A geometric representation of species concentrations in chemical kinetics

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The concept of ternary diagrams from equilibrium thermodynamics is applied to the geometric representation of species concentrations in dynamic systems. First, exact solutions of three-species kinetic systems are studied. Constants of motion based on properties of chemical reactions such as mass balance are used to obtain 2D trajectories in place of 3D ones; the triangular simplex structure is convenient for geometric representation. Then application of a quasi-stationary state approximation for successive reactions introduces another constant of motion so that the trajectory becomes 1D. Finally, using acetaldehyde pyrolysis as an example it is shown how to apply this method to complex multicomponent systems in order to obtain the representation *vs.* time of three species or three groups of species concentrations in a triangular space.

Geometric representations are a good way to visualize some properties of the equilibrium states of physico-chemical systems. For instance, binary, ternary, ... diagrams illustrate very clearly phenomena such as ebullition, solubility, miscibility, ... of systems with 2, 3, ... components.[1,2] The ability to represent kinetic information rather than simply a static situation is certainly interesting and useful in kinetic research and teaching.

After the classical work of Poincaré on integral curves, many publications propose the representation of dynamic trajectories of conservative or dissipative systems; we can cite some books[3–5] the references in which refer to many original papers. Fraser *et al.*[6–9] have developed the underlying mathematical aspects of the question with application to some classic mechanisms. Our purpose is to show how to obtain the trajectories in the triangular simplex familiar to the chemist.

The paper is organized as follows. In the first section, we apply the method to closed three-species systems including consecutive, parallel and reversible reactions. A second section examines how the quasi-stationary state approximation, applied to consecutive reactions, reduces the trajectory to a line segment. Then, considering a multicomponent reaction, we show how to extend the method to the representation of three groups of species.

Representation of simple systems

Let us consider a closed chemical system with constant volume and temperature having three species A, B and C whose concentrations change *vs.* time. The rates of accumulation of the three species are respectively:

$$v_A = d[A]/dt$$

$$v_B = d[B]/dt$$

$$v_C = d[C]/dt$$

If during the reaction the relation $v_A + v_B + v_C = 0$ is satisfied, then:

$$[A] + [B] + [C] = \text{constant} = K \qquad (1)$$

This equation corresponds to the mass balance and constitutes a constant of motion; then the 3D trajectory representing the three concentrations *vs.* time becomes a 2D one. A triangular diagram seems to be appropriate to represent the evolution of the system. Let us consider three perpendicular axes O*xyz*, which correspond respectively to the reduced concentrations $[A]/K$, $[B]/K$, $[C]/K$ *vs.* time, all of which are in the interval [0,1]. Eqn. (1) defines a plane, intercepting the axes at points *a*, *b*, *c* [Fig. 1(a)]. The triangle *abc* is called the

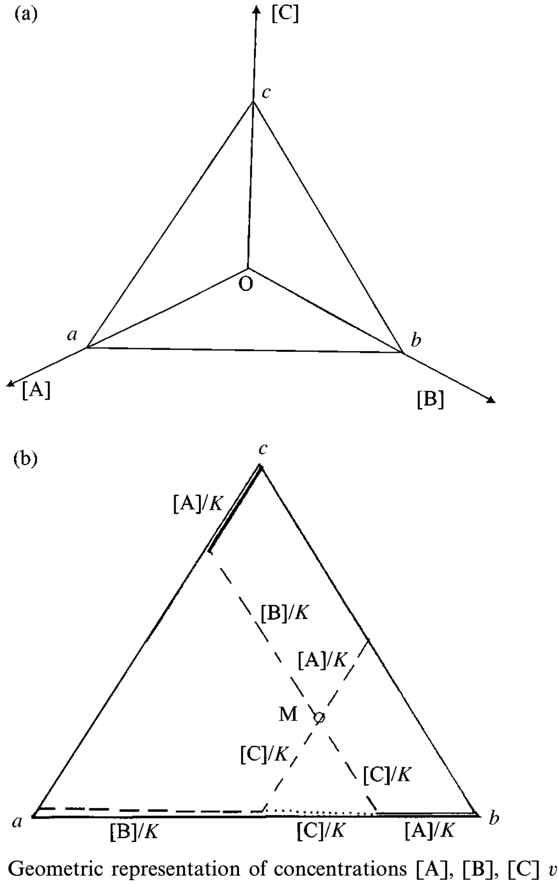

Fig. 1 Geometric representation of concentrations [A], [B], [C] *vs.* time. (a) 3D representation. (b) Reduced concentrations $[A]/K$, $[B]/K$, $[C]/K$ corresponding to point M in the simplex.

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"simplex" of the reaction. It is evidently easier to adopt a planar representation of the system in the simplex rather than the full 3-dimensional space. The set of three concentrations is represented by a point inside the equilateral triangle *abc*. The apices correspond to 100% of each species; for example the apex *a* represents 100% of species A. Then the concentrations are measured as shown in Fig. 1(b) with length *ab* now taken as unity. This property is classically used in equilibrium thermodynamics for the representation of ternary systems having three species A, B and C, as the molar fractions satisfy the equation $N_A + N_B + N_C = 1$. In chemical kinetics, the representative point of the system *vs.* time moves along a plane trajectory. If the chemical system comprises other variables such as the temperature and/or concentration of other species, the trajectory is described in a phase space having more than 3 dimensions. However, if eqn. (1) holds, the three concentrations can be represented in the sub-space O*xyz* by a plane trajectory previously defined, as will be seen later.

Hereafter we will mostly deal with the following conditions: initial conditions: $[A](0) = [A]_0 = 1$ and $[B](0) = [C](0) = 0$; rate constants: $k_1 = k_2 = \ldots = 1$ except when specified (arbitrary unit of time); orders: $n_1 = n_2 \ldots = 1$ except when specified.

Consecutive reactions

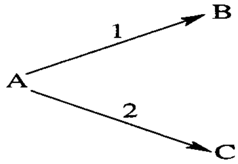
Chemical reactions generally involve many elementary steps; consecutive reactions constitute a very frequent case. Let us consider the set of 2 such reactions:

$$A \xrightarrow{1} B \xrightarrow{2} C$$

with rate constants k_1 and k_2, orders n_1 and n_2, respectively. The well known kinetic equations satisfy eqn. (1). Fig. 2(a) corresponds to a numerical example; the trajectory begins at point *a* and ends at point *c*. One can determine the concentrations for a point; for example with [A] = 0.5, [B] is equal to 0.35 and [C] equal to 0.15.

Parallel reactions

Consider the kinetic scheme and the corresponding equations



$$d[A]/dt = -k_1[A]^{n_1} - k_2[A]^{n_2}$$

$$d[B]/dt = k_1[A]^{n_1}$$

$$d[C]/dt = k_2[A]^{n_2}$$

eqn. (1) holds and the point representing the system moves along a curve in the "simplex" joining the initial point *a* to a point placed between *b* and *c* (because [A] is zero at the end of the reaction).

If $n_1 = n_2$, we obtain $d[B]/d[C] = k_1/k_2$ entailing $[B]/[C] = k_1/k_2$ due to the initial values. This corresponds to a new constant of motion $k_2[B] - k_1[C] = 0$. The 2D trajectory becomes 1D and this establishes that point **M** moves on a straight line emanating from *a*; this is an accidental degeneracy. Fig. 2(b) shows a numerical example.

Successive and reversible reactions

This mechanism is often encountered in chemical kinetics for acid–base catalysis, enzyme catalysis, transition state theory,

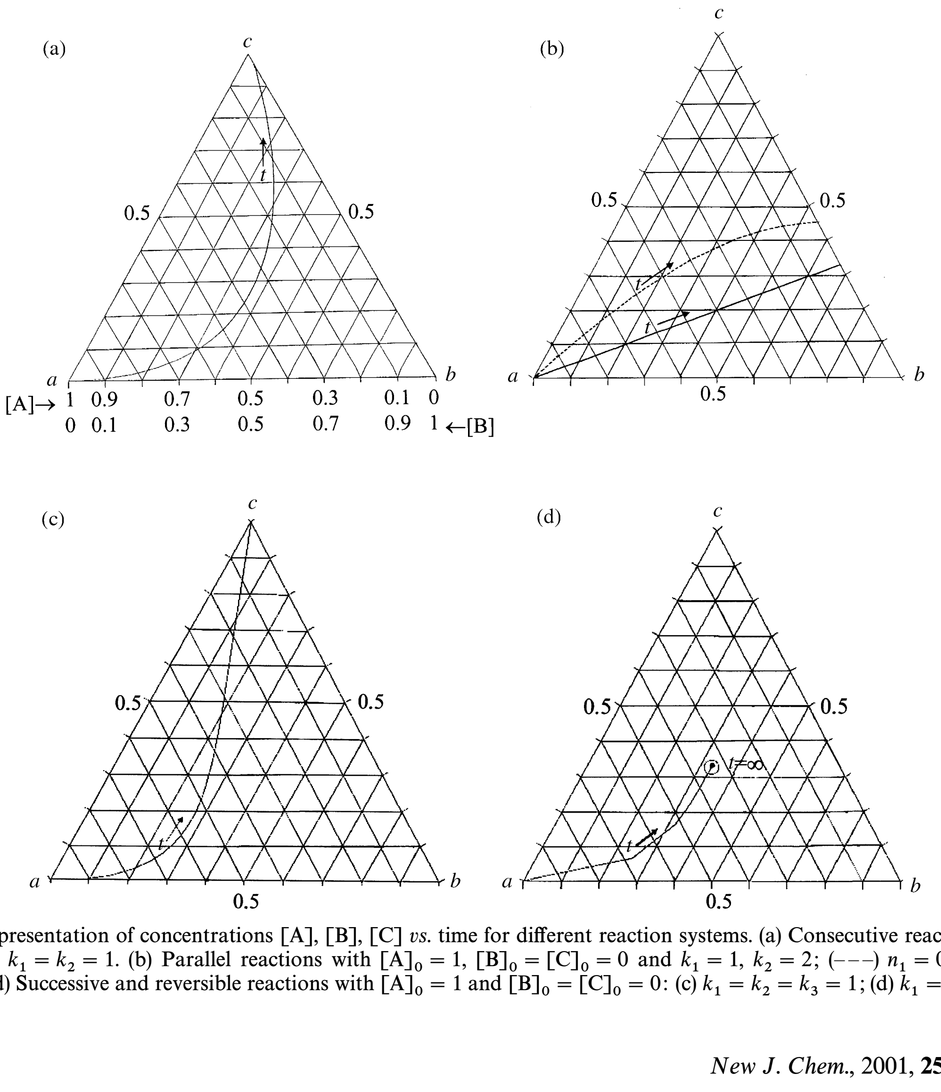


Fig. 2 Geometric representation of concentrations [A], [B], [C] *vs.* time for different reaction systems. (a) Consecutive reactions with $[A]_0 = 1$, $[B]_0 = [C]_0 = 0$ and $k_1 = k_2 = 1$. (b) Parallel reactions with $[A]_0 = 1$, $[B]_0 = [C]_0 = 0$ and $k_1 = 1$, $k_2 = 2$; (- - -) $n_1 = 0$, $n_2 = 1$ and (——) $n_1 = n_2 = 1$. (c) and (d) Successive and reversible reactions with $[A]_0 = 1$ and $[B]_0 = [C]_0 = 0$: (c) $k_1 = k_2 = k_3 = 1$; (d) $k_1 = k_2 = k_3 = k_4 = 1$.

quasi-unimolecular reaction theory by Lindemann, and in nucleophilic and electrophilic substitutions.

Let us study the very simple case where each reaction concerns only one species and is of first order:

$$\mathrm{A} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{B} \xrightarrow{3} \mathrm{C}$$

It is not necessary to write the kinetic equations to verify that eqn. (1) is fulfilled as it is only the mathematical expression of mass balance. The trajectory starts at the apex *a* and finishes at the apex *c* [Fig. 2(c)].

Similarly, we can also obtain the trajectories corresponding to the mechanism

$$\mathrm{A} \underset{2}{\overset{1}{\rightleftharpoons}} \mathrm{B} \underset{4}{\overset{3}{\rightleftharpoons}} \mathrm{C}$$

which leads finally to a chemical equilibrium represented by a point inside the simplex; the graph corresponds to Fig. 2(d). With the numerical values chosen, the three concentrations are 0.33 at equilibrium.

In summary, the graphs showing the dynamic trajectories are in the equilateral triangle *abc* because the relationship (1) is obeyed. If the medium contains only three species it is convenient to introduce the molar fractions N which satisfy the condition $N_A + N_B + N_C = 1$, whatever the nature of the chemical reactions between the different compounds. If the reactions include different stoichiometric coefficients or more than three species, the constant of the motion must take this into account, as shown later for acetaldehyde pyrolysis.

Application of the quasi-stationary state approximation (QSSA)

In the previous mode of representation it is also useful to introduce this approximation, usually made in chemical kinetics.[6,8,10–14]

Consider again the mechanism:

$$\mathrm{A} \xrightarrow{1} \mathrm{B} \xrightarrow{2} \mathrm{C};$$

Fig. 3 depicts the trajectories for different values of k_2. The graph allows the simultaneous visualisation of concentrations [A], [B] and [C] and so to decide which concentration is predominant in the system or which can be neglected at each moment. As can be seen, the larger the ratio k_2/k_1, the more the graph approaches the line *ac*, showing that the mechanism approaches that of the reaction

$$\mathrm{A} \xrightarrow{k_1} \mathrm{C}.$$

This is the essence of QSSA.

The kinetic equations are:

$$\mathrm{d[A]}/\mathrm{d}t = -k_1[\mathrm{A}]$$

$$\mathrm{d[B]}/\mathrm{d}t = k_1[\mathrm{A}] - k_2[\mathrm{B}] = 0$$

$$\mathrm{d[C]}/\mathrm{d}t = k_2[\mathrm{B}]$$

The question that now arises is how the geometric representation is modified when the differential system is solved with the help of QSSA. The two constraints of motion are: $k_1[\mathrm{A}] = k_2[\mathrm{B}]$, entailing $[\mathrm{B}]/[\mathrm{A}] = \text{constant}$ and $\mathrm{d[A]}/\mathrm{d}t + \mathrm{d[C]}/\mathrm{d}t = 0$, entailing $[\mathrm{A}] + [\mathrm{C}] = \text{constant} = K$. With these two relations, the system is confined to 1D. Its position can be determined as follows. The equation [B]/[A] defines a plane P′ including the Oz axis. The second equation corresponds to a plane P parallel to the Oy axis, dependent on the value of K. It is clear that the constant K has different values according to the initial conditions adopted. Case i: $K = K_{\mathrm{i}} = [\mathrm{A}]_0$ (plane $\mathrm{P_i}$) and Case ii: $K = K_{\mathrm{ii}} = [k_2/(k_1 + k_2)][\mathrm{A}]_0$ (plane $\mathrm{P_{ii}}$). These values imply the following. Case i: $[\mathrm{A}](0) = [\mathrm{A}]_0$; $[\mathrm{B}](0) = (k_1/k_2)[\mathrm{A}]_0$; $[\mathrm{C}](0) = 0$. Hence $[\mathrm{A}](0) + [\mathrm{B}](0) + [\mathrm{C}](0) = [(k_1 + k_2)/k_2][\mathrm{A}]_0$. With this hypothesis, the initial concentrations of A and C are correct, but [B](0) is fictitious and mass balance is not observed at the initial time.

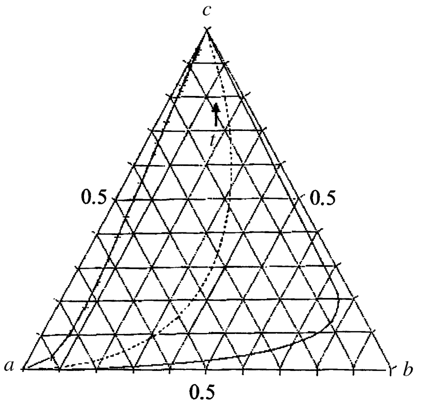


Fig. 3 Geometric representation of concentrations [A], [B], [C] *vs.* time for successive reactions with $[\mathrm{A}]_0 = 1$ and $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$, $k_1 = 1$ with different values of k_2: (——) $k_2 = 0.1$, (– – –) $k_2 = 1$; (+ + +) $k_2 = 10$.

Case ii: $[\mathrm{A}](0) = [k_2/(k_1 + k_2)][\mathrm{A}]_0$; $[\mathrm{B}](0) = [k_1/(k_1 + k_2)][\mathrm{A}]_0$; $[\mathrm{C}](0) = 0$. At the initial time, the mass of the system and the concentration of C are exact but those of A and B are fictitious. These initial conditions have been discussed previously.[10]

The dynamic trajectory of the system is a straight line since it is the intersection of two planes. The straight lines Δ_{i} and Δ_{ii} are the intersections of planes $\mathrm{P_i}$ and $\mathrm{P_{ii}}$ with plane P′ and represent the variation of the concentrations with time of the species A, B and C with the QSSA and the conditions i or ii, respectively [Fig. 4(a)]. In both cases, the trajectory is a line segment that starts at a point included in the xOy plane and ends at a point located on the Oz axis with the coordinates $[\mathrm{C}](\infty) = [\mathrm{A}]_0$ for case i and $[\mathrm{C}](\infty) = [k_2/(k_1 + k_2)][\mathrm{A}]_0$ for case ii. Fig. 4(b) depicts simultaneously the 2D trajectory (exact solution) and the 1D trajectories (with QSSA) that cross the plane of the simplex; Fig. 5 compares the exact values of [A] + [C] with K_{i} and K_{ii} corresponding to both conditions i and ii. It can easily be deduced which conditions are better according to the progress of the reaction.

In summary, QSSA is a useful approximation that simplifies both the analytical equations and the geometric representation. The graph in Fig. 5 shows the error introduced.

Application to a complex system: acetaldehyde pyrolysis

Fraser *et al.*[6–9] have studied the dynamic trajectories corresponding to some "classic" mechanisms such as those of Lindemann for quasi-unimolecular reactions or of Michaelis–Menten–Henri for enzymatic catalysis. They use the fact that "constants of motion can always be found by addition of appropriate equations from the complete reaction scheme",[6] such as atom, mass or catalyst (enzyme) conservation to simplify the graphic representation of the dynamic trajectory.

In this section we examine how the graphic representation of more complex systems such as chain reactions can be simplified by the use of "constants of motion". These constants correspond either to conservation laws or to approximations. Conservation laws (mass or atom) exist for all chemical

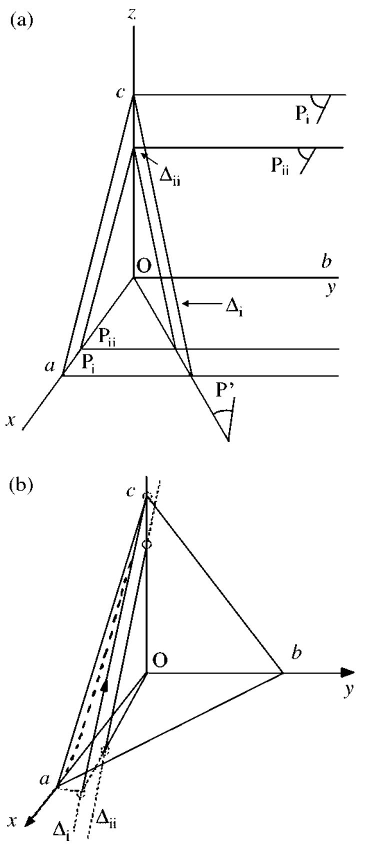


Fig. 4 QSSA applied to the mechanism $A \rightarrow B \rightarrow C$. (a) The planes P_i and P_{ii} correspond to the relation $[A] + [C] = K$ with different initial conditions: $K_i = A_0$; $K_{ii} = [k_2/(k_1 + k_2)][A]_0$. The plane P' corresponds to the relation $[B]/[A] = k_1/k_2$. (b) The segments Δ_i and Δ_{ii} represent the dynamical trajectories for fictitious initial conditions i and ii. The exact trajectory is represented by the bold dashed line.

systems while approximations correspond to experimental or particular conditions such as QSSA, catalysis, first steps of reaction, large excess of a reactant, *etc.*

We will consider a multicomponent system such as acetaldehyde pyrolysis in order to show how atom balances and approximations can be combined to obtain plane trajectories. The Rice–Herzfeld mechanism[15] describes the experimental results.

The reaction sequence is:

Chain initiation

$$CH_3CHO \rightarrow CH_3 + CHO$$

Chain propagation

$$CHO + M \rightarrow H + CO + M$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$$

$$H + CH_3CHO \rightarrow H_2 + CH_3CO$$

$$CH_3CO + M \rightarrow CH_3 + CO + M$$

Chain termination

$$CH_3 + CH_3 \rightarrow C_2H_6$$

where M represents all the species. This mechanism contains successive and parallel reactions. The determination of the 9 species concentrations is obtained by the resolution of a system of 9 stiff ordinary differential equations (ODEs). The geometric representation is in a multidimensional space. However 7 constants of motion can be found. First, applying QSSA to the atom and radical concentrations of H, CH_3, CHO and CH_3CO introduces 4 constants[16]; second, the atom balances (H, C, O) introduce 3 more constants. The system can then be described by $9 - 7 = 2$ independent variables. As a consequence, the trajectory is confined in a 2D space.

Integration of the ODEs according to Gear's method[17] with the rate constants recommanded by Gardiner[18] has been performed at three temperatures with an initial acetaldehyde of concentration 10^{-5} mol cm^{-3}. As supposed by QSSA, the stationary radical concentrations are very small; for example, at 800 K, they are:[19] $[CHO] = 4.5 \times 10^{-16}$; $[CH_3] = 1.37 \times 10^{-13}$; $[H] = 1.55 \times 10^{-19}$; $[CH_3CO] = 7.6 \times 10^{-13}$ mol cm^{-3}. If these species are neglected, the balances for the atoms H, C and O are respectively:

$$4[CH_3CHO] + 4[CH_4] + 6[C_2H_6] + 2[H_2] = 4[CH_3CHO]_0 \quad (2)$$

$$2[CH_3CHO] + [CO] + [CH_4] + 2[C_2H_6] = 2[CH_3CHO]_0 \quad (3)$$

$$[CH_3CHO] + [CO] = [CH_3CHO]_0 \quad (4)$$

The combination 4[eqn. (3) – eqn. (4)] – eqn. (2) shows that $[H_2] = [C_2H_6]$.

As the system evolution has to be represented by 2 independent variables, for the geometric representation we can choose an equilateral triangle with 3 interdependent variables, either $[CH_3CHO]$, $[CH_4]$, $2[C_2H_6]$ corresponding to eqn. (2) or $2[CH_3CHO]$, $[CO]$, $([CH_4] + 2[C_2H_6])$ corresponding to eqn. (3).

We report the evolution of the reduced concentrations at three temperatures: 800, 1100 and 1200 K for the first case because it is interesting to follow the transformation of acetaldehyde into the two hydrocarbons CH_4 and C_2H_6 issued from the radical CH_3. Fig. 6 shows the evolution of the three species as a function of temperature and progress of reaction. The ratio $2[C_2H_6]/[CH_4]$ increases with temperature, as

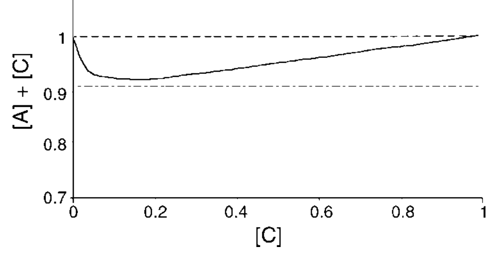


Fig. 5 In $A \rightarrow B \rightarrow C$ the exact and approximate (QSSA) solutions of $[A] + [C]$ *vs.* $[C]$ with $k_1 = 1$ and $k_2 = 10$: (——) exact solution, (– – –) initial conditions i; (– • – • –) initial conditions ii.

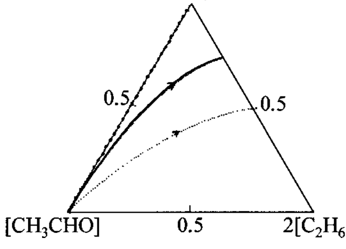


Fig. 6 Representation of the reduced concentrations $[CH_3CHO]/[CH_3CHO]_0$, $[CH_4]/[CH_3CHO]_0$; $2[C_2H_6]/[CH_3CHO]_0$ at different temperatures: (•••) 800, (——) 1100, (······) 1200 K.

shown experimentally by Colket *et al.*;[20] it is of the order of 10^{-3} at 800 K and 0.5 at 1200 K.

In summary, the example chosen shows the possibility of giving a plane representation even for complex systems having more than 3 species, based on the condition that a sufficient number of constants of motion can be found by using atom conservation in closed systems and, when possible, by applying QSSA to intermediate species. Then the triangular diagram seems to be the most appropriate to represent the time evolution of the system.

Conclusions

Geometric representation of concentrations *vs.* time for complex reactions concerning three or more species has to be done in a multidimensional space of species concentrations. Introduction of constants of motion such as mass or atom balances or the quasi-stationary state approximation reduces the dimension of the graph. We have chosen to represent the dynamic trajectories in a triangular simplex having the advantage of giving the concentrations of three linked species or three groups of species simultaneously and highlighting some properties of dynamic systems, as do ternary diagrams in thermodynamic equilibria. First we have demonstrated the method in the elementary case of three symbolic species with different reaction schemes. Then QSSA is used to introduce another constant of motion. Finally, with the example of acetaldehyde pyrolysis, we have developed the method for a complex system in which atom balances as well as QSSA are introduced to allow triangular representation of the evolution of three non-independent concentrations. This example illustrates a general method, which is the following: (i) determination of all the species concentrations; (ii) introduction of motion constraints based on mass or atom balances and on kinetic reasons such as QSSA or catalyst balance; this reduces the number of independent concentrations; and (iii) if the composition of the system depends only on two independent variables, the triangular simplex is attractive and appropriate to represent the dynamic trajectory of three now independent concentrations or of three groups of concentrations.

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