Introduction to Chemical Reaction Networks

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July 17, 2023

Organization

Preliminaries

- Chemical reaction network theory (CRNT) was initiated at the beginning of the 1970's by Martin Feinberg, Fritz Horn und Roy Jackson. Since then it has continued to be developed further, with Feinberg playing a central role.
- CRNT is an area of applied mathematics that attempts to model the behavior of chemical and biochemical systems.
- Chemical systems-chemical mixtures comprising a netwotk or set of interacting molecules
- For instance the reaction $2H_2 + O_2 \rightarrow 2H_2O$-summary of the reaction which takes place in the combustion of hydrogen.
- Biochemical systems are chemical reactions taking place inside living organisms
- Formulating the description of the reactions mathematically amounts to modelling.

Preliminaries...contd

- This modelling takes the form of (a system) differential equations.
- Models are usually built upon simplifying assumptions
- CRNT is concerned with the study of the solutions of ordinary differential equations where the unknowns are the concentrations of the substances involved as functions of time.
- Thus, one of the main focuses of the CRN theory is about the existence and stability of equilibria, or steady states.
- Major results are the deficiency theorems and the global attractor conjecture

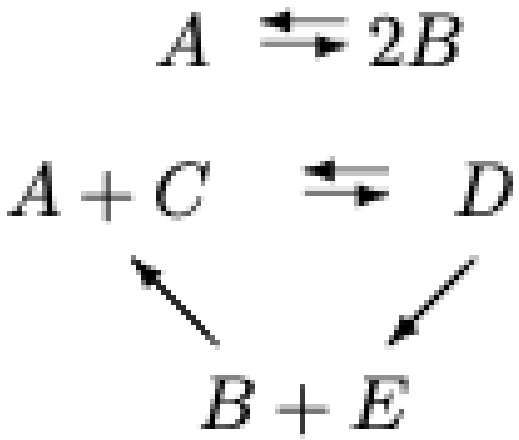
The S,C,R Notation

- The case of the combustion of hydrogen may be considered as a reaction of the form

$$2A + B \rightarrow 2C \tag{1}$$

  involving substances A, B and C.
- Two molecules of A come together with one molecule of B and two molecules of C are produced.
- The interactions (arrows) in the diagram can represent a range of processes, such as chemical binding or unbinding, reaction catalysis, or regulation of activity.

The S,C,R Notation-contd



$$A \rightleftharpoons 2B$$
$$A + C \rightleftharpoons D$$
$$B + E \tag{2}$$

- In the set of reactions in Eqn (2) a molecule of substance A is consumed to produce two molecules of B. Two molecules of B decompose into a molecule of A and so on.

The S,C,R Notation-contd

Definition

Species: A chemical species is a chemical substance that is involved in a reaction, either as a reactant or a product, or both.

- If there are in total s species in some reactions and we label them by $S_1, ..., S_s$, then we say

$$\mathcal{S} = \{S_1, ..., S_s\} \tag{3}$$

with

$$|\mathcal{S}| = s$$

is the set of chemical species involved in this reaction network.

- For Eqn (1), $\mathcal{S} = \{A, B, C\}$ while for Eqn (2) $\mathcal{S} = \{A, B, C, D, E\}$

The S,C,R Notation-contd

- Simply stated, a complex is the object at a head or a tail of a reaction arrow, as in Eqn (1).
- For instance, the complexes in Eqn (1) are $2A + B$ and $2C$. The complex set is thus given by

$$\mathcal{C} = \{2A + B, 2C\} \tag{4}$$

- For simplicity, we say that the number of complexes is n, so

$$|\mathcal{C}| = n$$

.

Definition

Complex: A complex y_k is a non-negative vector that represents the number of units of each species consumed or created in the $k - th$ reaction. The set of complexes is given by

$$\mathcal{C} = \{y_k\} \tag{5}$$

The S,C,R Notation-contd

- Often we denote the source vector by y_k and the product vector by $y_k^{'}$, but both y_k and $y_k^{'}$ belong to $\mathcal{C}$.
- We can write the reactants and products in Eqn (1) as column vectors: $y_k = [2, 1, 0]^T$ and $y_k = [0, 0, 2]^T$
- Each y_k is associated with a linear combination of the species, and the coefficient of S_i is given by y_{ki}.
- In chemistry the numbers y_{ki} are called stoichiometric coefficients. (e.g, if $y_k = [2, 1, 0]^T$, then the coefficient of S_2 is 1.)

The S,C,R Notation-contd

- The complexes in a reaction network form a finite subset $\mathcal{C}$ of the vector space $F(\mathcal{S})$ of real- valued functions on $\mathcal{S}$ with pointwise addition.
- The space $F(\mathcal{S})$ has a natural basis which is given by the characteristic functions of the points of $\mathcal{S}$.
- The characteristic function of the point with index i is denoted by ω_i.
- In this way the vector space can be identified with $\mathbb{R}^m$, where m is the number of elements of $\mathcal{S}$. In Eqn(1), m $= 3$ and the complexes are represented by the vectors $[2, 1, 0]^T$ and $[0, 0, 2]^T$.

Definition

Reaction: A reaction is an ordered pair of complexes.
A reaction $\mathcal{R}_k$ is given by $\mathcal{R}_k = y_k \rightarrow y_k^{'}$, where y_k and $y_k^{'}$ are complexes defined as above.
The set of all reactions are given by (denote the size of the set by r):

$$\mathcal{R} = \{y_k \rightarrow y_k^{'} : y_k, y_k^{'} \in \mathcal{C}\}, \tag{6}$$

where

$$|\mathcal{R}| = r$$

Identify the species, the complexes and the reactions for the CRN given by Eqn (2)

The S,C,R Notation-contd

- The first element is the left hand side with the substances which go into the reaction (often called educts or reactants) and the second with the products of the reaction.
- The reaction which transforms y_k into $y_k^{'}$ can also be thought of as a function on $\mathcal{C}$ with the value -1 at the point y_k and the value $+1$ at the point $y_k^{'}$.
- The space $F(\mathcal{S})$ of real-valued functions on $\mathcal{C}$ also has a natural basis given by characteristic functions and can be identified with $\mathbb{R}^n$, where n is the number of complexes.
- Because the reactions which occur in a model are often a combination of several elementary reactions it is useful to extend the definition of complexes to be non-negative real-valued functions on $\mathcal{S}$ which do not have to take their values in the integers.

The S,C,R Notation-contd

- The function which is identically zero also defines a complex which is often denoted by 0.
- A reaction where the left hand side is 0 is a source, where certain substances are introduced into the system.
- One where the right hand side is 0 is a sink where certain substances are removed from the system.
- In a continuous flow stirred tank reactor reactions of these type always occur.

Chemical Reaction Networks

- $\mathbb{R}_+^s$ will denote the set of positive real numbers
- $\overline{\mathbb{R}}_+^s$ will denote the set of nonnegative real numbers.
- For the index set of species $\mathcal{S}$, it becomes clear that

$$y_k \in \overline{\mathbb{R}}_+^s$$

.

- We shall regard a network to be specified by its set $\mathcal{S}$ of species, by its set $\mathcal{C}$ of complexes, and by a "reacts to" relation $\mathcal{R}$ that indicates how the complexes are joined by reaction arrows.
- That is, specification of $\mathcal{R}$ amounts to specification of a subset of $\mathcal{C} \times \mathcal{C}$, the set of all ordered pairs of complexes.
- We will require, naturally, that no complex reacts to itself and that no complex is isolated i.e, that each complex lies either at the head or at the tail of some reaction arrow.

Chemical Reaction Networks-contd

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 $y^{'}$.

Chemical Reaction Networks-contd

- A path from y_k to $y_k^{'}$ is a sequence y^i,$0 \leq i \leq k$ of complexes with the properties that $y^0 = y$, $y^k = y^{'}$ and for each i either $y^i \rightarrow y^{i+1}$ or $y^{i+1} \rightarrow y^i$ belongs to $\mathcal{R}$.
- If $y^i \rightarrow y^{i+1}$ is always in $\mathcal{R}$ the path is called directed. The trivial case $k = 0$ is allowed.

Definition

Reversibility: A network is called reversible if the fact that $y \rightarrow y^{'}$ is in the network implies that $y^{'} \rightarrow y$ is in the network.

Definition

Weak reversibility:
A network is called weakly reversible if the existence of a directed path from y to $y^{'}$ implies the existence of a directed path from $y^{'}$ to y.

Chemical Reaction Networks-contd

- The reaction networks considered above are referred to as closed, meaning that there are no reactions whose products or reactants lie outside of the network. The steady-state behaviour of such networks is thermal equilibrium, a state in which all net reaction rates are zero.
- According to a precise formalism, each reaction network gives rise to its own first-order system of differential equations that governs the evolution of the various species concentrations
- Reaction networks arise naturally in biology, in the manufacture of new materials, in energy production, in environmental dynamics, and in commerce generally.

General Kinetics

- For Eqn (2) we suppose that various amounts of the species go into a reaction.
- Assume the container or pot is stirred constantly so that its contents remain spatially homogeneous for all time
- Suppose also that the contents of the pot are forever maintained at fixed temperature and total volume.
- the occurrence of chemical reactions will serve to consume certain species and generate others.
- the temporal evolution of the composition?
- Denote the values of the molar concentrations of the species at time t by $c_A(t), c_B(t), c_C(t), c_D(t)$, and$c_D(t)$,
- Define this set as the "composition vector" $c(t)$.

General Kinetics -contd

- We would like to write down differential equations that describe the evolution of the five molar concentrations of the species in Eqn (2). Since chemical reactions are the source of composition changes-How rapidly are they occurring?
- What is generally assumed is that the instantaneous occurrence rate of each reaction depends in its own way on the instantaneous mixture composition vector, c.
- Thus, we presume, for example, the existence of a non-negative real-valued rate function $\kappa_{A\to 2B}(.)$ such that $\kappa_{A\to 2B}(c)$ is the instantaneous occurrence rate of reaction $A \to 2B$(per unit volume of mixture) when the instantaneous mixture composition is given by the vector c.
- Similarly, we presume the existence of a rate function $\kappa_{2B\to A}(.)$ for the reaction $2B \to A$, a rate function $\kappa_{A+C\to D}(.)$ for the reaction $A + C \to D$, and so on.
- A kinetics for a reaction network is an assignment of a rate function to each reaction in the network.

General Kinetics -contd

- Once we presume that network Eqn (2) is endowed with a kinetics, we are in a position to write down the system of differential equations that govern our reactor.
- Suppose that, at some instant, the reactor is in some composition state c.
- Let us begin by thinking about the instantaneous rate of change of c_A. Every time the reaction $A \to 2B$ occurs, we lose a molecule of A, and that reaction has an occurrence rate $\kappa_{A\to 2B}(c)$.
- On the other hand, every time the reaction $2B \to A$ occurs, we gain a molecule of A, and that reaction occurs at rate $\kappa_{2B\to A}(c)$. Similarly, the reactions $B + E \to A + C$ and $D \to A + C$ produce a molecule of A with each occurrence, while each occurrence of the reaction $A + C \to D$ results in the loss of a molecule of A. Thus we write

General Kinetics -contd

$$\frac{dc_A}{dt} = -\kappa_{A\to 2B}(c) + \kappa_{2B\to A}(c) - \kappa_{A+C\to D}(c) + \kappa_{D\to A+C}(c) + \kappa_{B+E\to A+C}(c) \quad (7)$$