Simplest Kinetic Models for Bistability of Antipodal Mixtures

I. Gutman

Faculty of Science, University of Kragujevac, Yugoslavia

A. Klemm

Max-Planck-Institut für Chemie (Otto-Hahn-Institut),
Mainz, Federal Republic of Germany

Z. Naturforsch. **42 a,** 899–900 (1987);
received May 11, 1987

Three choices of three rate coefficients out of the six coefficients occurring in the general second order rate equation for interacting antipodes (e.g. enantiomers) can provide bistability with incomplete demixing. Once choice of two rate coefficients can provide bistability with complete demixing.

In this note we consider stationary states of mixtures of interacting antipodes (e.g. enantiomers) with the mole fractions x and $1-x$ and look for simplest models of incomplete demixing ($x \neq 0, 1/2, 1$) and complete demixing ($x = 0, 1$). We assume second order rate equations to be valid:

$$\mathrm{d}[n\,x]/\mathrm{d}t = e + n\,[f_1\,x + f_2(1-x)] + n^2\,[g_1\,x^2 + g_2\,x\,(1-x) + g_3(1-x)^2], \qquad (1)$$

$$\mathrm{d}[n\,(1-x)]/\mathrm{d}t = e + n\,[f_1(1-x) + f_2\,x] + n^2\,[g_1(1-x)^2 + g_2\,x\,(1-x) + g_3\,x^2], \qquad (2)$$

where t is the time and n the total amount of the antipodes. If suitable, n can also be defined as an amount per unit volume or unit area. The coefficients e, f_2 and g_3 are assumed to be positive because negative values would mean that particles are disappearing at a rate that is independent of the number of particles present. This is clearly impossible if there are no particles, and if there are particles it would be possible but it would not comply with the mass law. Table 1 shows possible reactions which correspond to the rate coefficients.

In the stationary state, n and x remain constant in time. By adding (1) and (2) and putting $\mathrm{d}n/\mathrm{d}t = 0$ one obtains

$$2e + n(f_1 + f_2) + n^2\,[g_1 + g_3 - 2(g_1 - g_2 + g_3)\,x\,(1-x)] = 0, \qquad (3)$$

and by subtracting (1) from (2) and putting

$$\mathrm{d}[n\,(1-2x)]/\mathrm{d}t = 0$$

one obtains

$$(1-2x)\,[(f_1 - f_2) + n\,(g_1 - g_3)] = 0. \qquad (4)$$

The value of n in case of monostability (n_M, $x = 1/2$) results from (3):

$$n_\mathrm{M} = -\frac{f_1 + f_2}{g_1 + g_2 + g_3}\left[1 + \sqrt{1 - \frac{4e\,(g_1 + g_2 + g_3)}{(f_1 + f_2)^2}}\,\right]. \qquad (5)$$

In case of bistability (n_B, $x \neq 1/2$) it results from (4):

$$n_\mathrm{B} = -(f_1 - f_2)/(g_1 - g_3). \qquad (6)$$

Insertion of (6) into (3) gives

$$4x\,(1-x) = A\,(e, f_1, f_2, g_1, g_2, g_3), \qquad (7)$$

where

$$A = \frac{4}{g_1 - g_2 + g_3}\left[\frac{e\,(g_1 - g_3)^2}{(f_1 - f_2)^2} - \frac{f_2\,(g_1 - g_3)}{f_1 - f_2} + g_3\right]. \qquad (8)$$

A system defined by the values of the rate coefficients is bistable if $n_\mathrm{B} > 0$ and $0 < A < 1$.

The evolution towards stationary was studied in [1] for cases where n, e, f_2, g_1, g_2 and g_3 are constant, the constancy of n beig procured by allowing f_1 to vary with x according to (3). In these evolutions a parameter

$$q = 1 - \frac{4}{g_1 - g_2 + g_3}\left[\frac{e}{n^2} + \frac{f_2}{n} + g_3\right] \qquad (9)$$

remains constant while x and f_1 vary during the evolution. It was shown that for $q < 0$ and $q > 1$ the final state is racemic (i.e. $x = 1/2$) while for $0 < q < 1$ the final state is non-racemic (i.e. $x \neq 1/2$).

In the following we use the functions

$$Q_\mathrm{M}(e, f_1, f_2, g_1, g_2, g_3) \quad \text{and} \quad Q_\mathrm{B}(e, f_1, f_2, g_1, g_2, g_3)$$

instead of $q\,(n, e, f_2, g_1, g_2, g_3)$. Q_M and Q_B are obtained by eliminating n in (9) by means of (5) and (6), respectively. It turns out that

$$Q_\mathrm{B} = 1 - A. \qquad (10)$$

When putting $n_\mathrm{M} = n_\mathrm{B}$ and using (5) and (6) one obtains the same relation between the rate coefficients as when putting $A = 1$ and using (8). Therefore

$$n_\mathrm{M} = n_\mathrm{B} \quad \text{for} \quad Q_\mathrm{M} = Q_\mathrm{B} = 0. \qquad (11)$$

In terms of Q_M and Q_B, a system defined by the values of the rate coefficients is bistable if $n_\mathrm{B} > 0$ and $0 < Q_\mathrm{B} < 1$, it is monostable if $n_\mathrm{M} > 0$ and $Q_\mathrm{M} < 0$ or $Q_\mathrm{M} > 1$, and it can be in a stationary state if $n_\mathrm{M} > 0$ and $0 < Q_\mathrm{M} < 1$. The latter state, however, is unstable against small deviations of x from 1/2. Figure 1 shows the dependence of x on Q_M and Q_B.

Table 1. Possible reactions and the corresponding rate coefficients (positive and negative). The enantiomers L and D can be interchanged. $k, l = 0, 1, 2, \ldots$. X and Y sum up other substances possibly involved in the reactions.

$X \rightarrow Y + kD + (1+l)\,L$	$e > 0$
$L + X \rightarrow Y + kD + (2+l)\,L$	$f_1 > 0$
$L + X \rightarrow Y + kD$	$f_1 < 0$
$D + X \rightarrow Y + kD + (1+l)\,L$	$f_2 > 0$
$2L + X \rightarrow Y + kD + (3+l)\,L$	$g_1 > 0$
$2L + X \rightarrow Y + kD + (0, 1)\,L$	$g_1 < 0$
$L + D + X \rightarrow Y + kD + (2+l)\,L$	$g_2 > 0$
$L + D + X \rightarrow Y + kD$	$g_2 < 0$
$2D + X \rightarrow Y + kD + (1+l)\,L$	$g_3 > 0$

Reprint requests to Prof. Dr. A. Klemm, Saarstraße 23, D-6500 Mainz.

0932-0784 / 87 / 0800-0899 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 2. 3-coefficient models of bistability with incomplete demixing (f_1 is negative, g_1, e, f_2 and g_3 are positive).

Coefficients	Q_B	n_B	Q_M	n_M	$n_M = n_B$ for $Q_n = Q_B = 0$	$n_M = 2\,n_B$ for $Q_M = Q_B = 1$
f_1, g_1, e	$1 - \frac{4\,e\,g_1}{f_1^2}$	$-\frac{f_1}{g_1}$	$1 - \frac{4\,e}{g_1\,n_M^2}$	$-\frac{f_1}{g_1}(1 + \sqrt{1 - 4\,e\,g_1/f_1^2})$	$-\frac{f_1}{g_1}$	$-2\,\frac{f_1}{g_1}$
f_1, g_1, f_2	$1 + \frac{4 f_2}{f_1 - f_2}$	$-\frac{f_1 - f_2}{g_1}$	$1 + \frac{2 f_2}{f_1 + f_2}$	$-2\,\frac{f_1 + f_2}{g_1}$	$-\frac{4}{3}\,\frac{f_1}{g_1}$	$-2\,\frac{f_1}{g_1}$
f_1, g_1, g_3	$1 - \frac{4 g_3}{g_1 + g_3}$	$-\frac{f_1}{g_1 - g_3}$	$1 - \frac{4 g_3}{g_1 + g_3}$	$-2\,\frac{f_1}{g_1 + g_3}$	$-\frac{3}{2}\,\frac{f_1}{g_1}$	$-2\,\frac{f_1}{g_1}$

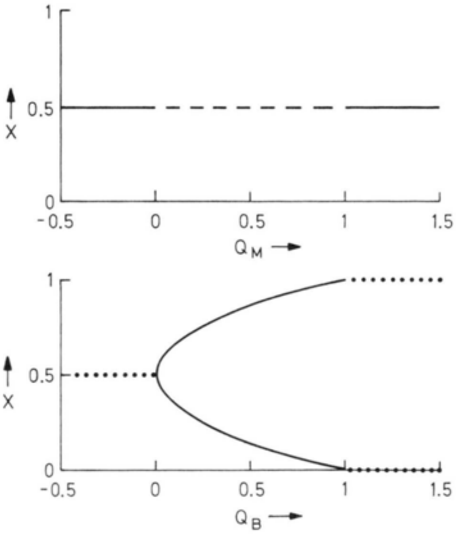

Fig. 1. Mole fractions x vs. $Q_M(e, f_1, f_2, g_1, g_2, g_3)$ and $Q_B(e, f_1, f_2, g_1, g_2, g_3)$. The figure relates to real systems if the corresponding values of n_M and n_B are positive. Solid lines: Stationary stable states. Dashed line: Stationary unstable states. Dotted lines: Non-stationary states.

At $Q_M = Q_B = 0$, provided $n_M = n_B > 0$, a system can pass in a quasi stationary way from monostability to bistability or back, due for example to a slow change of the temperature or the amount of a subrate involved in the reactions, such as X in Table 1. Even at a very slow change, howeveer, temporary non-stationarities will occur while the system passes the bifurcation point because there one has $dx/dQ_B = \pm\,\infty$. Kondepudi and coauthors [2–5], who also included small biased influences and noise, have studied this behaviour near the bifurcation point.

In [2] and [3] a model with four rate coefficients, (e, f_1, g_1, g_2) was considered, where e and f_1 are positive and varying while g_1 and g_2 are negative and constant. In future discussions of bistability with incomplete demixing it might be useful to consider models with a minimal number of rate coefficients. From (8) and $0 < A < 1$ it is evident that in such models at least three of the six rate coefficients must be non-zero.

In Table 2, out of the twenty possible coefficient triplets the three triplets allowing for bistability are listed together with their corresponding values of Q_B, n_B, Q_M, n_M, $n_M = n_B$ for $Q_M = Q_B = 0$, and $n_M = 2\,n_B$ for $Q_M = Q_B = 1$. Other triplets do not belong in the table because they do not comply with the requirements $n_B > 0$ and $0 < Q_B < 1$.

Complete demixing, i.e. $Q_B = 1$ can be realized for the doublet f_1, g_1 with $f_1 < 0$ and $g_1 > 0$. This doublet provides the simplest model for stationary monostrophic states and may explain many of the bistabilities occurring in the biosphere of the earth. Helicity conservation in the sexual replication of DNA is an example. Usually only one of the two stationary states exists on earth. Both states exist in the case of the land snail partula suturalis mentioned in [1].

A quasi stationary transition through the bifurcation point has not yet been observed in nature or the chemical or biological laboratory. Also an example of Frank's inherently non-stationary model (the doublet f_1, g_2 with $f_1 > 0$ and $g_2 < 0$) is not known because opposite enantiomers usually do not interact, i.e. $g_2 = 0$.

The island Moorea with its different helicities of the land snail partula in the different valleys of the island can be considered as a model of the earth or some other birth place of life at an early stage. When one day the populations of the valleys will have mixed, only one helicity of partula will be left. Today nobody can predict which one it will be. This final state of the island will correspond to the present state of the molecular biosphere of the earth as regards helicity.

[1] A. Klemm, Z. Naturforsch. **40 a,** 1231 (1985).

[2] D. K. Kondepudi and G. W. Nelson, Physica **124 A,** 465 (1984).

[3] D. K. Kondepudi and G. W. Nelson, Nature London **314,** 438 (1985).

[4] D. K. Kondepudi, F. Moss, and P. V. E. McClintock, Phys. Lett. **114 A,** 68 (1986).

[5] D. K. Kondepudi and M.-J. Gao, Phys. Rev. A **35,** 340 (1987).