Deterministic Differential Equations of Chemical Reactions

Lawi George

(The University Of Choice)

Department of Mathematics
Masinde Muliro University of Science and Technology

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Chemical Reaction Networks-Revisited

Definition

Reaction Network:

A chemical reaction network consists of three sets:

(i) a finite set $\mathcal{S}$, elements of which are the species of the network

(ii) a finite set $\mathcal{C}$ of vectors in $\overline{\mathbb{R}}_+$ called the complexes of the network

(iii) a finite set $\mathcal{R} \subset \mathcal{C} \times \mathcal{C}$ with the properties:

(a) for each $y \in \mathcal{C}$, $(y, y) \notin \mathcal{R}$

(b) for each $y \in \mathcal{C}$ there is a $y^{'} \in \mathcal{C}$ such that $(y, y^{'}) \in \mathcal{R}$ or $(y^{'}, y) \in \mathcal{R}$

Members of $\mathcal{R}$ are the reactions of the network. When $(y, y^{'}) \in \mathcal{R}$, we say that complex y reacts to complex $y^{'}$. The vector y is called the reactant complex of the reaction $y \longrightarrow y^{'}$, and $y^{'}$ is called its product complex. The vector $y^{'} - y$ is called the reaction vector.

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Remark: The component y_s (corresponding to species $s \in \mathcal{S}$) of the complex $y \in \mathbb{R}_+^s$ is usually called by chemists the *stoichiometric coefficient* of species s in complex y. For example, in the complex B+E of Eqn (2) (Previous lecture), the stoichiometric coefficient of B is 1, the stoichiometric coefficient of E is 1, and the stoichiometric coefficients of A, D, and C are 0. In the complex 2B, the stoichiometric coefficient of B is 2, and the stoichiometric coefficients of A, C, D, and E are 0.

Definition

The support of y, denoted supp y is the set of species that have nonzero stoichiometric coefficients in complex y. Thus, for example, supp A + B = {A, B} and supp 2B = {B}. The support of a complex is, in effect, the set of species that "appear in" that complex.

Definition

A kinetics for a reaction network $\{\mathcal{S}, \mathcal{C}, \mathcal{R}\}$ is an assignment to each reaction $y \longrightarrow y' \in \mathcal{R}$ of a continuously differentiable rate function $\mathcal{K}_{y \longrightarrow y'} : \mathbb{R}_+^{\mathcal{S}} \to \overline{\mathbb{R}}_+$ such that

$$\mathcal{K}_{y \longrightarrow y'}(c) > 0 \text{ if and only if supp } y \subset \text{supp c} \tag{1}$$

- Recall $\mathcal{K}_{y \longrightarrow y'}(c)$ was the occurrence rate of the reaction $y \longrightarrow y'$ when the mixture under study had composition c. There we required only that the rate functions take nonnegative values.

- In condition given in the definition above, we go a little further by delineating those $c \in \overline{\mathbb{R}}_+^{\mathcal{S}}$ for which the function $\mathcal{K}_{y \longrightarrow y'}(\cdot)$ takes positive values.

- In words, then, in the definition above implies this: Reaction $y \longrightarrow y'$ proceeds at nonzero rate, however slowly, if and only if all species appearing in the reactant complex y are actually present in the mixture.

- For example, $A + C \rightarrow D$ proceeds at nonzero rate if and only if c_A and c_C are both positive.

- We will say that c is a *positive composition* if it is a member of $\mathbb{R}_+^{\mathcal{S}}$ — that is, if all species concentrations are strictly positive. In this case supp c $= \mathcal{S}$, whereupon supp y $\subset$ supp c for all $y \in \mathcal{C}$. Thus, if c is a positive composition, we have

$$\mathcal{K}_{y \longrightarrow y'}(c) > 0, \ \forall \ y \longrightarrow y' \in \mathcal{R} \qquad (2)$$

Definition

A kinetic system $\{\mathcal{S}, \mathcal{C}, \mathcal{R}, \mathcal{K}\}$ is a reaction network $\{\mathcal{S}, \mathcal{C}, \mathcal{R}\}$ taken with a kinetics $\mathcal{K}$.

Mass action Kinetics

Definition

A kinetics $\mathcal{K}$ for a reaction network $\{\mathcal{S}, \mathcal{C}, \mathcal{R}\}$ is *mass action* if, for each $y \longrightarrow y^{'} \in \mathcal{R}$,there is a positive number $\mathcal{K}_{y \longrightarrow y^{'}}$ such that

$$\mathcal{K}_{y \longrightarrow y^{'}}(c) \equiv \kappa_{y \longrightarrow y^{'}} \prod_{s \in \mathcal{S}} c_s^{y_s} \tag{3}$$

- In Eqn (3), y_s is the stoichiometric coefficient of species s in the reactant complex y in the reaction $y \longrightarrow y^{'}$
- The number $\kappa_{y \longrightarrow y^{'}}$ is the rate constant for the reaction $y \longrightarrow y^{'}$
- With Eqn(3) in mind, then for example in the reaction $A + C \rightarrow D$

$$\mathcal{K}_{A+C \rightarrow D}(c) \equiv \kappa_{A+C \rightarrow D}(c_A)^1(c_B)^0(c_C)^1(c_D)^0(c_E)^0$$
$$= \kappa_{A+C \rightarrow D}(c_A)^1(c_C)^1$$

- Similarly in the reaction $2B \rightarrow A$

$$\mathcal{K}_{2B \rightarrow A}(c) \equiv \kappa_{2B \rightarrow A}(c_A)^0(c_B)^2(c_C)^0(c_0)^0(c_E)^0$$
$$= \kappa_{2B \rightarrow A}(c_B)^2$$

If we define c^y as follows:

$$c^y := \prod_{s \in \mathcal{S}} c_s^{y_s}$$

- Thus, mass action rate functions take the form

$$\mathcal{K}_{y \rightarrow y'}(c) \equiv \kappa_{y \rightarrow y'} c^y$$

NB:A *mass action system* $\{S, C, R, \kappa\}$ is a chemical reaction network $\{S, C, R\}$ taken with a rate constant specification $\kappa \in \mathbb{R}_+^{\mathcal{R}}$.

Definition

For a kinetic system $\{\mathcal{S}, \mathcal{C}, \mathcal{R}, \mathcal{K}\}$, the species-formation-rate function $f(\cdot)$ is defined by the requirement that, for all $c \in \overline{\mathbb{R}}_+^{\mathcal{S}}$

$$f(c) = \sum_{\mathcal{R}} \mathcal{K}_{y \to y'}(c)(y' - y). \tag{4}$$

A composition $c^* \in \overline{\mathbb{R}}_+^{\mathcal{S}}$ is an equilibrium of the kinetic system if $f(c^*) = 0$. A positive equilibrium is an equilibrium in $\mathbb{R}_+^{\mathcal{S}}$

Interpretation: If, in our homogeneous reactor, the instantaneous composition is c, then, for each $s \in S$, $f_s(c)$ gives the instantaneous rate of generation (per unit volume of mixture) of moles of species s due to the simultaneous occurrence of all reactions in $\mathcal{R}$.

Note that

$$f_s(c) = \sum_{\mathcal{R}} \mathcal{K}_{y \to y'}(c)(y'_s - y_s). \tag{5}$$

so that $f_s(c)$ is obtained by summing all the reaction occurrence rates, each weighted by the net number of molecules of s produced with each occurrence of the corresponding reaction. This is essentially the idea we used in chapter 2. At an equilibrium, the generation rate of every species is zero.

Note that the species-formation-rate function for the mass action kinetic system $\{\mathcal{S}, \mathcal{C}, \mathcal{R}, \kappa\}$ takes the form

$$f(c) = \sum_{\mathcal{R}} \kappa_{y \to y'} c^y (y' - y). \tag{6}$$

The Differential Equations for a Kinetic System

By the differential equation for a kinetic system, we mean

$$\dot{c} = f(c), \tag{7}$$

where the overdot denotes time differentiation and $f(\cdot)$ is the species-formation-rate function. That is, for a kinetic system $\{\mathcal{S}, \mathcal{C}, \mathcal{R}, \mathcal{K}\}$ the corresponding differential equation is

$$\dot{c} = \sum_{\mathcal{R}} \mathcal{K}_{y \to y'}(c)(y' - y). \tag{8}$$

This vector equation of course encodes a system of scalar equations, one for each species:

$$c_s = \sum_{\mathcal{R}} \mathcal{K}_{y \to y'}(c)(y'_s - y_s) \forall s \in S \tag{9}$$

Written for network Eqn(2), the system Eqn(9) is equivalent to Eqn(10).

$$\frac{dc_A}{dt} = -\mathcal{K}_{A\to 2B}(c) + \mathcal{K}_{2B\to A}(c) - \mathcal{K}_{A+C\to D}(c) + \mathcal{K}_{D\to A+C}(c)+$$
$$\mathcal{K}_{B+E\to A+C}(c) \tag{10}$$

$$\frac{dc_B}{dt} = 2\mathcal{K}_{A\to 2B}(c) - 2\mathcal{K}_{2B\to A}(c) + \mathcal{K}_{D\to B+E}(c) - \mathcal{K}_{B+E\to A+C}(c)$$

$$\frac{dc_C}{dt} = -\mathcal{K}_{A+C\to D}(c) + \mathcal{K}_{D\to A+C}(c) + \mathcal{K}_{B+E\to A+C}(c)$$

$$\frac{dc_D}{dt} = \mathcal{K}_{A+C\to D}(c) - \mathcal{K}_{D\to A+C}(c) - \mathcal{K}_{D\to B+E}(c)$$

$$\frac{dc_E}{dt} = \mathcal{K}_{D\to B+E}(c) - \mathcal{K}_{B+E\to A+C}(c)$$

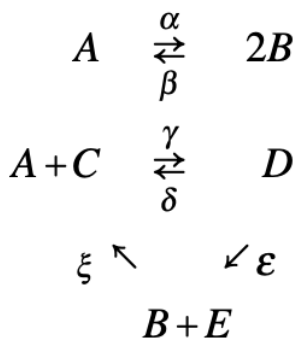For a mass action system $\{\mathcal{S}, \mathcal{C}, \mathcal{R}, \kappa\}$, the governing vector differential equation becomes

$$\dot{c} = \sum_{\mathcal{R}} \kappa_{y \to y'} c^y (y' - y). \tag{11}$$

The component form is

$$\dot{c}_s = \sum_{\mathcal{R}} \kappa_{y \to y'} c^y (y'_s - y_s) \; \forall s \in S \tag{12}$$

With mass action kinetics the rate functions become

$$\mathscr{K}_{A \to 2B}(c) \equiv \alpha c_A \quad \mathscr{K}_{2B \to A}(c) \equiv \beta (c_B)^2 \quad \mathscr{K}_{A+C \to D}(c) \equiv \gamma c_A c_C$$
$$\mathscr{K}_{D \to B+E}(c) \equiv \varepsilon c_D \quad \mathscr{K}_{D \to A+C}(c) \equiv \delta c_D \quad \mathscr{K}_{B+E \to A+C}(c) \equiv \xi c_B c_E$$

$$\tag{13}$$

$$A \quad \underset{\beta}{\overset{\alpha}{\rightleftarrows}} \quad 2B$$

$$A + C \quad \underset{\delta}{\overset{\gamma}{\rightleftarrows}} \quad D$$

$$\xi \nwarrow \qquad \swarrow \varepsilon$$

$$B + E$$

$$(14)$$

Using Eqn(12) with definition Eqn(13) the system of differential equations induced is given by

$$\frac{dc_A}{dt} = -\alpha c_A + \beta(c_B)^2 - \gamma c_A c_C + \delta c_D + \xi c_B c_E$$

$$\frac{dc_B}{dt} = 2\alpha c_A - 2\beta(c_B)^2 + \varepsilon c_D - \xi c_B c_E$$

$$\frac{dc_C}{dt} = -\gamma c_A c_C + \delta c_D + \xi c_B c_E \qquad (15)$$

$$\frac{dc_D}{dt} = \gamma c_A c_C - \delta c_D - \varepsilon c_D$$

$$\frac{dc_E}{dt} = \varepsilon c_D - \xi c_B c_E$$

1. M. A. Feinberg, *Lectures on Chemical Reaction Networks*. University of Rochester, 1979.
2. Jeremy Gunawardena, *Chemical reaction network theory for in-silico biologists*

THE END

WHAT NEXT?