CHEMICAL ENGINEERING AND COMPLEXITY, AN UNDISSIPATED STRUCTURE...YET.

J. L. AGUILAR-ARIAS[1]

[1] Universidad Nacional de Colombia, Chemical Engineering Department.
E-mail: jlaguilara@unal.edu.co

ABSTRACT – One of the main contributions of Ilya Prigogine, Nobel Prize in Chemistry in 1977, was the understanding of the three fields of thermodynamics, that is, the thermodynamics of systems in equilibrium, near equilibrium, and far from equilibrium. This last field, which is called the complexity sciences (CC), opened the understanding of creating order out of chaos with Prigogine's Dissipative Structures. This paper presents the basics of the CC with the perspective of Chemical Engineering, presenting its utility in unstable simple reactions and in reactive distillation. All within the framework of education and training of chemical engineers, with the view that the Sciences of Complexity, more than a tool, constitute an approach that can transform the performance of engineering and the role we engineers play in the society.

1. DISSIPATIVE STRUCTURES

The concept of Dissipative Structures was proposed by Ilya Prigogine in 1930 as a consequence of unexplained phenomena found in chemical reactions, such as the production of enantiomers, or oscillatory reactions. His explanation was in terms of that far from equilibrium, nature tends to find new forms of organization that seem to be unpredictable, but that in the end by self-organization, a new ordered structure is created, dissipating energy[9].

1.1. Stability Criteria

The basic foundation for the Dissipative Structures is that, since for a system in a stationary state (that could be an equilibrium state) its entropy must not be changing in time, so that the stability under perturbation for this stationary state is determined by the nature of second order variations in entropy, that is, if the second derivative is positive, then the system is under an unstable state, and a perturbation will take it out of it.

For chemical reactions, the entropy change can be expressed as:

$$\delta S = \frac{1}{T}\delta U + \frac{P}{T}\delta V + \sum_i \frac{\mu_i}{T}\delta N_i$$

For the second order change we have:

$$\delta^2 S = \frac{\partial}{\partial U}\frac{1}{T}(\delta U)^2 + \frac{\partial}{\partial V}\frac{P}{T}(\delta V)^2 + \frac{1}{T}\sum_i \frac{\partial \mu_i}{\partial N_i^\alpha}(\delta N_i)^2$$

For chemical reactions is convenient to use the reaction coordinate: $dN_i = \nu_i d\varepsilon$. For U and V constant, the expressions become:

$$\delta S = \frac{1}{T}\sum_i \nu_i \mu_i \, \delta\varepsilon = \frac{A}{T}\delta\varepsilon$$

Where $A = \sum_i \upsilon_i \mu_i$ is called the Affinity of the reaction.

It may be also expressed as:

$$\delta S = \left(\frac{\partial S}{\partial \varepsilon}\right)_{U,V} \delta\varepsilon = \frac{A}{T}\delta\varepsilon$$

For the second order change in entropy:

$$\delta^2 S = \left(\frac{\partial}{\partial \varepsilon}\left(\frac{A}{T}\right)\right)_{U,V} (\delta\varepsilon)^2$$

For the change in entropy after a perturbation, considering the second order term.

$$\Delta S = S - S_o = \delta S + \frac{1}{2}\delta^2 S$$

If the initial state was an equilibrium state, then the first order δS must vanish, since the entropy in equilibrium states reaches a maximum. Moreover, for the second order variation to be a stable change, must be negative, in order to be necessary an increase in entropy to come back in equilibrium, that is, for perturbations in systems under stable equilibrium:

$$\frac{1}{2}\delta^2 S = \frac{1}{2T}\frac{\partial A}{\partial \varepsilon}(\delta\varepsilon)^2 < 0$$

To use this expression for the analysis of stationary states, is necessary to derivate with respect of time, obtaining for one simple reaction:

$$\frac{1}{2}\frac{d\delta^2 S}{dt} = \frac{\delta A}{T}\delta\upsilon > 0$$

Where $A = RT\ln(R_f/R_r)$, $\upsilon = R_f - R_r$ and with R_f and R_r being the forward and reverse velocities of reaction.

Consider for instance the autocatalitic reaction:

$$2X + Y \underset{k_r}{\overset{k_f}{\rightleftarrows}} 3X$$

In this case: $R_f = k_f[X]^2[Y]$, $R_r = k_r[X]^3$

And the stability criteria is:

$$\frac{1}{2}\frac{d\delta^2 S}{dt} = \frac{\delta A}{T}\delta v = -R\left(2k_f[X]_s[Y]_s - 3k_r[X]_s^2\right)\frac{(\delta X)^2}{[X]_s} > 0$$

In this case, if $k_f >> k_r$ the left side may become negative, and in this case the reaction may become unstable, being possible to occur the reaction called "Brusselator". For the details in this topic, please refer to Kondepudi and Prigogine[9].

1.2. Bifurcation Analysis

One of the possible system responses to the lack of stability is through bifurcations. When a system is under stationary state conditions, but far from equilibrium, a perturbation may drive the system out of its stationary conditions, having the possibility to find two or more possible new stable conditions and the new final state will depend on the little differences in variables that could be in the moment of the occurrence of the perturbation.

A practical application to the bifurcation analysis was proposed by Doherty et al.[18] for Reactive distillation. In several works he and his research group show that bifurcation analysis is very important in order to study this process[7; 8].

However, there is not yet a clear and definitive space for the application of the Sciences of Complexity, or simply *Complexity*, in the field of Chemical Engineering, maybe due to the nature of the conventional chemical processes, or the fact that in industrial production it is not practical to work under unstable or complex conditions.

2. OPPORTUNITIES FOR CHEMICAL ENGINEERS IN COMPLEXITY

In contrast, other fields, such as biology, economy, health sciences, among other, have found practical applications of *Complexity* in their disciplines. The purpose of this work is to show some possible applications of *Complexity*, not necessarily in the traditional field of Chemical Engineering, but where clearly Chemical Engineers can uniquely contribute due to our formation and basic elements of thermodynamics, and processes analysis, compared to other disciplines, in matters of study that are not the classical Chemical Engineering applications, but where their application is necessary, even not being chemical processes.

As an example, Muller[14] proposes a simple social model based on thermodynamics, and presents as example the racism phenomena as a situation like a two immiscible phases occurring in society. This work, for instance, opens the question on how to apply thermodynamic fundamentals to increase the phase solubility in these cases.

Recently created journals, like the International Journal of Human Thermodynamics facilitate the diffusion of theories about applications of thermodynamics in social sciences. One example of these theories is the proposal of a social equation of state, as presented by Mohsen-Nia[13], where he establish an analogy for pressure, temperature and volume to laws, motivation, and freedom in societies, as well as other analogies for other thermodynamic properties as shown in Table 1. Also proposes a non ideal equation of state based on a second virial coefficient, which can be calculated using statistical mechanics by defining a potential function (social) where the distance *r* corresponds to a interpersonal personality distance.

Table 1. Analogies for thermodynamic variables proposed by Mohsen[13]

Symbol	Thermodynamics	Mohsen Analogy
U	Internal Energy	Energy Stored in Societies
Q	Heat	Energy flowing due to difference of society excitement
P	Pressure	Social Rules (Laws, Culture, Religion, etc.)
V	Volume	Freedom
T	Temperature	Motivation in society
W	Work	Energy necessary for making a regular social system
S	Entropy	Social system desorder

Another example for the application of *Complexity* with Chemical Engineering approach corresponds to economic dynamics in markets. The discipline associated to this field is called thermoeconomics, or Complexity Economics, and has several exponents with different points of view, in particular about the matters to study, and their applications[1; 5; 6].

Bryant[5], states also analogies for thermodynamic properties related to economic variables, and shows how some economic phenomena can be described as corresponding to thermodynamic processes involving work, heat, and entropy exchange, related to trading or sales, as presented in Table 2. The interesting point in this approach is to include variable analogy and process analysis, even being based on reversible processes.

Table 2. Analogies for thermodynamic variables proposed by Bryant[5]

Symbol	Thermodynamics	Bryant Analogy
U	Internal Energy	Internal Value, depending on T
Q	Heat	Entropic Value
P	Pressure	Unit price
V	Volume	Units per unit of time
T	Temperature	Index of trading value
W	Work	Work Value per unit of time
S	Entropy	Entropy
k	Boltzmann constant	Productive content

A wider scope is to consider non equilibrium processes in Economy, where can be mentioned the work conducted in the Santa Fe Institute[1]. Their studies in complexity have expanded the perspective in economics. Brian Arthur is one of the most prominent researchers in this field, and states that one of the major problems in classical economy is that all the theories have been based in equilibrium systems, and that non equilibrium states cannot be important in economy, and cites Samuelson[16]: “Positions of unstable equilibrium, even if they exist, are transient, non-persistent states. … How many times has the reader seen an egg standing on its end?.”

Brian Arthur is in total disagree with this statement, being based on two factors that make economics systems moving under non equilibrium conditions. The first is the uncertainty of the variables and processes inherent in economy, such as public perception of products/services, competence strategies, government regulations, etc. The second factor, according to Arthur, is the technological change, which is considered to have a cyclic effect, being the new technologies a direct result of the previous ones.

In the scope of chemical engineering, it could be said that there is some kind of confusion in economy about equilibrium states, and stationary states, it is easier to understand in chemical processes that a system remains its variables unchanged in time, but that it is not necessarily in equilibrium, and that is what must be happening in an economic system when it seems to be stable, by their unchanging variables, but that indeed it may be far from equilibrium.

An anecdotic (and relevant) fact, is the strong debate including Economy Nobel Prize winners such as Kenneth Arrow (winner in 1972), and Paul Krugman (winner in 2008), the first in favor and the last against the application of complexity in Economics[10; 11]. This debate is agitated by the use of defiant expressions used by the authors, such as they have “changed economic thinking”[17], which generates comments like other one “has just invented…economics”[12]. This work, by the way, doesn’t want to generate such comments, instead, its purpose is to reinforce arguments to the fields of action that Chemical Engineers can, and must be prepared to participate.

Turning back to bifurcation analysis, this one has already been used in economy, as well as chaos and indeterminacy[2; 3; 4], but as Brian Arthur states, these works are based on equilibrium ecnonomics.

3. BIFURCATION ANALYSIS APPLIED TO CHIRAL SYMMETRY

Just to put some numbers, and to give a concrete example on how bifurcation analysis is applied, in this section are presented some refinements on the interesting, although theoretical, example proposed by Prigogine[9] about the chiral symmetry and the formation of enantiomers. In this example, L and D enantiomers are produced in the following hypothetical autocatalytic reaction mechanism:

$$S + T \underset{k_{1r}}{\overset{k_{1f}}{\rightleftarrows}} X_L \qquad (1)$$

$$S + T + X_L \underset{k_{2r}}{\overset{k_{2f}}{\rightleftarrows}} 2X_L \qquad (2)$$

$$S + T \underset{k_{1r}}{\overset{k_{1f}}{\rightleftarrows}} X_D \qquad (3)$$

$$S + T + X_D \underset{k_{2r}}{\overset{k_{2f}}{\rightleftarrows}} 2X_D \qquad (4)$$

$$X_L + X_D \underset{k_3}{\rightarrow} P \qquad (5)$$

Where S and T correspond to the achiral reactants (e.g. Glucose and Fructose), X_L and X_D correspond to the L and D enantiomers (e.g. L-Sucrose and D-Sucrose), k_{if} and k_{ir} correspond to the forward and reverse reaction constants, and P is a product representing the removal of enantiomers, for simplifying equations. It must be noted that the reaction constants for the production of enantiomers are the same, that is, for reactions (1) and (3), and for reactions (2) and (4). These two last reactions (2) and (4), correspond to the autocatalytic reactions, meaning that the reaction constant k_{2f} must be dominant over the remaining constants.

Since reaction constants are the same for the production of L and D enantiomers are the same, the concentration of these products must be the same if the initial (or inlet) concentrations of the reactants are the same, or about the same. But it is found that the final (or outlet) concentrations clearly differ when the stationary state under certain condition is unstable, and the initial concentrations slightly differ.

In the model is considered that reactants S and T, and product P are fed and removed in such rates that the concentration of S and T remain constant in time. This makes possible to transform variables, obtaining the following system of non linear differential equations[9]:

$$\frac{d\alpha}{dt} = -k_{1r}\alpha + k_{2f}\lambda\alpha - 2k_{2r}\alpha\beta \tag{6}$$

$$\frac{d\beta}{dt} = k_{1f}\lambda - k_{1r}\beta + k_{2f}\lambda\beta - k_{2r}(\beta^2 + \alpha^2) - k_3(\beta^2 - \alpha^2) \tag{7}$$

Donde:

$$\lambda = [S][T] \tag{8}$$

$$\alpha = \frac{[X_L] - [X_D]}{2} \tag{9}$$

$$\beta = \frac{[X_L] + [X_D]}{2} \tag{10}$$

Applying the Lyapunov theory of stability[15], is possible to find the value for λ that makes the stationary states unstable:

$$\lambda_C = \frac{s + \sqrt{s^2 - 4k_{2f}^2 k_{1r}^2}}{2k_{2f}^2} \tag{11}$$

$$s = 2k_{2f}k_{1f} + \frac{4k_{2r}^2 k_{1r}}{k_3 - k_{2r}} \tag{12}$$

In the Table 3 are shown the parameters required for the simulation of the enantiomers production.

Table 3. Adjusted Parameters to attain unstable conditions

Reaction Constants	
k_{1f}	0.05
k_{1r}	0.01
k_{2f}	0.7
k_{2r}	0.1
k_3	0.5

Reactants Concentration		**Initial Product Concentrations**	
[S]	0.5	X_{Lo}	0.0001
[T]	0.5	X_{Do}	0
Stability Parameters			
s			0.019
λ_C			0.032

Using these parameters, the condition for autocatalytic reaction is given so that k_{2f} is greater than the other constants, and since $\lambda = [S][T] = 0.25$, and $\lambda > \lambda_C$, the system has unstable steady concentrations for both L and D. Units both for time and concentration are arbitrary, and initial concentrations of the enantiomers differ very slightly. The problem was solved using Polymath software, version 5.1, and results are shown in Figure 1, where can be seen that the unstable steady concentrations for both L and D are close to 0.34, and after a while concentrations bifurcate, the one for L growing to 1.63, while for D falling to 0.019.

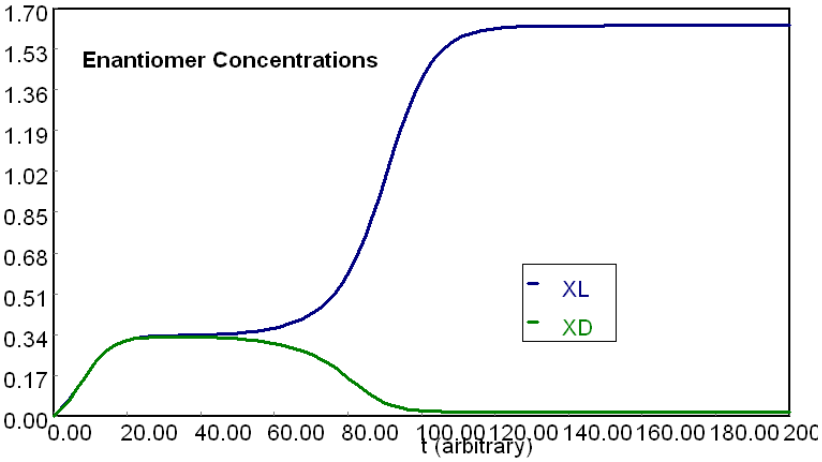

Figure 1. Enantiomer concentrations as a function of time in the unstable region.

4. CONCLUSIONS

In this paper have been presented elements to show that *complexity* is an emerging science, that has several applications and theories under development and verification. Also has been presented that due to the essence of *complexity*, being based on processes that are far from equilibrium, where the examples of chemical reactions are so close, and where thermodynamic analysis is so important, the opportunity and necessity of more Chemical Engineering teams working on this development and verification is very important.

The ongoing challenges include to find the way to verify the current models proposed, as well as to improve them, maybe including analogies for Gibbs free energy, what must give better tools for analysis and prediction of complex systems than the current models based on entropy.

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