DYNAMIC BEHAVIOR OF COMPLEX REACTING SYSTEMS: ROLE OF NONLINEARITY

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Summary

The most important concepts involved in the kinetic description of complex networks of reactions are introduced in this article. The approach to the formulation of material and energy balances is then considered, stressing the role of transport phenomena.

The dynamic analysis of various nonlinear systems, in which both diffusion and chemical reactions occur, reveals similarities both in mechanism and in mathematical description. This peculiar behavior is represented by the emergence of different steady states beyond certain bifurcation points, which exhibit less symmetry than the steady state before the bifurcation.

A comprehensive description of these aspects stresses the analogy with equilibrium critical phase transitions.

1. Introduction

The purpose of chemical kinetics is the description of the evolution over time of systems in which chemical transformations take place. These include practically all systems, on Earth and in cosmic clouds. Life itself depends on a very delicate and subtle balance between different chemical reactions.

At first glance the description of chemical transformations might appear simple—and it can be, if we are interested only in a few of the components present in the system. This could be a poor description, however, and sometimes not a very useful one. In fact, most chemical transformations occurring in nature imply the presence of a huge number of simple, or elementary, reactions that interact together in a very complex network.

Let us take one example. If we bring the simplest of the hydrocarbons—methane—together at relatively high temperature with oxygen, water and carbon dioxide are obtained through the overall reaction:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

In fact, the transformation takes place through a complex network of reactions that implies the presence of a range of different components, all present in very small amounts (see *Organic Synthesis*). A proposed scheme is illustrated in Figure 1, where the presence of intermediate radical species with an unpaired electron such as $CH_3\bullet$ and OH• is seen, and where an unpaired electron is indicated with a dot.

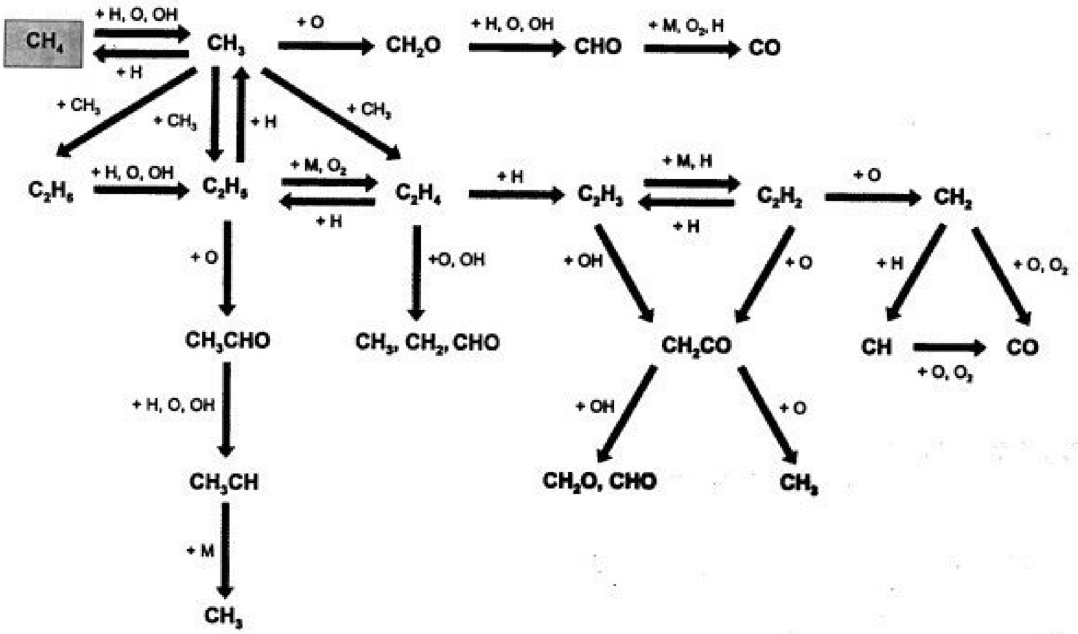
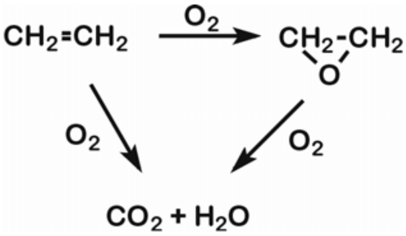


Figure 1. Schematic description of the reaction paths involved in methane combustion. M indicates an inert gaseous species.

Moreover, it is interesting to observe that some hydrocarbons with higher molecular weight than methane, such as ethane and ethylene, are also present. In any case, the complete oxidation to carbon monoxide (which eventually yields carbon dioxide) takes place through a set of intermediate oxidised products, such as alcohols and aldehydes.

In some important industrial processes, the oxidation of hydrocarbons is performed in order to isolate partial oxidation products that are useful for several applications. One interesting example is provided by the transformation of ethylene to ethylene oxide, usually described through a triangular scheme, like the previous one. The reaction, carried out in the presence of a solid catalyst constituted by supported silver, still implies the formation of several intermediate species adsorbed on the catalyst.



Another example of an industrially relevant process is the catalytic dehydrogenation of hydrocarbons to yield olefins. For instance, n-butane is transformed in the presence of a solid catalyst into butadiene, which is employed in the production of polymers. In fact, the process takes place through a reaction pattern involving both dehydrogenation and isomerization reactions, as described in the scheme given in Figure 2. Many cracking side-reactions also take place in the formation of coke and light hydrocarbons.

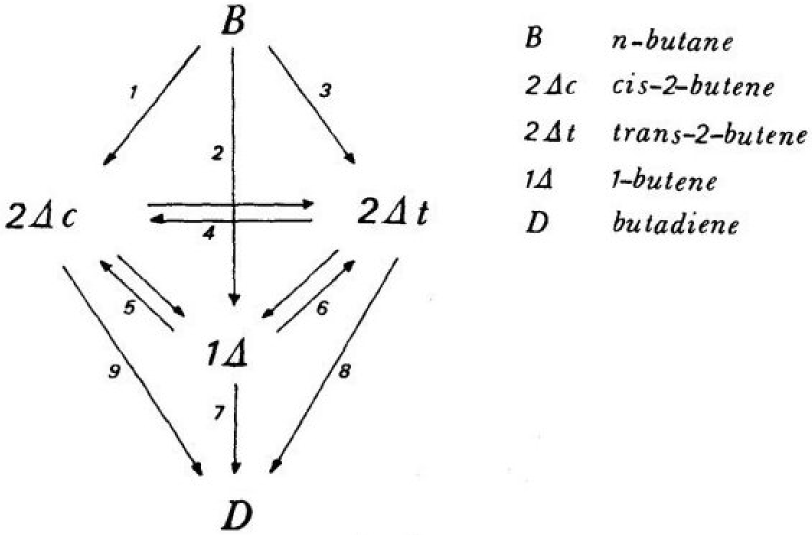


Figure 2. Reaction network of dehydrogenation of n-butane to butadiene. The different intermediates mentioned in the figure are involved in the overall transformations.

The transformations occurring in the cells of living systems are more complex. An important, and impressive, example is offered by the transformation of the main products of hydrolysis and the oxidation of carbohydrates into carbon dioxide and water. This takes place through a cyclic system of reactions that is called the *Krebs cycle* or *respiratory cycle*, which is localized within mitochondria. It has been defined as the focus at which all metabolic paths meet, and it is illustrated in Figure 3. Its important feature is the transformation of substances with a high energy content to other substances by driving certain other cycles which require energy: for instance, the contraction of muscle. Then it can again be considered a slow, cold combustion process, which represents the source of energy necessary for biosynthetic processes.

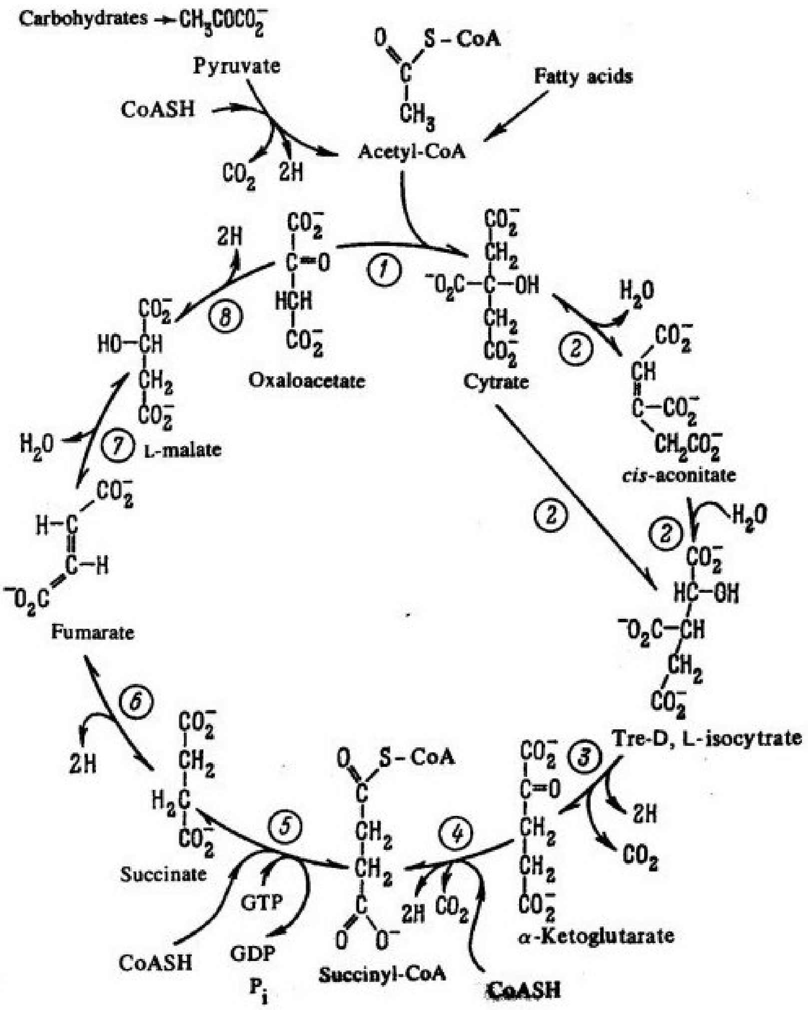
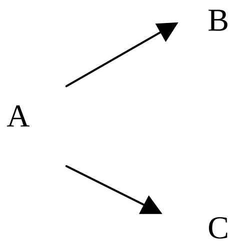


Figure 3. The Krebs cycle, by which carbohydrates are transformed in carbon dioxide and water in the cells of living systems

2. Rate Law of Chemical Reactions



In a complex reaction network the formation or disappearance of a given species is due to the combination of different simultaneous reactions, which occur through a set of *parallel* and *consecutive*

$$A \rightarrow B \rightarrow C$$

paths.

This occurrence can easily be checked in the cases of the above-mentioned examples involving oxidation and dehydrogenation.

Let us consider a reacting system in which M reactions take place with the participation of N species. From an algebraic point of view the set of chemical reactions can be represented in a very general form, as follows:

$$\begin{array}{l} \nu_{11}A_1 + \nu_{12}A_2 + \quad \ldots\ldots\ldots\ldots\ldots \quad + \ \nu_{1N}A_N = 0 \\ \nu_{21}A_1 + \nu_{22}A_2 + \quad \ldots\ldots\ldots\ldots\ldots \quad + \ \nu_{2}A_N = 0 \\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \nu_{M1}A_1 + \nu_{M2}A_2 + \quad \ldots\ldots\ldots\ldots\ldots \quad + \nu_{MN} \ A_N = 0 \end{array} \qquad (1)$$

or, more concisely:

$$\sum_{i=1}^{N} \nu_{ki}A_i = 0 \qquad , \qquad \mathrm{k} = 1,2,\cdots \mathrm{M} \qquad (2)$$

A_i indicates a generic component, while ν_{ki} is the corresponding stoichiometric coefficient in *k-th* reaction. Of course, since not all of the species involved participate in all the M reactions, most of the ν_{ki} are equal to zero.

Let us now indicate, with r_{ki}, the rate by which the species i is formed in the *k-th* reaction: that is, the amount of such a species formed per unit time and volume. By virtue of the stoichiometric restrictions, the rate of the *k-th* reaction can be defined as:

$$\frac{r_{k1}}{\nu_{k1}} = \frac{r_{k2}}{\nu_{k2}} = \cdots = \frac{r_{kN}}{\nu_{kN}} = r_k \qquad , \qquad k = 1, 2, \cdots M \qquad (3)$$

Then the rate of formation of species A_i will be given by:

$$R_i = \sum_{k=1}^{M} \nu_{ki} r_k \qquad (4)$$

The rate of a specific reaction depends on temperature and on species concentrations (see *Rate of Chemical Reactions: their Measurement and Mathematical Expressions*). An effective general method for accounting for their dependence on such variables implies the use of the following rate law:

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$$r_k = \vec{r}_k - \overleftarrow{r}_k = A_k e^{-E_k^{\neq}/RT} \Pi_i C_i^{q_i} \left(1 - \frac{1}{K_k} \Pi_i C_{ki}^{\nu_{ki}} \right) \tag{5}$$

where:

- $\vec{r}_k, \overleftarrow{r}_k$ the direct and forward rates of *k-th* reaction;
- $K_k = e^{-\Delta G_k^0/RT}$ is its equilibrium constant (see *Equilibrium in Multiphase Reacting Systems*);
- $E_k^{\pm}$ is the activation energy of the direct reaction;
- C_{ki} are the concentrations of the components which take part in the *k-th* reaction;
- q_{k_i} is the reaction order with respect to component *i*;
- A_k is the pre-exponential, or frequency, factor of the Arrhenius law; and
- ΔG_k^0 is the standard free energy change.

C_i includes, in principle, all components present in the system. In fact, only a few of those that take part to the *k-th* reaction are involved. For instance, in the first order reactions:

$$\Pi_i C_i^{q_i} \Rightarrow C \tag{6}$$

C is the concentration of the key species involved in the transformation.

3. Material and Energy Balances of Reacting Systems

Let us focus on the simplified situation illustrated in Figure 4. Here a well-mixed system is fed with a mixture of different reacting components, each of them at a concentration C_i^0 and temperature T_0. The system has a volume V; within it, concentrations and temperature have uniform values as a consequence of effective mixing. If Q is the volumetric flow rate of the feeding mixture, its residence time τ is given by the ratio V/Q. Such an idealized model is frequently employed to describe approximately the systems in which the gradients of intensive variables are negligible. It is called a *gradientless* or *continuous stirred tank reactor* (CSTR). The material balance of component *i* is given by:

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = \frac{1}{\tau}\left(C_i^0 - C_i\right) + R_i\left(C_i\right) \tag{7}$$

The *l.h.s.* represents the accumulation of component *i*, while the *r.h.s.* gives its variation due the flow and chemical reactions.

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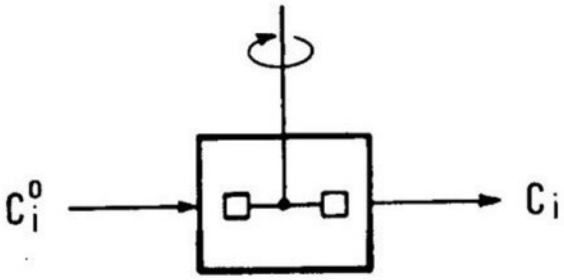

Figure 4. Continuous well-mixed, or gradientless, reactor (usually described using the acronym CSTR—continuous stirred tank reactor)

In stationary conditions $\left(\mathrm{d}C_i / \mathrm{d}t\right) = 0$, and in this case, the concentration C_i can be calculated by solving the algebraic equation so derived. For example, if the reaction rate is expressed by a first-order law, $R_i = kC_i$, it is:

$$C_i = \frac{C_i^0}{1 + k\tau} \qquad (8)$$

If we wish to account for the presence of gradients in the concentrations then the material balances must be performed on an elementary volume, as illustrated in Figure 5. The fluxes of the different components—in other words, the amount of the substance (in moles) passing through a unit of surface area in a unit of time—are expressed using the following expression:

$$\mathrm{N}_i = -D_i \nabla C_i + \mathrm{v} C_i \qquad (9)$$

where $\mathbf{v}(x, y, z, t)$ is the local fluid velocity.

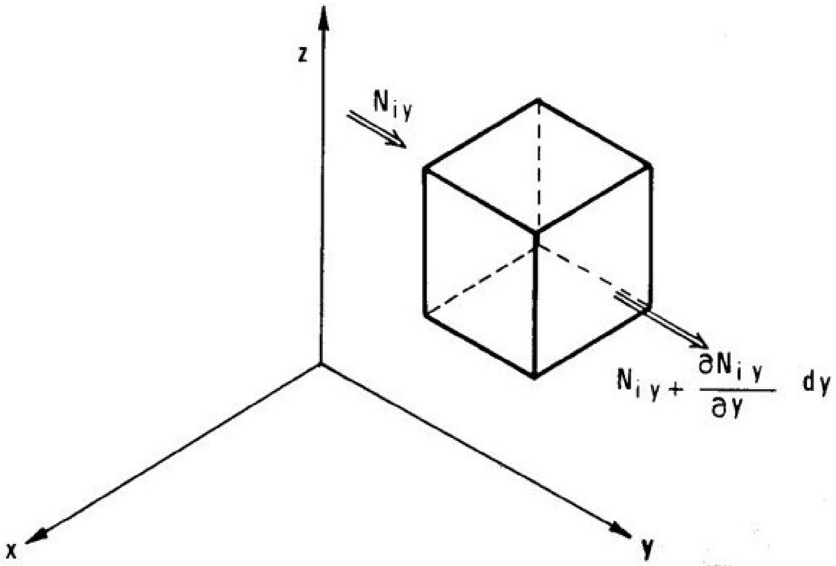

Figure 5. The arbitrary elementary volume for deriving the generalized mass balance

The second term in the *r.h.s.* represents the convective transport of component *i*, while the first term represent its diffusion (see *Microkinetics versus Macrokinetics: Role of Transport Phenomena in Reaction Rates*). The proportional constant D_i is regarded as a physical constant and is termed the *diffusion coefficient*. Moreover, the derivation is performed with respect to the co-ordinate in the direction of flux. The minus sign is used because the diffusion occurs in the direction of decreasing concentration.

The balance of component *i* in the elementary volume is stated by applying the conservation equation:

$$\begin{pmatrix}\text{Mass of Species } i\\ \text{Accumulating in dV}\end{pmatrix} = \begin{pmatrix}\text{Mass Flux of}\\ \text{species } i\\ \text{in minus that out}\end{pmatrix} + \begin{pmatrix}\text{Mass Produced}\\ \text{by chemical}\\ \text{reaction}\end{pmatrix} \qquad (10)$$

being $\mathrm{d}V = \mathrm{d}x\mathrm{d}y\mathrm{d}z$.

By considering the direction of the *z* axis, the first term on the *r.h.s.* yields:

$$N_{iz}\,\mathrm{d}x\mathrm{d}y - \left(N_{iz} + \frac{\partial N_{iz}}{\partial z}\,\mathrm{dz} \right)\mathrm{d}x\mathrm{d}y = -\frac{\partial N_{iz}}{\partial z}\,\mathrm{d}x\mathrm{d}y\mathrm{d}z \qquad (11)$$

By adding the terms corresponding to the three axes *x*, *y*, and *z*, and accounting for two other contributions, the following expression (after simplification) is created:

$$-\left(\nabla \cdot \mathrm{N}_i\right) + R_i = \frac{\partial C_i}{\partial t} \qquad (12)$$

At last, by introducing the specific expression of $\mathbf{N}_i$ the following differential equation is obtained:

$$\nabla \cdot \left(D_i \nabla C_i\right) - \nabla \cdot \left(\mathrm{v} C_i\right) + R_i = \frac{\partial C_i}{\partial t} \qquad (13)$$

Its boundary conditions are given by the rate of mass transfer at the boundary between the system and the surrounding environment. The initial conditions are expressed by the concentration's distribution at the initial time.

A similar treatment can be developed for energy transfer by expressing the amount of heat passing through a unit surface area in unit time, as follows:

$$\dot{\mathrm{q}} = -k_T \nabla T + \mathrm{v}\rho\, C_p T \qquad (14)$$

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Here k_T is the coefficient of thermal conductivity, which is regarded as a physical constant for a given material. Again the minus sign is used because the transfer of heat takes place in the direction of the decreasing temperature, according to the second law of thermodynamics. ρ is the fluid density and C_p the heat capacity when the mixture is at constant pressure.

The rate of local heat production (see *Thermodynamics Systems and State Functions*) is instead given by:

$$-\sum_i \Delta\tilde{H}_{fi} R_i \left(\frac{calories}{time\ volume}\right) \qquad (15)$$

where $\Delta\tilde{H}_{fi}$ is the molar heat of formation of component i.

In a similar manner to the previous development, if energy conservation is applied to an elementary volume the following equation is obtained:

$$\nabla \cdot \left(k_T \nabla T\right) - \nabla \cdot \left(\mathrm{v}\rho C_p T\right) - \sum_i R_i \Delta\tilde{H}_{fi} = C_p \rho \frac{\partial T}{\partial t} \qquad (16)$$

The boundary conditions of this equation are given by the rate of heat transfer at the boundary between the system and its environment. The initial conditions instead are given by the temperature profile at the initial time.

Another kind of information is actually needed to solve the examined problem; this concerns the determination of the fluid velocity as a function of position and time. This requirement can be fulfilled, at least in principle, by integrating the Navier–Stokes equation of fluid dynamics, which reflects the momentum balance on an elementary fluid volume. In actual fact, in the present treatment we are not interested in a detailed description of the motion of the fluid in which the transport processes occur, and the hydrodynamic conditions can be described in terms of average velocity values. A simple approximate approach is to assume (for instance) that the fluid velocity in a cylindrical reactor has a constant value along the reactor's axis. This approach, usually called *plug flow*, offers a simplified but effective model for describing the behavior of complex reacting systems, as will be shown in the next section.

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Biographical Sketch

Sergio Carrà was born in Milan in 1929, and is married with two sons and one grandson. He obtained a doctorate in Industrial Chemistry at the University of Milan in 1953. He has been both Assistant Professor and Associate Professor at the University of Milan. In 1968 he become full Professor of Physical

Chemistry at the University of Messina, and two years later at the University of Bologna. At present he is full rofessor of Chemical Engineering Thermodynamics at the Polytechnic of Milan. Some of his research and teaching activity has been in the USA.
Sergio Carrà has been President of the Italian Association of Physical Chemistry and Vice-President of the Italian Chemical Society, and is a member of the “Accademia Nazionale dei Lincei” and of the “Academia Europeaea”. He won the “Antonio Feltrinelli” award in 1991, the “Mario Giacomo Levi” in 1997, and the “Bonino” of the Divisione di chimica fisica della Società Chimica Italiana and the Gold Medal of the Scuola Normale Superiore di Pisa in 1999.

Sergio Carrà has had an important role in the organization of research activities performed with public financial support. He has also acted as a consultant for various companies (including Montedison, ENI, SnamProgetti, ENEL, SISAS, Atochem, and Dow) in the development of industrial projects. His research interest focuses on aspects of molecular thermodynamics, applied chemical kinetics, catalysis, and the modeling of chemical processes.

Sergio Carrà has published approximately 370 papers, six patents, and seven books.

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