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Generalized necessary scaling condition and stability of chemical reactors with several educts

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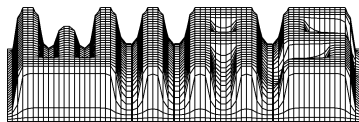
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Abstract

We present, for a class of industrially relevant chemical reactions with two educts the dependence of stability on important chemical parameters, such as coolant, dilution and diffusion rates. The main analytical tools are generalized upscaling balance condition for the equilibria concentrations and spectral properties of corresponding operators. Although we illustrate the stability analysis for a model reactor (2 educts, E_1 and E_2), it should be emphasized that our approach is applicable to more complex reaction mechanisms.

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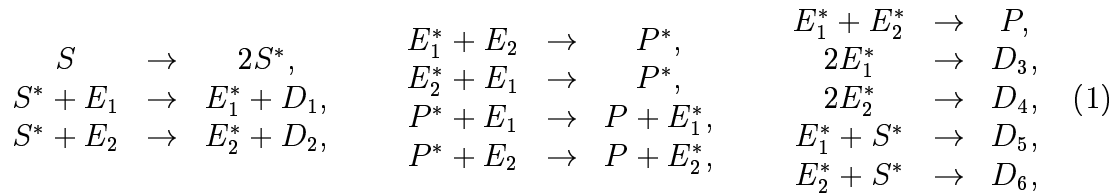
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1 Introduction

As an example of stability of chemical reactor we consider a class of chemical radical reactions with starter S , educts E_1, E_2 and chemical product of form



where by $D_i, i = 1(1)6$, denote by-products. The three blocks in (1) characterize starter, chain and reactions, respectively. Note, that the educt radicals E_1^* and E_2^* act ‘‘catalytically’’ even in low concentrations. Therefore these reactions are usually run with low starter concentrations S , Therefore these reactions are usually run with low starter concentrations S , already producing sufficient quantities of E_1^*, E_2^* .

We emphasize that, a reaction mechanism (2) is industrially relevant, and arise for example, in photosensitive chlorivation of aromates, where $E_1 = Cl_2, E_2$ Toluene. The chemical product of these reactions, Chlorbenzene, plays an important role both in food and pharmaceutical industries (see [5]).

In this paper we study stability of chemical reactor from important parameters, such as diffusion, dilution rates, when $\epsilon := S_0$ goes to zero.

We use the following designations

| | |
|--|--|
| S, E_1, E_2 | concentrations of starter and educts, |
| s, e_1, e_2 | corresponding radical concentrations, |
| $S_0, E_{1,0}, E_{2,0}$ | feed concentrations, |
| P, p | product and product radical, |
| $k_i(T) = k_i^* \exp\left(-\frac{\gamma_i}{T}\right), i = 1, \dots, 12,$ | Arrhenius law, |
| $d_S, d_{E_1}, d_{E_2}, d_s, d_{e_1}, d_{e_2}, d_p, d_T$ | diffusion rates, |
| $T, h_j, j = 1, \dots, 12,$ | temperature and reaction enthalpy, |
| v | velocity due to Navier-Stokes equations. |

The spatially heterogeneous evolution equations for (1) take the form (see [2])

$$\begin{aligned}
\frac{\partial S}{\partial t} &= d_S \Delta S + (v, \nabla)S + S_0 - k_1 S \\
\frac{\partial E_1}{\partial t} &= d_{E_1} \Delta E_1 + (v, \nabla)E_1 + E_{1,0} - k_2 s E_1 - k_5 e_2 E_1 - k_6 p E_1 \\
\frac{\partial E_2}{\partial t} &= d_{E_2} \Delta E_2 + (v, \nabla)E_2 + E_{2,0} - k_3 s E_2 - k_4 e_1 E_2 - k_7 p E_2 \\
\frac{\partial s}{\partial t} &= d_s \Delta s + (v, \nabla)s + 2k_1 S - k_2 s E_1 - k_3 s E_2 - k_{11} e_1 s - k_{12} e_2 s \\
\frac{\partial e_1}{\partial t} &= d_{e_1} \Delta e_1 + (v, \nabla)e_1 + k_2 s E_1 - k_4 e_1 E_2 + k_6 p E_1 - k_8 e_1 e_2 \\
&\quad - 2k_9 e_1^2 - k_{11} e_1 s \\
\frac{\partial e_2}{\partial t} &= d_{e_2} \Delta e_2 + (v, \nabla)e_2 + k_3 s E_2 - k_5 e_2 E_1 + k_7 p E_2 - k_8 e_1 e_2 \\
&\quad - 2k_{10} e_2^2 - k_{12} e_2 s \\
\frac{\partial p}{\partial t} &= d_p \Delta p + (v, \nabla)p + k_4 e_1 E_2 + k_5 e_2 E_1 - k_6 p E_1 - k_7 p E_2 \\
\frac{\partial T}{\partial t} &= d_T \Delta T + (v, \nabla)T + h_1 k_1 S + h_2 k_2 s E_1 + h_3 k_3 s E_2 + h_4 k_4 e_1 E_2 \\
&\quad + h_5 k_5 e_2 E_1 + h_6 k_6 p E_1 + h_7 k_7 p E_2 + h_8 k_8 e_1 e_2 + h_9 k_9 e_1^2 + h_{10} k_{10} e_2^2 \\
&\quad + h_{11} k_{11} e_1 s + h_{12} k_{12} e_2 s.
\end{aligned} \tag{2}$$

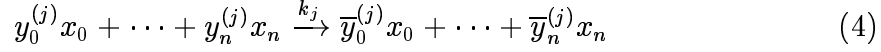
To investigate the stability of chemical (model) reactor (1) we distinguish laminar and turbulent zones of our reaction. In the laminar zone we consider partial differential equations of the form (2). In the turbulent zone, where fast mixing prevails, Equation (2) is averaged, spatially, to yield (see [2])

$$\begin{aligned}
\frac{\partial S}{\partial t} &= S_0 - k_1 S - D_0 S \\
\frac{\partial E_1}{\partial t} &= E_{1,0} - k_2 s E_1 - k_5 e_2 E_1 - k_6 p E_1 - D_1 E_1 \\
\frac{\partial E_2}{\partial t} &= E_{2,0} - k_3 s E_2 - k_4 e_1 E_2 - k_7 p E_2 - D_2 E_2 \\
\frac{\partial s}{\partial t} &= 2k_1 S - k_2 s E_1 - k_3 s E_2 - k_{11} e_1 s - k_{12} e_2 s - D_3 s \\
\frac{\partial e_1}{\partial t} &= k_2 s E_1 - k_4 e_1 E_2 + k_6 p E_1 - k_8 e_1 e_2 - 2k_9 e_1^2 - k_{11} e_1 s - D_4 e_1 \\
\frac{\partial e_2}{\partial t} &= k_3 s E_2 - k_5 e_2 E_1 + k_7 p E_2 - k_8 e_1 e_2 - 2k_{10} e_2^2 - k_{11} e_1 s - D_5 e_2 \\
\frac{\partial p}{\partial t} &= k_4 e_1 E_2 + k_5 e_2 E_1 - k_6 p E_1 - k_7 p E_2 - D_6 p \\
\frac{\partial T}{\partial t} &= h_1 k_1 S + h_2 k_2 s E_1 + h_3 k_3 s E_2 + h_4 k_4 e_1 E_2 + h_5 k_5 e_2 E_1 + h_6 k_6 p E_1 \\
&\quad + h_7 k_7 p E_2 + h_8 k_8 e_1 e_2 + h_9 k_9 e_1^2 + h_{10} k_{10} e_2^2 + h_{11} k_{11} e_1 s + h_{12} k_{12} e_2 s \\
&\quad - \chi(T - T_0).
\end{aligned} \tag{3}$$

Here $\vec{D} = (D_0, \dots, D_6)$ and χ indicates dilution and external cooling rate with coolant temperature T_0 , respectively.

2 Generalized necessary scaling condition

Following Feinberg [1] we write chemical reactions of species x_0, \dots, x_n as



with integer stoichiometric coefficients $y^{(j)}, \bar{y}^{(j)} \geq 0$ and positive real reaction rate coefficient k_j . Then the associate dynamics is given by

$$\dot{x} = \sum_{j=1}^M k_j x^y (\bar{y}^{(j)} - y^{(j)}). \quad (5)$$

Here $x = (x_0, \dots, x_n) \in \mathbb{R}^{n+1}$ is the vector of concentrations and $x^y := x_0^{y_0} \dots x_n^{y_n}$ represents the usual mass action kinetics.

We emphasize that the external feed concentrations can be incorporated in this model by adding formal reactions



Following mathematical convention we denote by $\epsilon := S_0$ ($0 \xrightarrow{k_0=\epsilon} S$) the feed concentration of the radical starter and $\alpha = (\alpha_0, \dots, \alpha_n)$ the scaling defined by

$$\begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_n \end{pmatrix} = \begin{pmatrix} \epsilon^{\alpha_0} & 0 & \dots & 0 \\ 0 & \epsilon^{\alpha_1} & \dots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & \epsilon^{\alpha_n} \end{pmatrix} \begin{pmatrix} \xi_0 \\ \xi_1 \\ \vdots \\ \xi_n \end{pmatrix}. \quad (7)$$

Substituting (7) into (5) we obtain

$$\epsilon^{\alpha_j} \dot{\xi}_j = \sum_{j=1}^M k_j \epsilon^{\alpha_0 y_0^{(j)} + \dots + \alpha_n y_n^{(j)}} \xi_0^{y_0^{(j)}} \dots \xi_n^{y_n^{(j)}} (\bar{y}^{(j)} - y^{(j)}). \quad (8)$$

Then the equilibrium equation takes the form

$$\sum_{j=1}^M k_j \epsilon^{\alpha y^{(j)}} \xi^{y^{(j)}} (\bar{y}^{(j)} - y^{(j)}) = 0 \quad (9)$$

for the scaled steady state $\xi = \xi(\epsilon)$, where by $\alpha y^{(j)}$ and $\xi^{y^{(j)}}$ we denote $\alpha y^{(j)} := \alpha_0 y_0^{(j)} + \dots + \alpha_n y_n^{(j)}$ and $\xi^{y^{(j)}} := \xi_0^{y_0^{(j)}} \dots \xi_n^{y_n^{(j)}}$, respectively.

In general, for a class of chemical reactions (1) the reaction rates k_j can often be determined only up to the order of magnitude. Therefore we make following ansatz:

$$k_j = k_{j,0} \epsilon^{\beta_j} + \mathcal{O}(\epsilon^{\beta_j}) \quad \text{with} \quad \epsilon := S_0. \quad (10)$$

Definition 1 We call a pair $(\alpha, \beta) = (\alpha_0, \dots, \alpha_n, \beta_1, \dots, \beta_M) \in \mathbb{R}^{n+1} \times \mathbb{R}^M$ a generalized scaling exponent for the steady state concentrations $x = (x_0, \dots, x_n)$ of (5), if there exists a sequence of scaled equilibria $\xi(\epsilon_l) = (\xi_0(\epsilon_l), \dots, \xi_n(\epsilon_l))$, $\epsilon_l \rightarrow 0$, $l \rightarrow \infty$ of (9), with k_j given by (10), such that for all $m = 0, \dots, n$ the following nondegeneracy conditions holds:

$$0 < \liminf_{l \rightarrow \infty} \xi_m(\epsilon_l) \leq \limsup_{l \rightarrow \infty} \xi_m(\epsilon_l) < \infty. \quad (11)$$

Theorem 1 Any generalized scaling exponent $(\alpha, \beta) \in \mathbb{R}^{n+1} \times \mathbb{R}^M$ satisfies

$$\min_{j: y_m^{(j)} \neq 0} \{(\alpha y^{(j)}) + \beta_j\} = \min_{i: \bar{y}_m^{(i)} \neq 0} \{(\alpha \bar{y}^{(i)}) + \beta_i\}. \quad (12)$$

Proof. Let $(\alpha, \beta) \in \mathbb{R}^{n+1} \times \mathbb{R}^M$ be any generalized scaling exponent. We rewrite Equation (9) for the scaled steady state $\xi = \xi(\epsilon)$ in components $m = 0, \dots, n$ as

$$\sum_{j=1}^M k_j \epsilon^{\alpha y^{(j)}} \xi^{y^{(j)}} y^{(j)} = \sum_{i=1}^M k_i \epsilon^{\alpha y^{(i)}} \xi^{y^{(i)}} \bar{y}^{(i)} \quad (13)$$

or equivalently

$$\sum_{j: y_m^{(j)} \neq 0} k_j \epsilon^{\alpha y^{(j)}} \xi^{y^{(j)}} y_m^{(j)} = \sum_{i: \bar{y}_m^{(i)} \neq 0} k_i \epsilon^{\alpha y^{(i)}} \xi^{y^{(i)}} \bar{y}_m^{(i)}. \quad (14)$$

Let $k_j = k_{j,0} \epsilon^{\beta_j} + \mathcal{O}(\epsilon^{\beta_j})$, $\epsilon := S_0$ (see (10)), and fix m . We sort the terms on each side of last equality by increasing powers $\alpha y^{(j)} + \beta_j$, $\alpha y^{(i)} + \beta_i$ of ϵ , respectively. Note, that all terms are strictly positive by the nondegeneracy assumption (11). Let

$$\min_{j: y_m^{(j)} \neq 0} \{(\alpha y^{(j)}) + \beta_j\} = \alpha y^{(j_o)} + \beta_{j_o} \quad \text{and} \quad \min_{i: \bar{y}_m^{(i)} \neq 0} \{(\alpha \bar{y}^{(i)}) + \beta_i\} = \alpha \bar{y}^{(i_o)} + \beta_{i_o}$$

in (14). Then the leading (alias: lowest) power of ϵ in the m -th component of (14) is given by $\alpha y^{(j_o)} + \beta_{j_o}$ on the left, as compared to $\alpha \bar{y}^{(i_o)} + \beta_{i_o}$ on the right. Note, that these leading powers may in fact be realized by several other terms $\alpha y^{(j)} + \beta_j$, $\alpha \bar{y}^{(i)} + \beta_i$ in addition. Comparing coefficients, we divide (14) by ϵ to the powers

$$\min \{ \alpha y^{(j_o)} + \beta_{j_o}, \alpha \bar{y}^{(i_o)} + \beta_{i_o} \}$$

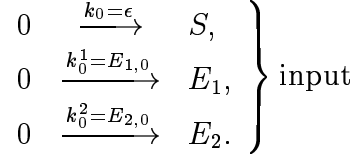
and let $\epsilon \rightarrow 0$. This immediatly yields

$$\alpha y^{(j_o)} + \beta_{j_o} = \alpha \bar{y}^{(i_o)} + \beta_{i_o}$$

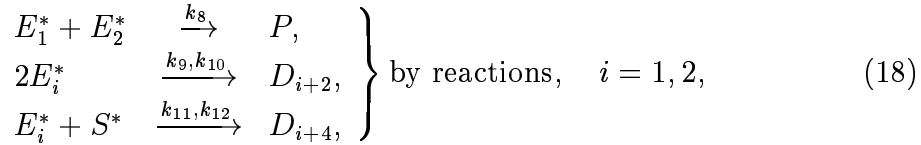
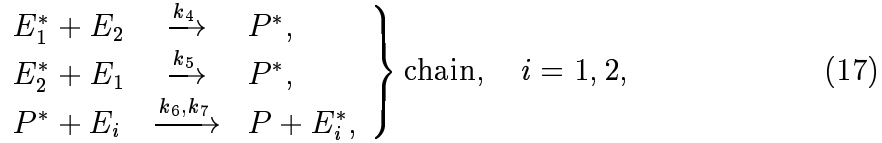
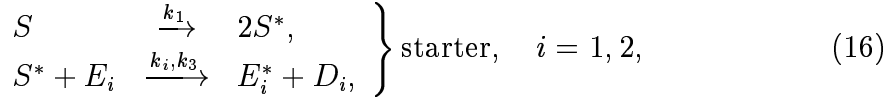
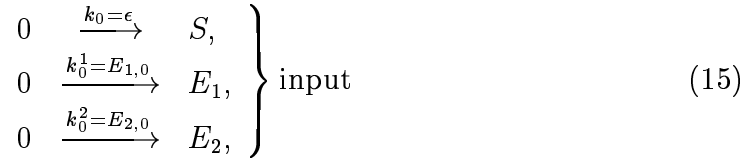
by positivity of all terms in the sums. This proves the Theorem 1.

3 Necessary scaling exponent for a model reactor with two educts: full picture

In this section we apply Theorem 1 to concrete reaction mechanism (1). We start our analysis in the case $k_j = \mathcal{O}(1)$, that is $\beta_j = 0$, $j = 1, \dots, M$, and $D = 0$. For very spatial case, that is chemical reactions for 1 (one) educt (see [4]). Based on mass action kinetics we add to reaction mechanism (1) following terms



Hence we consider the following radical reaction



with $\epsilon := S_0 > 0$. Note, that photosensitive chlorivation of aromate is a specific example of mechanism (15) - (18) (see [5]).

With $x = (x_0, \dots, x_6) = (S, E_1, E_2, s, e_1, e_2, p)$ and $\beta_j = 0$ and $\epsilon = S_0$, the generalized necessary scaling condition (12) for the scaling exponent $\alpha = (\alpha_0, \dots, \alpha_6) := (\alpha_S, \alpha_{E_1}, \alpha_{E_2}, \alpha_s, \alpha_{e_1}, \alpha_{e_2}, \alpha_p)$ takes the following form

$$\alpha_S = 1, \quad (19a)$$

$$\min \{ \alpha_{E_1} + \alpha_s, \alpha_{E_1} + \alpha_{e_2}, \alpha_{E_1} + \alpha_p \} = 0, \quad (19b)$$

$$\min \{ \alpha_{E_2} + \alpha_s, \alpha_{E_2} + \alpha_{e_1}, \alpha_{E_2} + \alpha_p \} = 0, \quad (19c)$$

$$\min \{ \alpha_{E_1} + \alpha_s, \alpha_{E_2} + \alpha_s, \alpha_s + \alpha_{e_1}, \alpha_s + \alpha_{e_2} \} = \alpha_S, \quad (19d)$$

$$\min \{ \alpha_{E_2} + \alpha_{e_1}, \alpha_{e_1} + \alpha_{e_2}, 2\alpha_{e_1}, \alpha_s + \alpha_{e_1} \} = \min \{ \alpha_{E_1} + \alpha_s, \alpha_{E_1} + \alpha_p \}, \quad (19e)$$

$$\min \{ \alpha_{E_1} + \alpha_{e_2}, \alpha_{e_1} + \alpha_{e_2}, 2\alpha_{e_2}, \alpha_s + \alpha_{e_2} \} = \min \{ \alpha_{E_2} + \alpha_s, \alpha_{E_2} + \alpha_p \}, \quad (19f)$$

$$\min \{ \alpha_{E_1} + \alpha_p, \alpha_{E_2} + \alpha_p \} = \min \{ \alpha_{E_2} + \alpha_{e_1}, \alpha_{E_1} + \alpha_{e_2} \}. \quad (19g)$$

Theorem 2 Let $\alpha = (\alpha_S, \alpha_{E_1}, \alpha_{E_2}, \alpha_s, \alpha_{e_1}, \alpha_{e_2}, \alpha_p)$ be any scaling exponent of (15) -(18). Then $\alpha = (1, \alpha_{E_1}, -\frac{1}{2}, 1 - \alpha_{E_1}, \frac{1}{2}, -\frac{1}{2} - 2\alpha_{E_1}, -\alpha_{E_1})$ with $\alpha_{E_1} \leq -\frac{1}{2}$.

Proof. We distinguish two cases:

- (a) $\alpha_{E_1} < \alpha_{E_2}$,
- (b) $\alpha_{E_1} = \alpha_{E_2}$.

Let us start with the case (a). Then we rewrite (19e) and (19f) as

$$\begin{aligned}\alpha_{e_1} + \min\{\alpha_{E_2}, \alpha_s, \alpha_{e_1}, \alpha_{e_2}\} &= \alpha_{E_1} + \min\{\alpha_s, \alpha_p\}, \\ \alpha_{e_2} + \min\{\alpha_{E_1}, \alpha_s, \alpha_{e_1}, \alpha_{e_2}\} &= \alpha_{E_2} + \min\{\alpha_s, \alpha_p\}.\end{aligned}\tag{20}$$

From (20) follows that $\alpha_{e_1} < \alpha_{e_2}$.

Next we prove $\alpha_{e_1} < \alpha_p$. Assume contrary, i.e. $\alpha_{e_1} \geq \alpha_p$. Then from (19b) and (19c) we obtain

$$\begin{aligned}\alpha_{E_1} + \min\{\alpha_s, \alpha_p\} &= 0, \\ \alpha_{E_2} + \min\{\alpha_s, \alpha_p\} &= 0.\end{aligned}$$

Hence $\alpha_{E_1} = \alpha_{E_2}$ contradicting $\alpha_{E_1} < \alpha_{E_2}$. Note, that $\alpha_s + \alpha_{E_2} \geq 1$ due to Equation (19d) and (19a). Thus Equation (19c) takes the form

$$\alpha_{E_2} + \min\{\alpha_{e_1}, \alpha_p\} = \alpha_{E_2} + \alpha_{e_1} = 0,$$

that is $\alpha_{e_1} = -\alpha_{E_2}$.

As a result Equation (19g) can be written as

$$\alpha_p + \alpha_{E_1} = \min\{\alpha_{e_1} + \alpha_{E_2}, \alpha_{E_1} + \alpha_{e_2}\} = \min\{0, \alpha_{E_1} + \alpha_{e_2}\}.$$

Last equality implies $\alpha_p + \alpha_{E_1} = 0$, since $\alpha_{E_1} + \alpha_{e_2} \geq 0$ (due to Equation (19b)), that is $\alpha_p = -\alpha_{E_1}$. Next we show $\alpha_{E_2} \leq 0$. To this end we emphasize that $\alpha_{e_1} < \alpha_s$, because otherwise we get contradiction

$$0 = \alpha_{e_1} + \alpha_{E_2} \geq \alpha_s + \alpha_{E_2} \geq \alpha_S = 1$$

due to (19a) and (19d). To obtain $\alpha_{E_2} \leq 0$ we rewrite Equation (19e) in the form

$$\alpha_{e_1} + \min\{\alpha_{E_2}, \alpha_{e_2}, \alpha_{e_1}, \alpha_s\} = \min\{\alpha_s + \alpha_{E_1}, \alpha_p + \alpha_{E_1}\}.$$

With $\alpha_p = -\alpha_{E_1}$, $\alpha_{e_1} < \alpha_{e_2}$, $\alpha_{e_1} < \alpha_s$, $\alpha_s + \alpha_{E_1} \geq 1$ last equality yields

$$\alpha_{e_1} + \min\{\alpha_{E_2}, \alpha_{e_1}\} = 0$$

or equivalently, with $\alpha_{e_1} = -\alpha_{E_2}$

$$\min\{\alpha_{e_1} + \alpha_{E_2}, 2\alpha_{e_1}\} = \min\{0, -2\alpha_{E_2}\} = 0,$$

which in turn implies $\alpha_{E_2} \leq 0$. Let us prove that $\alpha_s = 1 - \alpha_{E_1}$. Indeed (19d) can be written as

$$\alpha_s + \min \{ \alpha_{E_1}, \alpha_{E_2}, \alpha_{e_1}, \alpha_{e_2} \} = 1, \quad (21)$$

so that taking into account $\alpha_{E_1} < \alpha_{E_2} \leq 0$ and $\alpha_{e_2} > \alpha_{e_1} = -\alpha_{E_2} \geq 0$, we obtain from (21) that $\alpha_s = 1 - \alpha_{E_1}$. To express α_{e_2} through α_{E_1} and α_{E_2} we rewrite Equation (19f) as follows

$$\alpha_{e_2} + \min \{ \alpha_{E_1}, \alpha_{e_1}, \alpha_{e_2}, \alpha_s \} = \alpha_{E_2} + \min \{ \alpha_s, \alpha_p \} \quad (22)$$

Due to $\alpha_{e_1} < \alpha_{e_2}$, $\alpha_{e_1} < \alpha_s$, $\alpha_{E_1} < \alpha_{e_1}$, $\alpha_p = -\alpha_{E_1}$, and $\alpha_p < \alpha_s$, it follows from (22) that

$$\alpha_{e_2} + \alpha_{E_1} = \alpha_{E_2} - \alpha_{E_1}$$

or equivalently $\alpha_{e_2} = \alpha_{E_2} - 2\alpha_{E_1}$. Thus we obtain

$$\alpha = (1, \alpha_{E_1}, \alpha_{E_2}, 1 - \alpha_{E_1}, -\alpha_{E_2}, \alpha_{E_2} - 2\alpha_{E_1}, -\alpha_{E_1}) \quad \text{with} \quad \alpha_{E_2} \leq 0.$$

To prove Theorem 2 it remains to show that $\alpha_{E_2} = -\frac{1}{2}$. To this end, we consider the equations $\dot{e}_1 = 0$, $\dot{e}_2 = 0$, $\dot{p} = 0$, that is

$$\begin{aligned} 0 &= \dot{e}_1 = k_2 s E_1 - k_4 e_1 E_2 + k_6 p E_1 - k_8 e_1 e_2 - 2k_9 e_1^2 - k_{11} e_1 s, \\ 0 &= \dot{e}_2 = k_3 s E_2 - k_5 e_2 E_1 + k_7 p E_2 - k_8 e_1 e_2 - 2k_{10} e_2^2 - k_{12} e_2 s, \\ 0 &= \dot{p} = k_4 e_1 E_2 + k_5 e_2 E_1 - k_6 p E_1 - k_7 p E_2. \end{aligned} \quad (23)$$

Adding these equations we obtain

$$k_2 s E_1 + k_3 s E_2 = 2k_8 e_1 e_2 + 2k_9 e_1^2 + 2k_{10} e_2^2 + k_{11} e_1 s + k_{12} e_2 s. \quad (24)$$

Comparing powers ϵ in (24)

$$1 = \min \{ -2\alpha_{E_1}, -2\alpha_{E_2}, 2(\alpha_{E_2} - 2\alpha_{E_1}), 1 - \alpha_{E_1} - \alpha_{E_2}, 1 - 3\alpha_{E_1} + \alpha_{E_2} \}.$$

Therefore $\alpha_{E_2} = -\frac{1}{2}$ and

$$\alpha = \left(1, \alpha_{E_1}, -\frac{1}{2}, 1 - \alpha_{E_1}, \frac{1}{2}, -\frac{1}{2} - 2\alpha_{E_1}, -\alpha_{E_1} \right) \quad \text{with} \quad \alpha_{E_1} < -\frac{1}{2}. \quad (25)$$

This proves Theorem 2 in the case (a) $\alpha_{E_1} < \alpha_{E_2}$.

In the same manner (even simple) we prove that, if $\alpha_{E_1} = \alpha_{E_2}$ (case (b)), then scaling exponent

$$\alpha = \left(1, -\frac{1}{2}, -\frac{1}{2}, \frac{3}{2}, \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \right).$$

4 Stability of chemical reactor in the presence of diffusion

For simplicity we restrict ourselves to the case, when the dilution vector $\vec{D} := (D_1, \dots, D_6) = 0$ and $\beta = 0$. Moreover we assume that the bulk of reactor to be well-mixed. Let G be a reactor volume and $\Omega \subset G$ be a domain where laminar flow prevails. We denote by

$$u^*(\epsilon) = (S(\epsilon), E_1(\epsilon), E_2(\epsilon), s(\epsilon), e_1(\epsilon), e_2(\epsilon), p(\epsilon), T^*(\epsilon))$$

homogeneous equilibrium of (3). Due to the Theorem 2 we have following (for simplicity we restrict ourselves to the case $\alpha_{E_1} = \alpha_{E_2} = -\frac{1}{2}$) asymptotic expansions for equilibrium $u^*(\epsilon)$, that is

$$\begin{aligned} S(\epsilon) &\sim \epsilon + \mathcal{O}(\epsilon), & E_1(\epsilon) &\sim \epsilon^{-\frac{1}{2}} + \mathcal{O}(\epsilon^{-\frac{1}{2}}), \\ E_2(\epsilon) &\sim \epsilon^{-\frac{1}{2}} + \mathcal{O}(\epsilon^{-\frac{1}{2}}), & s(\epsilon) &\sim \epsilon^{\frac{3}{2}} + \mathcal{O}(\epsilon^{\frac{3}{2}}), \\ e_1(\epsilon) &\sim \epsilon^{\frac{1}{2}} + \mathcal{O}(\epsilon^{\frac{1}{2}}), & e_2(\epsilon) &\sim \epsilon^{\frac{1}{2}} + \mathcal{O}(\epsilon^{\frac{1}{2}}), \\ p(\epsilon) &\sim \epsilon^{\frac{1}{2}} + \mathcal{O}(\epsilon^{\frac{1}{2}}). \end{aligned} \quad (26)$$

The equation $\dot{T} = 0$ yields an ϵ -expansion of the steady state temperature $T^*(\epsilon)$, that is

$$T^*(\epsilon) \sim \frac{E_{1,0} + E_{2,0}}{2} + \chi T_0 + \mathcal{O}(\epsilon). \quad (27)$$

We rewrite Equation (2) in the absence of transport terms (∇, v) in the following abstract form

$$\frac{\partial \vec{u}}{\partial t} = D\Delta \vec{u} + \vec{F}(u), \quad \vec{u}|_{\partial\Omega} = u^*(\epsilon), \quad (28)$$

where $D = \text{diag}(d_S, d_{E_1}, d_{E_2}, d_s, d_{e_1}, d_{e_2}, d_p, d_T)$ and $u^*(\epsilon)$ is a homogeneous equilibrium mentioned above. Both due to equilibria concentrations and the bulk of reactor to be well-mixed. Let

$$\vec{u}(x, t) = u^*(\epsilon) + W(x, t).$$

Then $W(x, t)$ satisfies

$$\frac{\partial W}{\partial t} = D\Delta W + F'(u^*(\epsilon))W, \quad W|_{\partial\Omega} = 0, \quad (29)$$

where $F'(u^*(\epsilon))$ is the (8, 8)-matrix at $u^*(\epsilon)$, that is

$$F'(u^*(\epsilon)) = \begin{pmatrix} -k_1 & 0 & 0 & 0 & 0 & 0 & 0 & k'_1 S \\ 0 & \sigma_1 & 0 & -k_2 E_1 & 0 & -k_5 E_1 & -k_6 E_1 & \Theta_1 \\ 0 & 0 & \sigma_2 & -k_3 E_2 & -k_4 E_2 & 0 & -k_7 E_2 & \Theta_2 \\ 2k_1 & -k_2 s & -k_3 s & \sigma_3 & -k_{11} s & -k_{12} s & 0 & \Theta_3 \\ 0 & k_2 s + k_6 p & -k_4 e_1 & k_2 E_1 - k_{11} e_1 & \sigma_4 & -k_8 e_1 & k_6 E_1 & \Theta_4 \\ 0 & -k_5 e_2 & k_3 s + k_7 p & k_3 E_2 - k_{12} e_2 & -k_8 e_2 & \sigma_5 & k_7 E_2 & \Theta_5 \\ 0 & k_5 e_2 - k_6 p & k_4 e_1 - k_7 p & 0 & k_4 E_2 & k_5 E_1 & \sigma_6 & \Theta_6 \\ h_1 k_1 & \gamma_1 & \gamma_2 & \gamma_3 & \gamma_4 & \gamma_5 & \gamma_6 & \Theta_7 \end{pmatrix}, \quad (30)$$

where

$$\begin{aligned}\sigma_1 &= -k_2s - k_5e_2 - k_6p, & \sigma_2 &= -k_3s - k_4e_1 - k_7p, \\ \sigma_3 &= -k_2E_1 - k_3E_2 - k_{11}e_1 - k_{12}e_2, & \sigma_4 &= -k_4E_2 - k_8e_2 - 4k_9e_1 - k_{11}s, \\ \sigma_5 &= -k_5E_1 - k_8e_1 - 4k_{10}e_2 - k_{12}s, & \sigma_6 &= -k_6E_1 - k_7E_2,\end{aligned}$$

$$\begin{aligned}\gamma_1 &= h_2k_2s + h_5k_5e_2 + h_6k_6p, \\ \gamma_2 &= h_3k_3s + h_4k_4e_1 + h_7k_7p, \\ \gamma_3 &= h_2k_2E_1 + h_3k_3E_2 + h_{11}k_{11}e_1 + h_{12}k_{12}e_2, \\ \gamma_4 &= h_4k_4E_2 + h_8k_8e_2 + 2h_9k_9e_1 + h_{11}k_{11}s, \\ \gamma_5 &= h_5k_5E_1 + h_8k_8e_1 + 2h_{10}k_{10}e_2 + h_{12}k_{12}s, \\ \gamma_6 &= h_6k_6E_1 + h_7k_7E_2,\end{aligned}$$

$$\begin{aligned}\Theta_1 &= -k'_2sE_1 - k'_5e_2E_1 - k'_6pE_1, \\ \Theta_2 &= -k'_3sE_2 - k'_4e_1E_2 - k'_7pE_2, \\ \Theta_3 &= 2k'_1S - k'_2sE_1 - k'_3sE_2 - k'_{11}e_1s - k'_{12}e_2s, \\ \Theta_4 &= k'_2sE_1 - k'_4e_1E_2 + k'_6pE_1 - k'_8e_1e_2 - 2k'_9e_1^2 - k'_{11}e_1s, \\ \Theta_5 &= k'_3sE_2 - k'_5e_2E_1 + k'_7pE_2 - k'_8e_1e_2 - 2k'_{10}e_2^2 - k'_{12}e_2s, \\ \Theta_6 &= k'_4e_1E_2 + k'_5e_2E_1 - k'_6pE_1 - k'_7pE_2, \\ \Theta_7 &= h_1k'_1S + h_2k'_2sE_1 + h_3k'_3sE_2 + h_4k'_4e_1E_2 + h_5k'_5e_2E_1 + h_6k'_6pE_1 + h_7k'_7pE_2, \\ &\quad + h_8k'_8e_1e_2 + h_9k'_9e_1^2 + h_{10}k'_{10}e_2^2 + h_{11}k'_{11}e_1s + h_{12}k'_{12}e_2s - \chi\end{aligned}$$

with

$$k'_j := \frac{d}{dT}k_j(T), \quad j = 1, \dots, 12.$$

Let $0 < \lambda_1 \leq \lambda_2 \leq \dots \leq \lambda_N \leq \dots$, $\lambda_N \rightarrow \infty$ as $N \rightarrow \infty$ be eigenvalues of $-\Delta$ (the Laplacian) with Dirichlet boundary conditions, that is

$$-\Delta e_k(x) = \lambda_k e_k(x), \quad e_k|_{\partial\Omega} = 0. \quad (31)$$

Hence stability of chemical reactor (1) in the presence of diffusion

$D = \text{diag}(d_S, d_{E_1}, d_{E_2}, d_s, d_{e_1}, d_{e_2}, d_p, d_T)$ will be governed by

$$\det\{F'(u^*(\epsilon)) - \lambda_1 \text{diag}(d_S, d_{E_1}, d_{E_2}, d_s, d_{e_1}, d_{e_2}, d_p, d_T) - \lambda I\} = 0, \quad (32)$$

where λ_1 is the first eigenvalue of $-\Delta$, and I is the identity matrix.

Note that in the absence of diffusion stability of (1) will be governed by

$$F'(u^*(\epsilon))\xi = \lambda\xi. \quad (33)$$

We begin our stability analysis by grouping the matrix $F'(u^*(\epsilon))$ according to its leading order in $\epsilon := S_0$. To this end we use asymptotic expansion (26). Therefore $F'(u^*(\epsilon))$ can be decomposed as

$$F'(u^*(\epsilon)) = \epsilon^{-\frac{1}{2}} \left[A_0 + \mathcal{O}\left(\epsilon^{\frac{1}{2}}\right) \right]. \quad (34)$$

It remains to compute $\lambda_j(A_0), j = 1, \dots$. Simple linear algebra computations show that for $\chi \geq \chi_c$ we have stability and $0 \leq \chi < \chi_c$ belongs to the instability interval. Here χ_c some positive number. Recall that by χ is denoted the coolant rate.

Now we are interested in stability of (1) in the presence of diffusion. To this end we consider equation (32), where $F'(u^*(\epsilon))$ is the same matrix as in (33). Taking into account that $\lambda_1 > 0$, it is not difficult to see that $\chi > \chi_c - \delta$, where χ_c the same number as above (in the absence of diffusion) and δ is some positive number depending on λ_1 and $\vec{D} = (d_S, d_{E_1}, d_{E_2}, d_s, d_{e_1}, d_{e_2}, d_p, d_T)$. We emphasize that the interval $\chi_c - \delta < \chi < \chi_c$ which provides stability of chemical reactor in the presence of diffusion, belongs to the instability interval in the diffusionless case.

Remark 1. In the same manner one can analyse influence of dilution rate to the stability of (1).

The following figures show the role of diffusion for the stability of chemical reactor (1) and confirm our theoretical observations. The graphs in the Figures 1 - 16 represent the eigenvalues (ordinate) of the matrices $F'(u^*(\epsilon))$ for the coolant rates $\chi = 0$ and $\chi = 100$ with $\alpha_{E_1} = -2.00, -1.99, \dots, -0.49, -0.50$ (abscissa, see (25)), $\epsilon = 10^{-4}$, $k_i = 1$, $h_i = 1$, $k'_i = 1$, $i = 1, \dots, 12$. The 8 eigenvalues of each matrix are sorted in ascending order.

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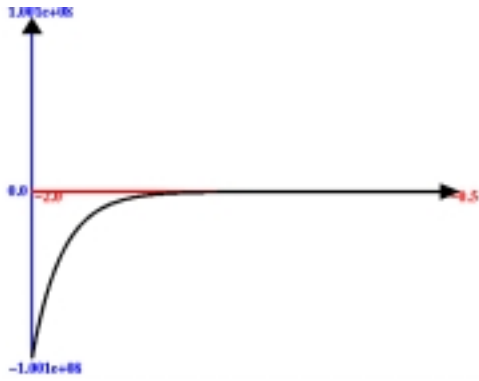


Figure 1: Eigenvalues $\lambda_1, \chi = 0$

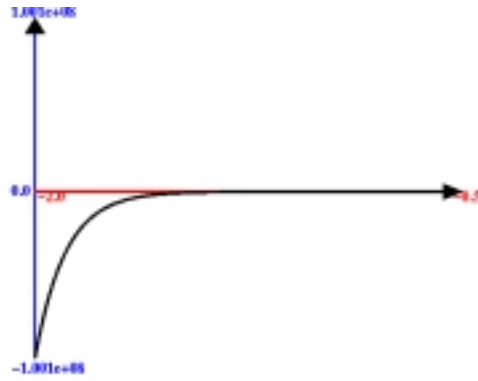


Figure 2: Eigenvalues $\lambda_1, \chi = 100$

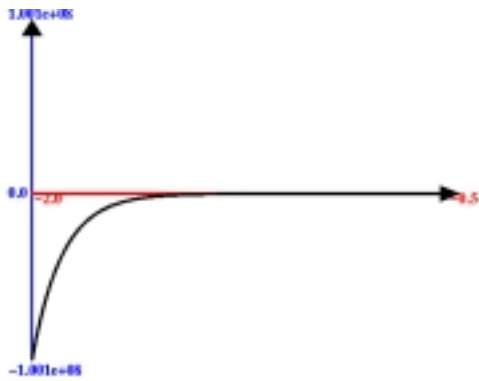


Figure 3: Eigenvalues $\lambda_2, \chi = 0$

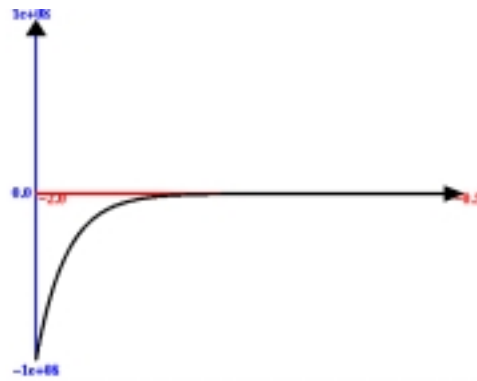


Figure 4: Eigenvalues $\lambda_2, \chi = 100$

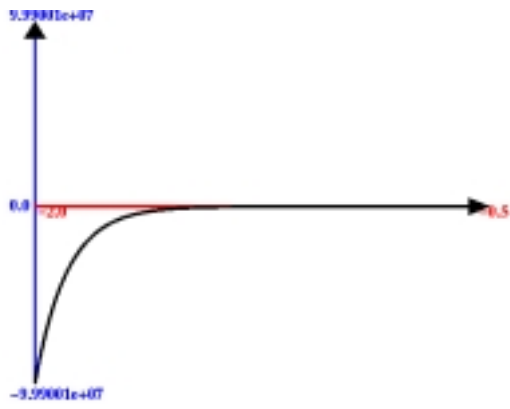


Figure 5: Eigenvalues $\lambda_3, \chi = 0$

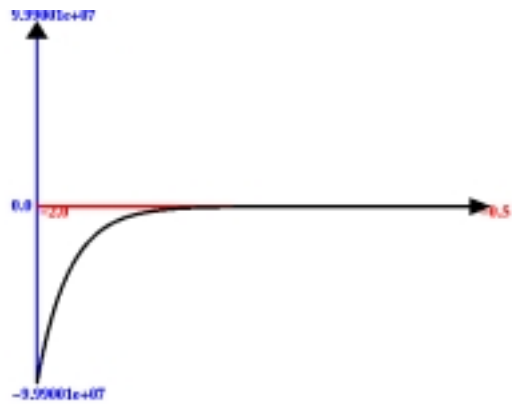


Figure 6: Eigenvalues $\lambda_3, \chi = 100$



Figure 7: Eigenvalues $\lambda_4, \chi = 0$

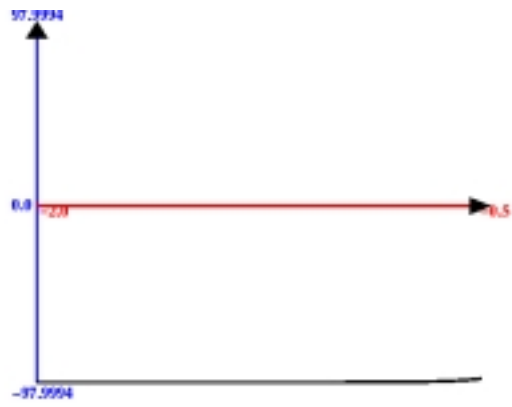


Figure 8: Eigenvalues $\lambda_4, \chi = 100$

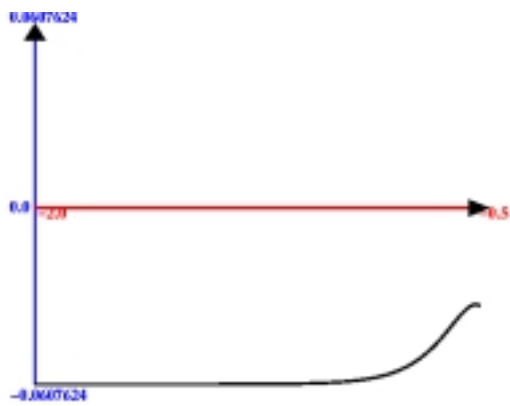


Figure 9: Eigenvalues $\lambda_5, \chi = 0$

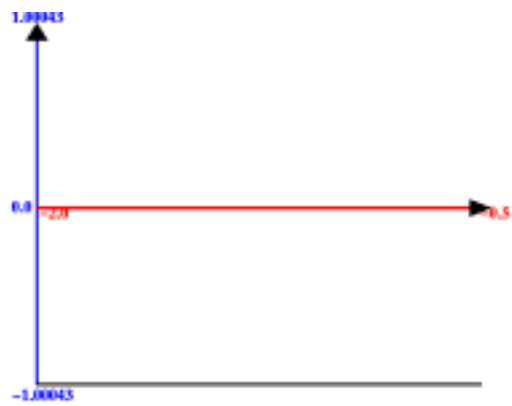


Figure 10: Eigenvalues $\lambda_5, \chi = 100$

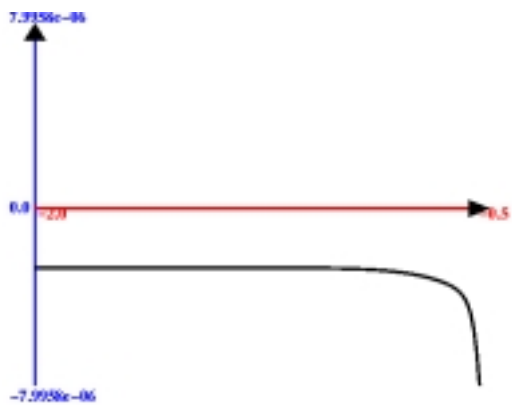


Figure 11: Eigenvalues $\lambda_6, \chi = 0$



Figure 12: Eigenvalues $\lambda_6, \chi = 100$

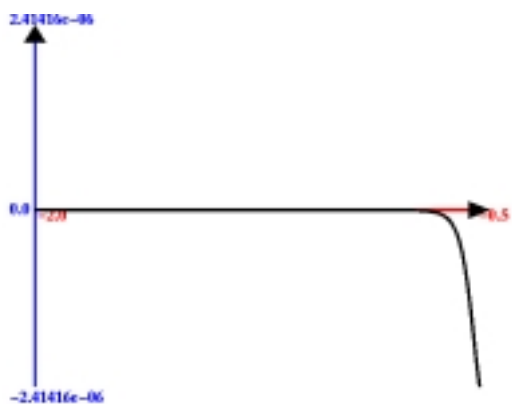


Figure 13: Eigenvalues $\lambda_7, \chi = 0$

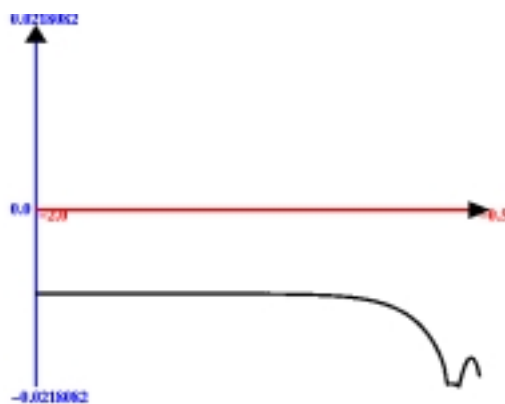


Figure 14: Eigenvalues $\lambda_7, \chi = 100$

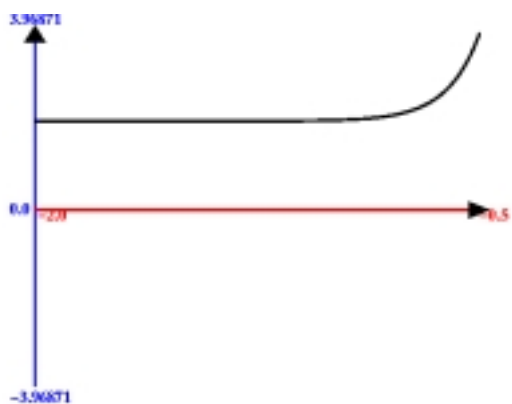


Figure 15: Eigenvalues $\lambda_8, \chi = 0$

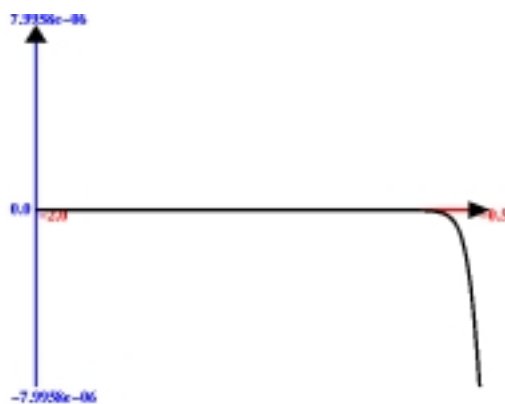


Figure 16: Eigenvalues $\lambda_8, \chi = 100$

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