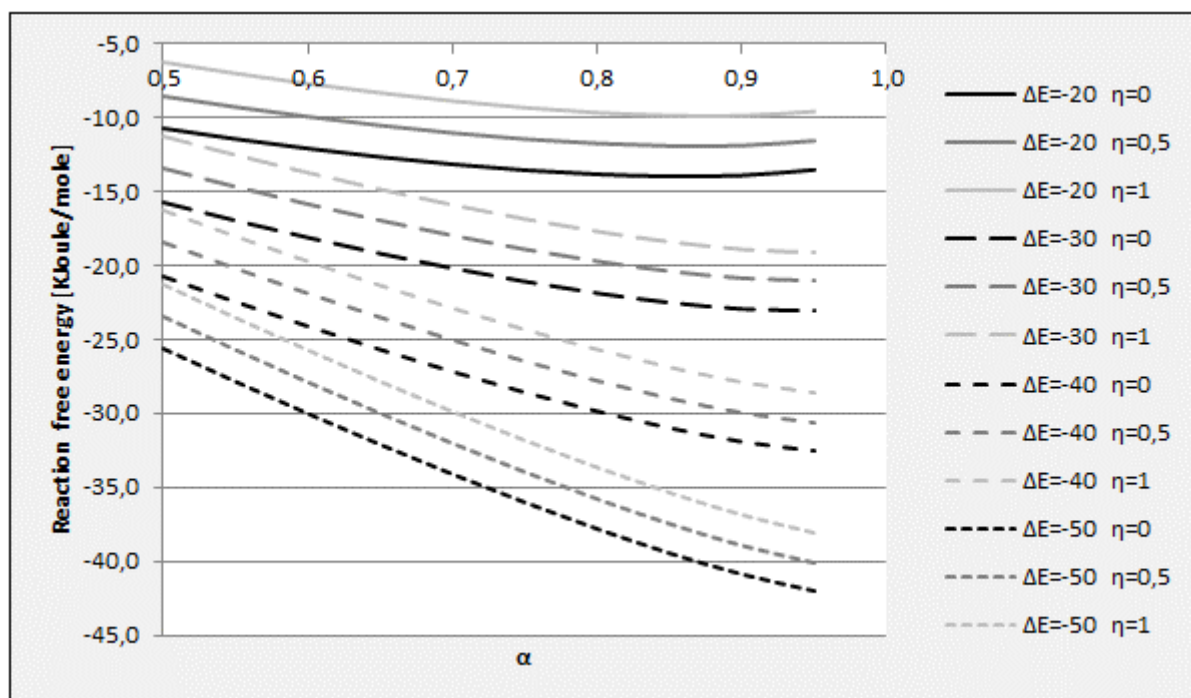


Figure 18. Complete codified autopoietic aggregation: $\Delta G_R(\alpha)$ trend for different values of η and ΔE ($h_O = h_{O^*} = 1,5$)

3. Heteropoietic aggregations

Let's now suppose that a certain system is characterized by a matrix of bonds such that, in autopoietic regime, the aggregative process develops with $\eta = \eta_a$ and $\Delta E = \Delta E_a$. Let us also suppose that entities external to the system itself, able to force the autopoietic orientation of the aggregative process, intervene by imposing their own code. Thus, we are in the case of heteropoietic aggregation and, within our model, the combination between IDEPs is therefore guided by a sequencer with memory. Its functioning logic does not derive from the matrices of the binding energies but rather from the special codifying attitude of these entities which do not strictly belong

to the reactive system: we call them *ordering agents*. So, let's indicate with η_h and with ΔE_h respectively, the coding factor and the molar energy balance in the heteropoietic regime.

Let us finally suppose that the ordering agents as such, produce a more orderly final state than that which the system would achieve if left free to aggregate in an autopoietic way, that is to say

$$\eta_h > \eta_a$$

If so, in what relation are ΔE_a and ΔE_h ? In the case of autopoietic aggregation the matrix of bonds $[l_{jk}^f]$ is certainly such as to maximize the energy dispersed, in order to make the system of aggregates reach the most stable condition possible. Given the matrix $[\varepsilon_{jk}^f]$, the value ΔE_a will be the highest value (in absolute value) that can be achieved according to [2/b]. Consequently, the forcing action exerted by the ordering agents on $[l_{jk}^f]$ can result only in a decrease (always in absolute value) of the molar formation energy E_f , that is

$$|\Delta E_h| \leq |\Delta E_a| \quad [27]$$

where the sign of equality applies only if the autopoietic aggregation is random⁸.

As far as the mathematical treatment of the model is concerned, nothing changes with respect to what was set up and developed in the case of autopoietic codified aggregation. Therefore, all the numerical results acquired for the autopoietic processes can be immediately applied to heteropoietic scenarios except the observation which closed the discussion on ΔS_R (both in the case of incomplete as well as complete aggregation) in the previous paragraph. In the case of heteropoietic aggregation, in fact, the direct comparison with codified autopoietic aggregation is feasible since the proposed scenario provides that the same system can actually evolve in several ways: as an autonomous and random evolutionary path if left to itself or as any of a multiplicity of heterodirected and variously codified paths if in the presence of appropriate codifying entities. But the system is always the same. In particular, it is always characterized by a unique set of values of the binding energies and therefore by values of the molar energy balance ΔE_a and ΔE_h , linked by [27]. That direct comparison which was precluded in the case of autopoietic systems, is now possible.

From this point of view, the results presented in Fig.15 can be schematically summarized as in Fig.19 where the reaction enthalpies ΔH_R , the reaction entropies ΔS_R and the reaction free energies ΔG_R have been apexed with "a" for the autopoietic codified aggregation (therefore characterized by $\eta = \eta_a$ and $\Delta E = \Delta E_a$) and with "h" for the heteropoietic codified aggregation induced by ordering agents and characterised by $\eta = \eta_h$ and $\Delta E = \Delta E_h$. In general, whatever the value of α , if the reaction is exothermic and $\eta_h > \eta_a$, then $\Delta E_h \geq \Delta E_a$ and $\xi_0^h < \xi_0^a$.

Consequently:

- for [8], it is always $\Delta H_R^h > \Delta H_R^a$ or, since the reaction enthalpies are always negative, $|\Delta H_R^h| < |\Delta H_R^a|$
- for the results shown in the table of Fig.15 it is always $\Delta S_R^h < \Delta S_R^a$

⁸ In this case, in fact, the molar energy balance does not depend in any way on the matrix of bonds as shown by [13]. In reality, it seems reasonable to suppose that the action of the ordering agents is all the easier the more uniform the matrix of bonds is: an autopoiesis close to random aggregation will certainly be easier to be forced than an autopoiesis with a high coding factor. Moreover, the aggregates produced will be more stable. On the other hand, a strong differentiation of the binding energies and therefore a high value of the autopoietic coding factor, will require a stronger action of the ordering agents and the whole complex of aggregates produced will be less stable.

- for the results shown in the same table and graphically represented in Fig.16 and in Fig.17, it is always $\Delta G_R^h > \Delta G_R^a$ or, for negative reaction free energies, $|\Delta G_R^h| < |\Delta G_R^a|$.

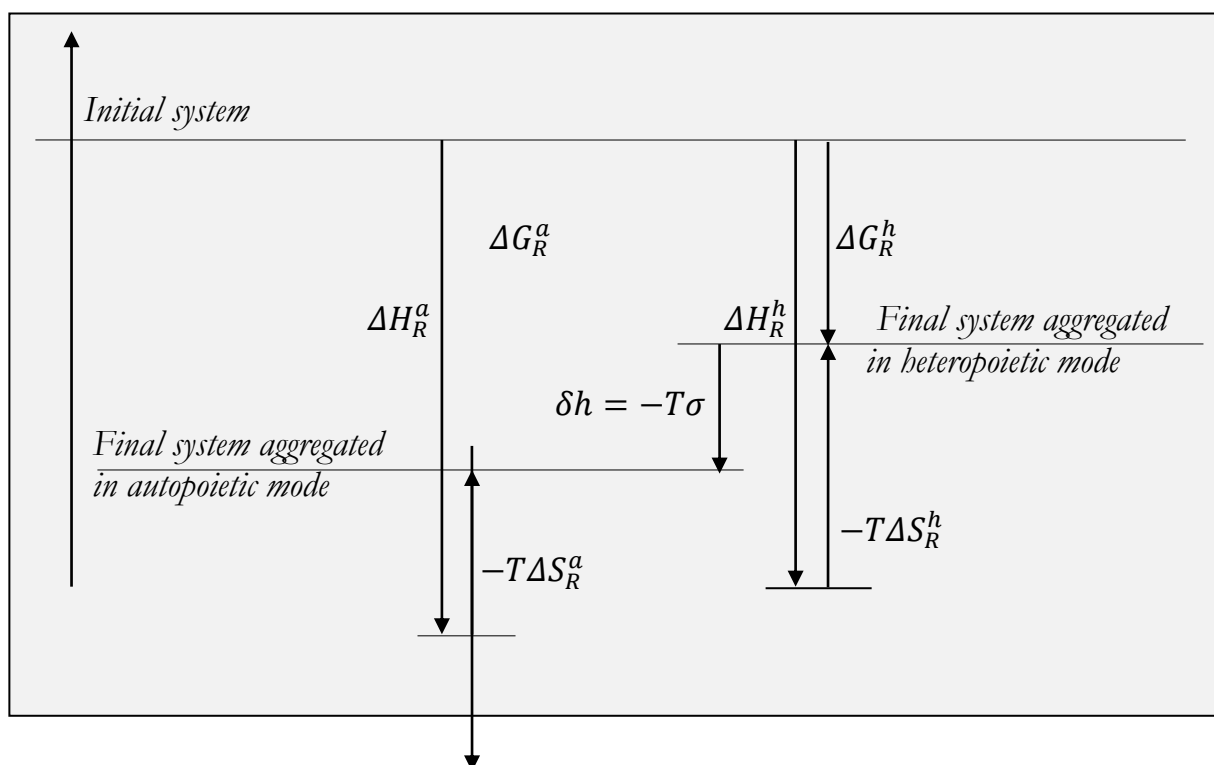


Figure 19. Qualitative comparison between the energy development of the same system following autopoietic and heteropoietic aggregative processes.

It should be noted, however, that for any aggregation mode, the spontaneity of the process is always implied. Then a question immediately arises. Why should the system evolve with heteropoietic mode if the state of minimum energy is reached only with autopoietic aggregation? How is it possible that the ordering force of external entities can win the competition with the natural attitude of the system to evolve in an autopoietic way if this second type of aggregation is such as to achieve a lower energy level? There can be only one explanation within a physics governed by the second principle of thermodynamics: it is the ordering agents themselves that, while bearing the aggregation code, at the same time must be the seat of an additional thermal dispersion. In the case of heteropoietic aggregation, the system on which to calculate the energy balance must necessarily be an *extended system* that also includes the ordering agents.

Fig.19 shows the gap between the reaction free energies in an autopoietic aggregation and a heteropoietic aggregation. This difference can be compensated for only if the ordering agents dissipate an amount of energy at least a little higher than δH , a dissipation to which an increase σ of entropy must correspond such that

$$\sigma = -\frac{\delta H}{T} > 0 \quad [28]$$

This minimum additional entropy is called *addressing entropy* and the associated negative enthalpy, δH , is called *compensatory dispersion*.

It is evident that the production of addressing entropy within the *extended system* (reactants + ordering agents) is a necessary and sufficient condition for a heteropoietic aggregation not to violate the second principle of thermodynamics: only in this way can the flow of information contained in the sequencer's code be channeled into the reagent system. On the contrary, should the thermodynamic contribution of the ordering agents be absent, the codified aggregation could not

take place for lack of the necessary compensatory dispersion and therefore an adequate increase of disorder in the extended system.

This observation opens the way to the thermodynamic interpretation of the aggregative processes of biological interest but at the same time raises profound questions about the possible dynamics of biogenesis.

Conclusions

The IdEP-IdLA model is able to provide a comprehensive description of complete and incomplete aggregation processes in closed systems, both in autopoietic (random or coded) and heteropoietic modes. In particular it remains proven that the heteropoietic mode of assembling implies that ordering agents are involved also in the energetic aspects of the reaction and not only in informative transmission of the code contents. Although external to the system, they are necessarily the site of specific dissipative processes, thus decisively contributing to the entropic balance. This makes the model promising for the study of biological aggregation processes but at the same time suggests the difficulty of explaining the birth of life on earth.

References

[Ref.1] V. Cocchi, R. Morandi – *Mathematical modeling for the simulation of aggregative processes*, Entropie, ISTE Open Science, DOI: 10.21494/ISTE.OP.2021.0667, 2021