PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 38, NOS. 1-2, PP. 133-138 (1994)

LINEAR SORPTION MODELLED BY A MARKOV PROCESS

Árpád PETHŐ

Institut für Technische Chemie
Universität Hannover
D-30167 Hannover, Germany

Received: July 23, 1994

Abstract

Consider a network of n compartments assuming that transition processes may occur between them: e.g. heat or mass transfer, or any kind of exchange of the first order. In fact, we have a Markov process with n states.

Keywords: linear sorption, Markov process.

1. Introduction

Consider a network of n compartments assuming that transition processes may occur between them: e.g. heat or mass transfer, or any kind of exchange of the first order. In fact, we have a Markov process with n states: $A_1, A_2, \ldots, A_n$; the state occupancies $x_1, x_2, \ldots, x_n$ (e.g. the distribution of 1 kg mass) obey the differential equations:

$$\frac{\mathrm{d}}{\mathrm{d}t}\begin{bmatrix} x_1 \\ \vdots \\ . \\ x_n \end{bmatrix} = \begin{bmatrix} k_{11} & \ldots & k_{1n} \\ k_{21} & \ldots & k_{2n} \\ \ldots & \ldots & \ldots \\ k_{n1} & \ldots & k_{nn} \end{bmatrix} \begin{bmatrix} x_1 \\ \vdots \\ . \\ x_n \end{bmatrix}; \qquad k_{ij} \geq 0, \qquad i \neq j \tag{1.1}$$

with

$$k_{ii} = -\sum_{j \neq i} k_{ji} \tag{1.2}$$

and the initial conditions [1]:

$$\text{for} \quad t = 0: \quad x_1 = 1, \quad x_2 = \ldots = x_n = 0. \tag{1.3}$$

In order to handle the problem we introduce the Laplace transforms

$$\mathcal{L}\{x_i(t)\} = \int_0^\infty e^{-st} x_i(t)\mathrm{d}t \equiv x_i(s); \quad i = 1, 2, \ldots, n. \tag{1.4}$$

Let us consider the partitioning (without any practical meaning for the time being)

$$A_1 : \quad \text{'mobile' phase and}$$
$$\{A_2, \ldots, A_n\} : \quad \text{'fixed' phase}$$

and let us calculate the ratio

$$\frac{x(s)}{x_1(s)} \equiv J(s), \tag{1.5}$$

where

$$x(s) = \sum_{i=1}^{n} x_i(s). \tag{1.6}$$

Using the rules

$$\mathcal{L}\left\{\frac{\mathrm{d}x}{\mathrm{d}t}\right\} = sx(s) - x(t)\Big|_{t=0}, \tag{1.7}$$

and

$$\mathcal{L}\{1\} = \frac{1}{s} \tag{1.8}$$

and applying Cramer's rule we immediately have from the transformed solution of (1.1) – (1.2) – (1.3):

$$J(s) = \frac{|sI - K|}{s\,|sI^1 - K^1|}, \tag{1.9}$$

where $K = [k_{ij}]$ and K^1 is obtained by deleting the first row and first column in K (and similarly I^1, too).

What we are interested in is whether or not J remains unchanged (invariant) by changing our model to a moving-phase one: the system being situated in a CSTR, or in a one-dimensional tube where convectional-diffusional transport takes place.

2. The Lumped-parameter System (CSTR)

Let us define the flux (with respect to phase A_1, which is now moving in fact):

$$y(t) = \omega x_1(t)\,[\mathrm{kg/s}], \tag{2.1}$$

with

$$\omega : \quad \text{flow rate}\,[1/\mathrm{s}]. \tag{2.2}$$

There holds the following

THEOREM 1: J, see (1.5), is independent of ω, i.e. J is an invariant [2] and can be calculated from (1.9).

As an application of this statement we determine the RTD (residence time distribution) of the tracer particles in the CSTR. The balance equation becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} + y = 0\,, \qquad \text{i.e.} \qquad \frac{\mathrm{d}x}{\mathrm{d}t} + \omega x_1 = 0\,. \tag{2.3}$$

Using the rule (1.7) we have

$$sx(s) + \omega x_1(s) = 1\,. \tag{2.4}$$

In view of (1.5) and Theorem 1, we immediately obtain

$$(J(s)s + \omega)\, x_1(s) = 1\,,$$

i.e.

$$y(s) = \omega x_1(s) = \frac{\omega}{J(s)s + \omega} = \left.\frac{\omega}{s + \omega}\right|_{s=J(s)s}\,. \tag{2.5}$$

We realize that if $n = 1$: $J = 1$ and denoting the flux in that case by y^1, we obtain the simple rule

$$y(s) = \left. y^1(s)\right|_{s=J(s)s}\,. \tag{2.6}$$

3. The Higher Moments of RTD

Obviously $y(s)$ in (2.6) is just the transformed density function of the RTD. Let us denote the first three so-called cumulants or semi-invariants (mean, variance and 3rd central moment) by

$$\kappa_1,\ \kappa_2 \qquad \text{and} \qquad \kappa_3 \tag{3.1}$$

and in the case of only one phase, by

$$K_1,\ K_2 \qquad \text{and} \qquad K_3\,, \tag{3.2}$$

respectively. Rewriting $J(s)$ as

$$J(s) = Cf(s) + 1 \qquad \text{with} \qquad f(0) = 1\,, \tag{3.3}$$

where C is the equilibrium constant between the 'fixed' and 'mobile' phase, we finally obtain the general formulae [3, 2]:

$$\kappa_1 = (C+1)K_1\,, \tag{3.4}$$

$$\kappa_2 = (C+1)^2 K_2 - 2Cf'(0)K_1\,, \tag{3.5}$$

$$\kappa_3 = (C+1)^3 K_3 - 6C(C+1)f'(0)K_2 + 3Cf''(0)K_1\,. \tag{3.6}$$

4. The Distributed Parameter System (Tube)

Let us define the flux as (the analogue of (2.1)):

$$y(z,t) = Lx_1(z,t)\,, \tag{4.1}$$

where z is the length coordinate [m] and L is a linear operator, e.g.

$$L = u - D\frac{\partial}{\partial z}\,, \tag{4.2}$$

with

$$u: \qquad \text{flow velocity [m/s]} \tag{4.3}$$

and

$$D: \qquad \text{diffusivity [m}^2\text{/s]}\,. \tag{4.4}$$

THEOREM 2:

$$\frac{x(z,s)}{x_1(z,s)} = J(s)\,, \tag{4.5}$$

with $J(s)$ as defined in (1.9). Once again, the left-hand side is independent of z and u as well as D (invariant).

As an application of this theorem [4] we determine the respective RTD. The balance equation becomes

$$\frac{\partial x}{\partial t} + \frac{\partial y}{\partial z} = 0 \tag{4.6}$$

and in the Laplace domain we have because of (4.5)

$$\left(J(s)s + \frac{\partial}{\partial z}L\right) x_1(z,s) = x_1(z,t)\Big|_{t=0}: \qquad \text{prescribed} \tag{4.7}$$

whose solution (depending on the boundary conditions) is to be substituted in the transformed equation (4.1):

$$y(z,s) = Lx_1(z,s)\,. \tag{4.8}$$

However, we realize that if $n = 1$: $J = 1$, and denoting the flux in that case by y^1, we have

$$y(z,s) = y^1(z,s)\Big|_{s=J(s)s} \tag{4.9}$$

which is the counterpart of (2.6). Once again, $y(z,s)$ is the transformed density function of RTD. For the first three cumulants the general relations (3.4) – (3.5) – (3.6) are valid.

References

1. KUMAR, S. — PETHŐ, Á. (1990): The Markov Process Approach to Modelling of Residence Time Distributions in Flow Systems, *Chem. Eng. Technol.*, Vol. 13, pp. 422–425.
2. PETHŐ, Á. (1991): A Simple Mathematical Treatment of Linear Sorption Modelled by a Markov Process, *Hung. J. Ind. Chem.*, Vol. 19, pp. 47–54.
3. PETHŐ, Á. (1990): Contributions to the Theory of Linear Multiphase Chromatography, *Chem. Biochem. Eng. Q.*, Vol. 4, pp. 67–72.
4. PETHŐ, Á. (1989): Residence Time and Displacement Distributions in the Case of Continuous Flow Combined with an Imbedded Markov Process in the Fixed Bed, *Hung. J. Ind. Chem.*, Vol. 17, pp. 509–521.

Appendix

1. The higher moments of RTD for a CSTR without sorption are given by the simple formula:

$$\mu_m = \frac{m!}{\omega^m}; \qquad m = 1, 2, \ldots \tag{A.1}$$

where

$$\mu_m = \int_0^\infty t^m y^1(t)\mathrm{d}t; \qquad m = 1, , 2, \ldots \tag{A.2}$$

Consequently the first 3 semi-invariants become

$$K_1 = \mu_1 = \frac{1}{\omega}, \qquad K_2 = \int_0^\infty (t-\mu_1)^2 y^1 \mathrm{d}t = \frac{1}{\omega^2},$$

$$K_3 = \int_0^\infty (t-\mu_1)^3 y^1 \mathrm{d}t = \frac{2}{\omega^3}. \tag{A.3}$$

Inserting these values in (3.4) – (3.5) – (3.6) we obtain at once the respective semi-invariants for a CSTR with an imbedded Markov process.

2. The first 3 semi-invariants of RTD in a continuous-flow one-dimensional tube reactor with diffusion are given by the simple formulae [3]:

$$K_1 = \frac{1}{u}z, \qquad K_2 = \frac{2D}{u^3}z, \qquad K_3 = \frac{12D^2}{u^5}z. \tag{A.4}$$

Once again, substituting these values in (3.4) – (3.5) – (3.6) we have the respective semi-invariants for the generalized linear chromatography [3].

3. Consider an arbitrary continuous-flow reactor (either of the above examples) with two phases (mobile and fixed) between which a Markov process according to the system matrix

$$K = \begin{bmatrix} -k_{21} & k_{12} \\ k_{21} & -k_{12} \end{bmatrix} \tag{A.5}$$

takes place. Then, in view of (1.9) and (3.3) we readily obtain

$$J(s) = \frac{s + k_{12} + k_{21}}{s + k_{12}}, \qquad f(s) = \frac{k_{12}}{s + k_{12}} \tag{A.6}$$

and

$$C = \frac{k_{21}}{k_{12}}, \qquad f_0' = -\frac{1}{k_{12}}, \qquad f_0'' = \frac{2}{k_{12}^2}. \tag{A.7}$$

4. The interested reader might put down the respective formulae (3.4) – (3.5) – (3.6) in the case of the imbedded Markov process for both types of continuous-flow reactors.

Notation

f see *Eq.* (3.3)
s Laplace transform variable, s^{-}1
t time, s
u flow velocity, m/s
x the total state occupancy (in the mobile plus fixed phase)
x_1 state occupancy in the mobile phase, kg (CSTR) or kg/m (tube)
y flux, kg/s
z length coordinate, m
C equilibrium constant, see *Eq.* (3.3)
D diffusivity, m^2/s
J see *Eq.* (1.5)
K system matrix, see *Eq.* (1.1)
K_i semi invariants in a system consisting only of one phase ($i = 1, 2, 3$)
κ_i semi invariants ($i = 1, 2, 3$)
ω flow rate, s^{-1}