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Abstract—Two different projection operators are found, projecting the state space of a continuous stirred tank reactor (C.S.T.R.) dynamic model on the space of asymptotically invariant states (or on the space of true invariant states for a batch reactor). The first projection gives an explicit expression for the invariants, but it requires a certain partitioning of the stoichiometric matrix. The other projection avoids this difficulty, but gives a description of the invariants by a set of equations which do not have full rank. Concerning the observability of the dynamical modes, it turns out that the invariants put certain restrictions on the observation matrix for the system to be observable. The corresponding conditions for the system to be controllable by feed composition control are briefly outlined. Certain properties of the solution of the linearized system are also analyzed.

1. INTRODUCTION

The study of chemical reactor dynamics becomes more and more important in the attempts to improve the production, the selectivity and the dynamic control of the reactors. The basic thermodynamic variables like composition and enthalpy are important state variables in the analysis of these phenomena.

A subset of reaction invariant variables may be found by a simple partitioning of the reactor equations. These variables are linear combinations of the basic concentrations and the temperature, even if the differential state equations are strongly nonlinear due to the reaction rates. The motion of these variables is linear and constrained to a subset orthogonal to the remaining state space. For a C.S.T.R., these variables may be called asymptotic invariants[1]. In a batch reactor, they are true invariants[2]. Hence, the dimensionality of such a state space description can be reduced, as has been realized for a long time for closed systems. Recently, conditions for such a reduction to be valid in

open, continuous flow reactors have been analyzed by Asbjørnsen and Fjeld[3], Fjeld[1] and Asbjørnsen[4]. For global stability analysis, all the states are necessary, unless special conditions are met. However, for stability analysis in the small, only a reduced number of state variables needs to be considered. In this paper, a closer study of the projection of the state space on the set of asymptotically invariants (eigenmodes) is made.

The concepts of observability and controllability are both very important for the control of dynamical systems. State observability is important also in parameter estimation schemes. It turns out that invariant states of chemical reactors are of interest in the analysis of state observability of such processes, and this is the topic studied in the last part of the paper.

2. INVARIANTS AND EIGENVECTORS

Consider a nonlinear system described by the differential equation

$$\dot{\mathbf{x}}(t) = \mathbf{f}(\mathbf{x}(t), \mathbf{u}(t), t) \qquad (1)$$

where for $t \geq 0$, $\mathbf{x} \in X \subset E_n$, $\mathbf{u} \in U \subset E_r$ and $\mathbf{x}(0) = \mathbf{x}_0$ $\in X$. Furthermore, $\mathbf{u}(\cdot) \in \mathcal{F}$, $\mathcal{F}$ is a given class of integrable functions. The solution of Eq. (1) is assumed to exist for all $t > 0$ and all $\mathbf{x}_0 \in X$. The notion of invariance is introduced as follows.

Definition 2.1

A *true invariant* of the solution Eq. (1) is a function $h(\mathbf{x})$ of the state vector $\mathbf{x}(t)$ such that $\dot{h} = \mathrm{d}h/\mathrm{d}t = \langle \mathrm{grad}\, h, \dot{\mathbf{x}} \rangle = \langle \mathrm{grad}\, h, \mathbf{f} \rangle = 0$.

If $\langle \mathrm{grad}\, h, \mathbf{f} \rangle$ is neither a constant nor equal to zero, but its limit as $t \to \infty$ is zero, then h is an *asymptotic invariant* of the solution of Eq. (1).

If $\mathbf{x}$ is the state vector of a chemical reactor and $h(t)$ does not explicitly depend on any reaction parameter, such as stoichiometric coefficients, kinetic parameters or heats of reactions, then an invariant, true or asymptotic, is called a true or asymptotic *reaction invariant*.

Linear systems

For linear autonomous systems, i.e. $\mathbf{f} = A\mathbf{x}$, it is easily seen that the projection on the nullspace of A is an invariant. Similarly it is found that the projection on the space spanned by the eigenvectors corresponding to stable eigenvalues is an asymptotic invariant.

Nonlinear systems

In attempting to extend this idea to the nonlinear case the deviation $\Delta\mathbf{x} = \mathbf{x} - \mathbf{x}_s$ is introduced; here $\mathbf{x}_s$ is a singular point at which $\mathbf{f}(\mathbf{x}_S, \mathbf{u}_S) = \mathbf{0}$. Then

$$\Delta\dot{\mathbf{x}} = \mathbf{f}(\mathbf{x}_s + \Delta\mathbf{x}) \triangleq \mathbf{h}(\Delta\mathbf{x}) \triangleq \mathbf{F}(\Delta\mathbf{x})\,\Delta\mathbf{x} \qquad (2)$$

where the matrix $\mathbf{F}$ has elements $F_{ij} = h_i(\Delta\mathbf{x})/\Delta x_j$. These are assumed to be uniformly bounded for finite Δx_j as the other $\Delta x_i \to 0$. For any fixed $\Delta\mathbf{x}$, the eigenvalue problem for F is

$$[\lambda I - F(\Delta\mathbf{x})]\mathbf{e} = \mathbf{0}. \qquad (3)$$

At $\mathbf{x} = \mathbf{x}_s$, i.e. as $\Delta\mathbf{x} \to \mathbf{0}$, F becomes the Jacobian of the functions $\mathbf{f}$ with respect to the variables $\mathbf{x}$ evaluated at the critical point. For the problem (3) the eigenvectors and eigenvalues will depend on $\Delta\mathbf{x}$ unless Eq. (1) is linear. However certain nonlinear systems, including chemical reactors in general, may have a subset of state space where linear motions take place. Certain eigenvalues and the corresponding eigenvectors will then be independent of $\Delta\mathbf{x}$. For an absolute invariant to be present there must be a zero eigenvalue. An asymptotic reaction invariant implies that an eigenmode becomes constant as $t \to \infty$ *independently of the reaction*.

3. STIRRED TANK REACTOR EQUATIONS

The dynamic mass and enthalpy balances for a stirred tank reactor has been studied in details by Asbjørnsen and Fjeld[3] and Asbjørnsen[4, 10] under isothermal and adiabatic operation, and under operation with heat exchange.

Provided all physical properties as well as the heat of reactions are constant, the enthalpy and species balances are combined in one single vector differential equation[3, 4]

$$\dot{\mathbf{x}} = \frac{1}{\tau}(\mathbf{x}_f - \mathbf{x}) - A\,\mathbf{r}(\mathbf{x}) \qquad (4)$$

where A for isothermal operation is the transpose of the stoichiometric matrix. For truly adiabatic operation, the adiabatic temperature rises for each reaction is added as an extra row, as a consequence of the inclusion of the temperature in state vector $\mathbf{x}$. This vector then comprises the temperature and the molar concentrations of the n participants of n_r truly independent chemical reactions[3, 4].

The characteristic feature of the differential equation describing the C.S.T.R. is that the nonlinear term at the right hand side of Eq. (4) maps as follows

$$A\,\mathbf{r} : E_n \overset{r}{\to} E_{n_r} \overset{A}{\to} E_n. \qquad (5)$$

This particular property of the stirred tank reactor equations is the basis for the analysis presented in this paper.

Provided the reactions are truly independent, the matrix A will have full rank n_r, and a square submatrix A_1, with rank n_r can always be found.

In this case, Asbjørnsen and Fjeld[3] showed by a partitioning procedure that a reaction invariant $\mathbf{z}(t)$ is obtained

$$\mathbf{z} = \mathbf{x}_2 - A_2 A_1^{-1}\mathbf{x}_1 \qquad (6)$$

where A_2 contains the remaining $n - n_r$ rows of A and $\dim(\mathbf{z}) = n - n_r$.

This variable is described by the differential equation for a stirred tank without any reactions

$$\dot{\mathbf{z}} = \frac{1}{\tau}(\mathbf{z}_f - \mathbf{z}). \qquad (7)$$

The solution for the reaction invariant is simply

$$\mathbf{z}(t) = \exp\left(-\int_0^t \mathrm{d}\upsilon/\tau\right)\mathbf{z}(0) + \int_0^t \exp\left(-\int_\theta^t \mathrm{d}\upsilon/\tau\right)\mathbf{z}_f(\theta)\,\mathrm{d}\theta \qquad (8)$$

which allows the parameter τ to be dependent of time[11].

Provided $\mathbf{z}_f$ is constant, then $\mathbf{z}(t)$ is an asymptotic

reaction invariant, since:

$$\lim_{t \to \infty}[\mathbf{z}(t)] = \mathbf{z}_f. \qquad (9)$$

If $1/\tau = 0$, i.e. for a batch reactor, $\mathbf{z}$ is a true invariant $\mathbf{z}(0)$. This leads to the following theorem[3, 4]:

Theorem 1. For a C.S.T.R. with n_r reactions between n species and with a stoichiometric matrix of full rank n_r, an asymptotic invariant exists, which is

$$\mathbf{z}(t) = \mathbf{x}_2(t) - A_2 A_1^{-1}\mathbf{x}_1(t) \qquad (10)$$

provided the feed is such that

$$\mathbf{z}_f = \mathbf{x}_{2f} - A_2 A_1^{-1}\mathbf{x}_{1f} \qquad (11)$$

is constant. For a batch reactor, $\mathbf{z}(t) = \mathbf{z}(0)$ is a true invariant.

Note that all concentrations and the temperature have to be positive

$$x_i \geq 0. \; x_{if} \geq 0, i = 1,2,\ldots\ldots, n. \qquad (12)$$

This constrains the states to a certain subset of E_n in the positive orthant E_n^+. This means that the state space is not a linear space, and therefore the term "subspace" should not be used for certain subsets of E_n.

The deviation from a steady state $\mathbf{x}_s$ is introduced as $\Delta\mathbf{x} = \mathbf{x} - \mathbf{x}_s$. A new set of state variables may be chosen, as $\Delta\mathbf{x}_1$ and $\Delta\mathbf{z}$. For a given $\mathbf{x}_f =$ constant, the n-dimensional non-linear reactor equation then becomes

$$\begin{bmatrix} \Delta\dot{\mathbf{x}}_1 \\ \Delta\dot{\mathbf{z}} \end{bmatrix} = -\frac{1}{\tau}\begin{bmatrix} \Delta\mathbf{x}_1 \\ \Delta\mathbf{z} \end{bmatrix} - \begin{bmatrix} A_1 \\ 0 \end{bmatrix}\Delta\mathbf{r} \qquad (13)$$

where

$$\Delta\mathbf{r} \triangleq \mathbf{r}(\mathbf{x}) - \mathbf{r}(\mathbf{x}_s). \qquad (14)$$

Furthermore

$$\Delta\bar{\mathbf{x}} \triangleq \begin{bmatrix} \Delta\mathbf{x}_1 \\ \Delta z \end{bmatrix} \text{ and } \Delta\mathbf{x} = \begin{bmatrix} I & 0 \\ A_2A_1^{-1} & I \end{bmatrix}\Delta\bar{\mathbf{x}}. \qquad (15)$$

4. INVARIANT SUBSETS AND STATE VARIABLES

4.1 *The partitioning procedure*

It is now seen that the subset on which $\Delta\mathbf{z} = 0$ defines a n_r-dimensional subset R_{n_r} of the state space $X \subset E_n^+$ which is invariant[5] under the non-linear transformation $F(\Delta\bar{\mathbf{x}})$, since Eqs. (18)–(19) may be written as

$$\Delta\bar{\mathbf{x}} = \begin{bmatrix} -\dfrac{1}{\tau}I - A_1 R(\Delta\bar{\mathbf{x}}) & -A_1 R_2(\Delta\bar{\mathbf{x}}) \\ 0 & -\dfrac{1}{\tau}I \end{bmatrix}\Delta\bar{\mathbf{x}} =$$
$$F(\Delta\bar{\mathbf{x}}) \, \Delta\bar{\mathbf{x}} \qquad (16)$$

where

$$\Delta\mathbf{r} \triangleq [R_1(\Delta\bar{\mathbf{x}}) \mid R_2(\Delta\bar{\mathbf{x}})]\,\Delta\mathbf{x} \qquad (17)$$

$$\dim(R_1) = n_r \times n_r, \quad \dim(R_2) = n_r \times (n - n_r).$$

The transformation projecting $\Delta\mathbf{x}(t)$ on the space of asymptotical invariants $\Delta\mathbf{z}(t)$ is given by Eq. (14) or

$$\Delta\mathbf{z}(t) = [-A_2A_1^{-1} \mid I]\,\Delta\mathbf{x}(t). \qquad (18)$$

Therefore, the invariant subset R_{n_r} is described through all those $\Delta\mathbf{x}$ satisfying the constraints (12) and the $n - n_r$ equations

$$V\Delta\mathbf{x} \triangleq [-A_2A_1^{-1} \mid I]\,\Delta\mathbf{x} = \mathbf{0} \qquad (19)$$

from which the simple relation follows:

$$R_{n_r} = \mathcal{N}(V)^+ \qquad (20)$$

The$^+$ reminds about the restrictions corresponding to Eq. (12). It is observed that the rows of V are linearly independent, and span a space R_{n-n_r} orthogonal to R_{n_r}.

The relation above may be expressed by the projection operator P_1. When $X = R_{n_r} \oplus R_{n-n_r}$ [care should be taken in the use the direct sum symbol $\oplus$ since the spaces are not linear because of Eq. (12)], $\Delta\mathbf{x}$ may be expressed as

$$\Delta\mathbf{x} = P_1\Delta\mathbf{x} + (I - P_1)\,\Delta\mathbf{x} \qquad (21)$$

where

$$P_1\Delta\mathbf{x} \in R_{n-n_r} \text{ and } (I - P_1)\Delta\mathbf{x} \in R_{n_r}$$

P_1 is a projection operator on R_{n-n_r} along R_{n_r} if and only if $P_1 = P_1^2$ when $R_{n-n_r} = \mathcal{R}(P_1)$ and $R_{n_r} = \mathcal{N}(P_1)$[5]. It is seen that the conditions are satisfied with

$$P_1 = \begin{bmatrix} 0 & 0 \\ -A_2A_1^{-1} & I \end{bmatrix}. \qquad (22)$$

Then

$$P_1\Delta\mathbf{x} = \left(\frac{\mathbf{0}}{\Delta\mathbf{x}_2 - A_2A_1^{-1}\Delta\mathbf{x}_1}\right)\left(\frac{\mathbf{0}}{\Delta\mathbf{z}}\right) \qquad (23)$$

$$(I - P_1)\Delta\mathbf{x} = \left(\frac{\Delta\mathbf{x}_1}{A_2A_1^{-1}\Delta\mathbf{x}_1}\right)\left(\frac{\Delta\mathbf{x}_1}{\Delta\mathbf{x}_2 - \Delta\mathbf{z}}\right) \qquad (24)$$

Note that neither $P_1\Delta\mathbf{x}$ nor $(I - P_1)\Delta\mathbf{x}$ are state vectors, but $\Delta\mathbf{z}$ and $\Delta\mathbf{x}_1$ are. The asymptotic invariants are explicitly given by the last $n - n_r$ components of $P_1\Delta\mathbf{x}$ as expressed by Eq. (2)

4.2 *Finding invariants through direct use of projections*

The problem of finding the reaction invariants has so far been solved through a particular choice of state variables. To get further insight into the problem another coordinate free solution is presented. The analysis will also result in a different

representation of the asymptotic invariants. This approach is motivated by the corresponding description of a batch reaction. i.e. $1/\tau = q(t)/V = 0$:

$$\dot{x}(t) = -A\, r[x(t)] \tag{25}$$

From matrix algebra, it is known that if A is a linear matrix transformation from E_{n_r} to E_n, then

$$E_n = \mathscr{R}(A) \oplus \mathscr{N}(A^T) \tag{26}$$

and

$$\mathscr{N}(A^T) = [\mathscr{R}(A)]^\perp \tag{27}$$

Let $\mathbf{w} \in \mathscr{N}(A^T)$, i.e. $\mathbf{w}$ satisfies $A^T\mathbf{w} = \mathbf{0}$, any vector $\mathbf{x}$ in E_n given by the solution of (25) can be expressed as

$$\mathbf{x} = \mathbf{w} + \mathbf{s} = \mathbf{w} + A\mathbf{v} \tag{28}$$

where $\mathbf{s} \in \mathscr{R}(A)$. The latter may simply be taken as $\mathbf{s} = A\mathbf{v}$, where $\mathbf{v}$ is a n_r-dimensional vector, in general with nonzero entries. The projection operator for the projection from E_n to $\mathscr{N}(A^T)$ is

$$P_2 = I - AA\dagger \tag{29}$$

Where $A\dagger$ is a pseudo-inverse of A. Since A has full rank, $A\dagger$ is simply:

$$A\dagger = (A^TA)^{-1}A^T \tag{30}$$

It is observed that P_2 satisfies all the conditions for P_2 to be a projection operator. Applying P_2 to Eq. (25),

$$P_2\dot{x}(t) = \dot{\mathbf{w}}(t) = \mathbf{0} \tag{31}$$

i.e.

$$\mathbf{w}(t) = \text{constant} = \mathbf{w}_0. \tag{32}$$

Further, the projection onto $\mathscr{R}(A) = \mathscr{N}(A^T)^\perp$ is $AA\dagger$, i.e.

$$(I - P_2)\dot{x}(t) = -A\, r(\mathbf{w}_0 + A\mathbf{v}) \tag{33}$$

that is

$$A\dot{\mathbf{v}}(t) = -A\, r(\mathbf{w}_0 + A\mathbf{v}). \tag{34}$$

Projecting again $A\dot{\mathbf{v}}$ on R_{n_r} by multiplying Eq. (34) with $A\dagger$ from the left (this projects $A\dot{\mathbf{v}}$ onto $\mathscr{R}(A^T) = \mathscr{N}(A)^\perp$, i.e. R_{n_r})

$$A\dagger A\dot{\mathbf{v}}(t) = \dot{\mathbf{v}}(t) = -r[\mathbf{w}_0 + A\mathbf{v}(t)]. \tag{35}$$

This result shows that the variable $\mathbf{v}$ is equivalent to the 'extent of reaction' so frequently referred to in the chemical engineering literature. To conclude, an arbitrary $\mathbf{x}(t)$ satisfying Eq. (25) can be expressed as

$$\mathbf{x}(t) = P_2\mathbf{x}(t) + (I - P_2)\mathbf{x}(t) = \mathbf{w}_0 + A\mathbf{v}(t) \tag{36}$$

where P_2 is an orthogonal projection operator. Note that rank $(P_2) = n - n_r$.

Theorem 2. For a stirred tank batch reactor with n_r reactions between n species and with a stoichiometric matrix of rank n_r, the function

$$\mathbf{w}(t) = [I - A(A^TA)^{-1}A^T]\mathbf{x}(t) \tag{37}$$

is a true reaction invariant.

Furthermore, the function

$$\mathbf{v}(t) = (A^TA)^{-1}A^T\mathbf{x}(t) \tag{38}$$

is the extent of reaction in the batch reactor.

The projection operator P_2 is applied to the C.S.T.R. equation, Eq. (4), which becomes

$$P_2\dot{x} = \frac{1}{\tau}(P_2\mathbf{x}_f - P_2\mathbf{x}) - P_2A\, r. \tag{39}$$

Since the properties of the pseudo-inverse $A\dagger$ is such that $A\dagger A = I$, the following equation is obtained

$$P_2\dot{x} = \frac{1}{\tau}(P_2\mathbf{x}_f - P_2\mathbf{x}). \tag{40}$$

Defining as before $\mathbf{w} = P_2\mathbf{x}$ and $\mathbf{w}_f = P_2\mathbf{x}_f$, it follows that

$$\dot{\mathbf{w}} = \frac{1}{\tau}(\mathbf{w}_f - \mathbf{w}). \tag{41}$$

Furthermore

$$(I - P_2)\dot{x} = AA\dagger\dot{x} = \frac{1}{\tau}AA\dagger(\mathbf{x}_f - \mathbf{x}) - A\, r. \tag{42}$$

Since Eq. (28) implies that $\mathbf{v} = A\dagger\mathbf{x}$ and $\mathbf{v}_f = A\dagger\mathbf{x}_f$, it follows that

$$A\dot{\mathbf{v}} = \frac{1}{\tau}A(\mathbf{v}_f - \mathbf{v}) - A\, r. \tag{43}$$

With $A\mathbf{v} \in \mathscr{R}(A)$, a projection of this vector on to $\mathscr{R}(A^T)$ as in Eq. (35), gives

$$\dot{\mathbf{v}} = \frac{1}{\tau}(\mathbf{v}_f - \mathbf{v}) - r. \tag{44}$$

Observe that $\mathbf{w}(0) \in \mathscr{N}(A^T)$ and $\mathbf{w}_f \in \mathscr{N}(A^T)$ implies that $\mathbf{w}(t)$ is invariant in this respect under the solution of Eq. (41) so $\mathbf{w}(t) \in \mathscr{N}(A^T)$. The solution is equivalent to Eq. (8), but with $\mathbf{z}$ replaced by $\mathbf{w}$

$$\mathbf{w}(t) = \exp\left(-\int_0^t dv/\tau\right)\mathbf{w}(0)$$
$$+ \int_0^t \exp\left(-\int_\theta^t dv/\tau\right)\mathbf{w}_f(\theta)\, d\theta. \tag{45}$$

Finally, $\mathbf{x}(t)$ is given by

$$\mathbf{x}(t) = \mathbf{w}(t) + A\mathbf{v}(t). \tag{46}$$

If the feed is such that $\mathbf{w}_f = P_2\mathbf{x}_f = \text{constant}$, then Eq. (41) implies that

$$\lim_{t\to\infty} \mathbf{w}(t) = \mathbf{w}_f. \tag{47}$$

In analogy to Eqs. (11), (12) and (13), this leads to the following theorem:

Theorem 3. For a C.S.T.R. with n_r reactions between n species, and with a stoichiometric matrix of full rank n_r, an asymptotic reaction invariant exists, which is

$$w(t) = [I - A(A^TA)^{-1}A^T] x(t) \qquad (48)$$

provided the feed is such that

$$w_f = [I - A(A^TA)^{-1}A^T]x_f \qquad (49)$$

is constant.

Remark. Theorem 3 includes Theorem 1 as a special case, which is demonstrated by the introduction of the partitioned forms of A and x. Then

$$[I - A(A^TA)^{-1}A^T]x$$
$$= \begin{bmatrix} x_1 - A_1(A_1{}^TA_1 + A_2{}^TA_2)^{-1}(A_1{}^Tx_1 + A_2{}^Tx_2) \\ -A_2(A_1{}^TA_1 + A_2{}^TA_2)^{-1}(A_1{}^Tx_1 + A_2{}^Tx_2) + x_2 \end{bmatrix} \qquad (50)$$

and it follows from Theorem 3 that for large t, the two vectors

$$x_2 - A_2(A_1{}^TA_1 + A_2{}^TA_2)^{-1}[A_1{}^Tx_1 + A_2{}^Tx_2] \rightarrow \text{constant} \qquad (51)$$

$$x_1(A_1(A_1{}^TA_1 + A_2{}^TA_2)^{-1}[A_1{}^Tx_1 + A_2{}^Tx_2] \rightarrow \text{constant}$$

are asymptotic reaction invariants. Eliminating the expression within the square brackets, gives

$$x_2 - A_2A_1{}^{-1}x_1 \rightarrow \text{constant}$$

which is equivalent to Theorem 1.

5. EXAMPLE

Some of the relationships in the previous sections is illustrated by a simple example, given by the stoichiometric matrix

$$A^T = \begin{bmatrix} -1 & 2 & | & 0 & 0 \\ 0 & -2 & | & 2 & 1 \end{bmatrix} \qquad (52)$$

From Eq. (19), the subset $R_{n_r} = R_2$ is obtained through

$$V\Delta x = \begin{bmatrix} 2 & 1 & | & 1 & 0 \\ 2 & 1 & | & 0 & 1 \end{bmatrix} \Delta x = 0 \qquad (53)$$

P_1 is given by

$$P_1 = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 2 & 1 & 1 & 0 \\ 2 & 1 & 0 & 1 \end{bmatrix} \qquad (54)$$

From Eq. (29), P_2 is given by

$$P_2 = \frac{1}{29} \begin{bmatrix} 20 & 10 & 8 & 4 \\ 10 & 5 & 4 & 2 \\ 8 & 4 & 9 & -10 \\ 4 & 2 & -10 & 24 \end{bmatrix} \qquad (55)$$

which has a rank equal two. $P_2\Delta x = 0$ can be reduced to Eq. (53), but the form $P_2\Delta x$ is not dependent on the condition that A_1 is nonsingular: Any rearrangement of the columns of A^T does not change the result.

6. LINEARIZED SOLUTION

The use of Eq. (53) leads to a particular simple form of the autonomous ($\Delta x_f = 0$) solution of a C.S.T.R. The linearized description can be found from Eq. (44) where $\Delta x_f = 0$ and hence $\Delta v_f = 0$

$$\Delta \dot{v} = -\frac{1}{\tau} \Delta v - \Delta r \qquad (56)$$

where Δr is replaced by $(\partial r / \partial v)\Delta v$

$$\frac{\partial \Delta r}{\partial \Delta v}\bigg|_{\substack{w=w_s \\ v=v_s}} = \frac{\partial r}{\partial x}\frac{\partial x}{\partial v}\bigg|_{\substack{x=x_s \\ v=v_s}} = RA. \qquad (57)$$

At steady state, one has from Eqs. (28), (41) and (44)

$$x_s = w_s + Av_s$$
$$w_s = w_f \qquad (58)$$
$$v_s = v_f - \tau r(x_s).$$

This leads to a linearized approximation to the n_r − dimensional differential equation for the vector Δv:

$$\Delta \dot{v} = -\frac{1}{\tau} \Delta v - RA\,\Delta v. \qquad (59)$$

The solution for $\Delta x = \xi(t)$ is

$$\xi(t) = \Delta w(t) + A\,\Delta v(t) \qquad (60)$$

that is:

$$\xi(t) = \exp(-t/\tau)\Delta w(0) + \exp\left[\left(-\frac{1}{\tau}I - RA\right)t\right]A\,\Delta v(0) \qquad (61)$$

7. EIGENVECTORS

7.1 *The nonlinear system*

Considering the non-linear system, the deviations in the reaction rate from its steady state value $r_s = r(x_s)$ are defined by

$$\Delta r(x_s + \Delta x) \triangleq R(x)\Delta x. \qquad (62)$$

Then the autonomous balance equations become

$$\Delta \dot{x}(t) = -\frac{1}{\tau}\Delta x(t) - AR(x)\Delta x(t) \qquad (63)$$

applying Eq. (3), the right column eigenvectors e_j satisfy (for given Δx) the equation

$$\left[\left(\lambda_j + \frac{1}{\tau}\right) I + AR(x)\right] e_j = 0 \qquad (64)$$

Similarly, the left row eigenvectors v_j satisfy the equation:

$$v_j\left[\left(\lambda_j + \frac{1}{\tau}\right) I + AR(x)\right] = 0. \qquad (65)$$

For $\lambda_j = -1/\tau$, Eq. (65) may be written as a matrix equation:

$$VAR(x) = [0] \qquad (66)$$

where V is the matrix of the $n - n_r$ left row eigenvectors belonging to the $n - n_r$ eigenvalues $-1/\tau$. Equation (66) is satisfied by

$$V = [-A_2 A_1^{-1} \quad I_{n-n_r}] \qquad (67)$$

independently of the matrix $R(x)$. Here I_{n-n_r} is the identity matrix of dimension $[n - n_r) x (n - n_r)]$. Hence, it follows

Theorem 4. The $n - n_r$ left eigenvectors of the non-linear C.S.T.R. equation belonging to the $n - n_r$ 'uncoupled' eigenvalues $-1/\tau$ are linearly independent and equal to the rows of the matrix V in Eq. (67). 'Uncoupled' eigenvalues meaning that the algebraic multiplicity is equal to the geometrical multiplicity, since the system matrix is diagonalizable in the $n - n_r$ eigenvalues $-1/\tau$, due to the properties of the reaction invariants.

The right column eigenvectors e_i corresponding to the $n - n_r$ left row eigenvectors above, can be found from the orthogonality condition

$$v_j e_i = \delta_{ji} \qquad (68)$$

7.2 *The linearized system*

The variable v in the partitioning $x = w + Av$, was shown by Eq. (41) to be described by a set of n_r non-linear equations which were given a linearised approximation in Eq. (59). This equation has n_r eigenvalues, which are assumed to be distinct. Correspondingly, there are n_r eigenvectors of this equation.

The basic balance equations, Eq. (4), in the variable x may be linearised in a similar way[3, 4] by defining as in Eq. (57)

$$\left.\frac{\partial \Delta r}{\partial \Delta x}\right|_{x=x_s} = R(x_s). \qquad (69)$$

Then the linearised approximation to Eq. (4) may be written for an autonomous system ($\Delta x_f = 0$[3, 4],

$$\Delta\dot{x} = -\frac{1}{\tau}\Delta x - AR\ \Delta x. \qquad (70)$$

It may be of interest to see how the eigenvectors of Eq. (59) (the Δv-system) are related to the eigenvectors of Eq. (70) (the Δx-system). The right eigenvectors of the Δx-system are given by

$$\left[\left(\lambda_i + \frac{1}{\tau}\right) I_n + AR\right] e_i = 0 \qquad (71)$$

where $\dim(e_i) = n$. Similarly, the right eigenvectors of the Δv-system are given by

$$\left[\left(\lambda_i + \frac{1}{\tau}\right) I_{n_r} + RA\right] \tilde{e} = 0, \lambda_i \neq -\frac{1}{\tau} \qquad (72)$$

where $\dim(\tilde{e}_i) = n_r$. Multiplying Eq. (71) from the left with R, it follows that

$$\left[\left(\lambda_i + \frac{1}{\tau}\right) I_{n_r} + RA\right] (Re_i) = 0, \lambda_i \neq \frac{1}{\tau}. \qquad (73)$$

Hence, if e_i is a right eigenvector of the Δx-system, e_i belonging to an eigenvalue $\lambda_i \neq -1/\tau$, then the corresponding right eigenvector of the Δv-system, $\tilde{e}_i$ belonging to the same eigenvalue, is given by

$$\tilde{e}_i = Re_i, i = 1,2,\ldots,n_r. \qquad (74)$$

The left row eigenvectors in the Δx-system satisfy the equation:

$$v_i\left[\left(\lambda_i + \frac{1}{\tau}\right) I_n + AR\right] = 0. \qquad (75)$$

Similarly, the left row eigenvectors of the Δv-system satisfy the equation

$$\tilde{v}_i\left[\left(\lambda_i + \frac{1}{\tau}\right) I_{n_r} + RA\right] = 0 \quad \lambda_i \neq -\frac{1}{\tau}. \qquad (76)$$

Multiplying Eq. (76) with R from the right, it follows

$$(\tilde{v}_i R)\left[\left(\lambda_i + \frac{1}{\tau}\right) I_{n_r} + AR\right] = 0, \quad \lambda_i \neq -\frac{1}{\tau}. \qquad (77)$$

In analogy to Eq. (73), it is clear that if $\tilde{v}_i$ is a left row eigenvector of the Δv-system, $\tilde{v}_i$ belonging to an eigenvalue $\lambda_i \neq -1/\tau$, then the corresponding left row eigenvector of the Δx-system, v_i belonging to the same eigenvalue, is given by

$$\tilde{v}_i R = v_i, i = 1,2,\ldots.n_r. \qquad (78)$$

Note that $e \notin \mathcal{N}(R)$ ($\Rightarrow Re \neq 0$, $\tilde{v}R \neq 0$) is implied by $\lambda_i \neq -1/\tau$. Therefore, only n_r eigenvalues come into this discussion. Furthermore, neither Re_i nor $\tilde{v}_i R$ are zero, when rank $(R) = n_r$.

This is true, however, only when the Jacobian of the reaction rate expressions indicates true independence between the expressions.

8. INVARIANTS AND OBSERVABILITY

Consider the linearized system given by Eq. (63),

$$\dot{\xi}(t) = \left[-\frac{1}{\tau} I - AR(\mathbf{x}_s) \right] \xi(t) = F\xi(t). \quad (79)$$

Lemma 1. Given (63), let y_i be an observation of the form $y_i = \mathbf{v}_i \mathbf{x}$, i.e.

$$y_i = \mathbf{v}_i(\mathbf{x}_s + \xi) = \mathbf{v}_i\mathbf{x}_s + \Delta y_i \quad (80)$$

i.e.

$$\Delta y_i = \mathbf{v}_i \xi \quad (81)$$

where $\mathbf{v}_i$ is a left row eigenvector of F. The rank of the observability matrix $\mathbf{O}$ [6] is equal to one, and the system Eq. (63) is not *locally observable* at the point $\mathbf{x}_s$ [6].

Proof. To prove this, we do not need to consider the term $\mathbf{v}_i\mathbf{x}_s$ in y_i, since this is a constant for each chosen $\mathbf{x}_s$. The observability matrix is then

$$\mathbf{O} = [\mathbf{v}_i{}^T \quad F^T\mathbf{v}_i{}^T \quad ------ \quad (F^T)^{n-1}\mathbf{v}_i{}^T]. \quad (82)$$

Since $\mathbf{v}_i$ is a left eigenvector,

$$\mathbf{v}_i F = \lambda_i \mathbf{v}_i$$

or

$$F^T \mathbf{v}_i{}^T = \lambda_i \mathbf{v}_i{}^T$$

that is,

$$(F^T)^k \mathbf{v}_i{}^T = \lambda_i{}^k \mathbf{v}_i{}^T. \quad (83)$$

This means that all $\mathbf{v}_i$ is contained in an F^T-invariant subset of E_n. For the observability matrix we have

$$\mathbf{O} = [\mathbf{v}_i{}^T \quad \lambda_i \mathbf{v}_i{}^T \quad ------ \quad \lambda_i{}^{n-1}\mathbf{v}_i{}^T]$$

which obviously has rank equal to one, and the system is not locally observable [6].

Remark. In particular, if $\mathbf{y} = V\mathbf{x}$, then $\mathbf{y}$ is an asymptotic reaction invariant vector of the non-linear system, and the system is neither locally nor globally observable.

Theorem 6. For the nonlinear system Eq. (4), given an observation in the neighbourhood of a steady state $\mathbf{x}_s$, such that

$$y = \mathbf{d}^T\mathbf{x} = \mathbf{d}^T[\mathbf{x}_s + \xi(t)] \quad (84)$$

i.e.

$$y = \mathbf{d}^T\xi \quad (85)$$

where $\xi(t)$ is given by the solution of Eq. (79). If $\mathbf{d}^T$ is contained in an F^T-invariant subspace of dimension less than n, then the system is not locally observable at $\mathbf{x}_s$.

Proof. The proof follows easily from Lemma 1. $y = \mathbf{d}^T\xi$ yields an observability matrix of rank less than n: since $\mathbf{v}_i$ is a basis, there exists numbers β_j, not all equal to zero, $j = 1,2,\ldots,q$, such that

$$\mathbf{d}^T = \sum_{j=1}^{q} \beta_j \mathbf{v}_j \quad (86)$$

where $q < n$. Therefore the rank of

$\mathbf{O} =$

$$\left[\sum_{j=1}^{q} \beta_j \mathbf{v}_j{}^T \quad F^T\sum_{j=1}^{q} \beta_j \mathbf{v}_j{}^T \quad ---- \quad (F^T)^{n-1}\sum_{j=1}^{n} \beta_j \mathbf{v}_j{}^T \right] \quad (87)$$

obviously has rank $q < n$ at most.

9. THE MINIMAL POLYNOMIAL OF F AND THE SOLUTION OF THE LINEARIZED SYSTEM

From matrix algebra it is known, if a matrix F is semisimple [7], the minimal polynomial of F is

$$' r(\lambda) = \Pi'(\lambda - \lambda_i) \quad (88)$$

where Π' denotes the product of all distinct factors. The direct solution of Eq. (79)

$$\xi(t) = e^{Ft}\xi(0) = e^{-(1/\tau\,I+AR)t}\xi(0) \quad (89)$$

may be expressed as

$$\xi(t) = \sum_{i=0}^{n-1} p_i F^i \xi(0) \quad (90)$$

by means of the theorem of Cayley–Hamilton. Assuming that F is semi-simple, F is diagonalizable with eigenvalues $\lambda_1, \lambda_2, \ldots, \lambda_{n_r}$ plus $(n - n_r)$ eigenvalues equal to $-1/\tau$. The minimal polynomial is hence at most of order $n_r + 1$. For a matrix function $f(F)$ we obtain

$$f(F) = \sum_{i=1}^{q} f(\lambda_i)H_i \quad (91)$$

where $q \leq n_r + 1$ and

$$H_i = \prod_{\substack{j=1 \\ j \neq i}}^{q} \frac{F - \lambda_j I}{\lambda_i - \lambda_j} \quad (92)$$

(Sylvester's Theorem). For the matrix exponential we then obtain

$$e^{Ft} = \sum_{j=1}^{q} e^{\lambda_i t}H_i \quad (93)$$

or more specifically

$$\xi(t) = [e^{\lambda_1 t}H_1 + e^{\lambda_2 t}H_2 + \ldots + e^{\lambda_{n_r} t}H_{n_r}$$
$$+ e^{(-1/\tau)t}H_{n_r+1}] \xi(0). \quad (94)$$

10. CONTROLLABILITY

10.1 *Feed flow rate control, constant feed composition*

When flow rate control is applied, the mean residence time will change, and Eqs. (7) or (40) may be written

$$\dot{\mathbf{z}}(t) = \frac{q(t)}{V}[\mathbf{z}_f(t) - \mathbf{z}(t)]. \tag{95}$$

It is a well-known feature of a stirred tank without any chemical reactions, that the thermodynamic states are insensitive to flow rate changes when the balance equation takes the form of Eq. (95)[11]. This is so, if the system operates at a steady state in $\mathbf{z}$, as then $\mathbf{z}(t) = \mathbf{z}_s = \mathbf{z}_f$ and $\dot{\mathbf{z}} = 0$. Consequently, the subset $R_{n_r}^{\perp}$ is uncontrollable for all t.

If, however, $\mathbf{z}(0) \neq \mathbf{z}_f$, then a certain transient control is possible, via $\mathbf{z}(0)$ initially, but gradually $R_{n_r}^{\perp}$ becomes uncontrollable as t approaches infinity.

### 10.2 Feed composition control, constant flow rate
From Eqs. (7) or (40)

$$\dot{\mathbf{z}}(t) = \frac{1}{\tau}[\mathbf{z}_f(t) - \mathbf{z}(t)] \tag{96}$$

where the parameter τ is constant, it is seen that the state $\mathbf{z}$ is controllable only via the input variable $\mathbf{z}_f$. Consequently, if the feed is such that $\mathbf{z}_f = \mathbf{0}$, i.e. $\mathbf{x}_f(t) \in \mathcal{N}(V)^+$, then $R_{n_r}^{\perp}$ is an uncontrollable subset for all t.

11. THE STOICHIOMETRIX DOES NOT HAVE FULL RANK

A general model for a set of chemical reactions involves parallel and consequtive mechanisms. Parallel reactions are in principle indicating different possible reaction paths to form the same products from the same original reactants. The stoichiometry along such parallel paths are linear combinations of each other, provided the reactants at the start and the final products at the end of a path are the same for the parallel paths. The rank of the stoichiometric matrix will in this case be less than the number of reactions. For example, the steam reforming of methane may be considered in the first approximation as two apparent parallel reactions.

$$(1) \quad CH_4 + 2H_2O - 4H_2 - CO_2 \rightleftarrows 0 \tag{97}$$

$$(2) \quad CH_4 + H_2O - 3H_2 - CO \rightleftarrows 0$$
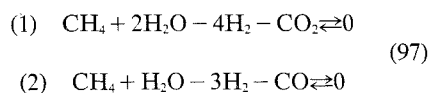
as far as methane, water vapour and hydrogen is concerned. However, they have linearly independent stoichiometry due to the formation of carbon monoxide and dioxide. If however, the water shift reaction takes place at the same time:

$$(3) \quad H_2O + CO - CO_2 - H_2 \rightleftarrows 0 \tag{98}$$

The stoichiometric conditions for this reaction is

just the difference between the other two. This is due to the fact that the shift reaction acts as an intermediate, consecutive reaction in two parallel paths both using methane and water to produce hydrogen and carbondioxide. The introduction of the shift reaction does not alter the rank of the stoichiometric matrix from 2, as it was before.

Another example on reaction models with several parallel paths, is the hydrogenation of fatty oils from soybeans. The stoichiometry along these paths is shown to be linear combinations of each other. The mechanism is best illustrated by a graph:

 (99)
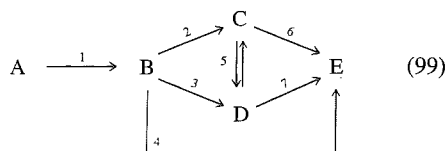
as shown by Hertzberg and Asbjørnsen[9]. Here A is linolenic, B linoleic, C *trans*-oleic, D *cis*-oleic and E stearic acid.

As it is stoichiometric there are seven reactions suggested, five components, while the stoichiometric matrix in the equation:

$$Nm = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 & -1 \\ 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & -1 \end{bmatrix} \begin{bmatrix} A \\ B \\ C \\ D \\ E \end{bmatrix} \rightarrow \mathbf{0} \tag{100}$$

is seen to have the rank four. Let the rows in N be $\mathbf{a}_i$ and the columns $\mathbf{b}_i$. By developing the echelon matrix, the following relationships appear: $\mathbf{a}_5 = \mathbf{a}_3 - \mathbf{a}_2$, $\quad \mathbf{a}_6 = \mathbf{a}_4 - \mathbf{a}_2$, $\quad \mathbf{a}_7 = \mathbf{a}_4 - \mathbf{a}_3$ $\quad$ and $\quad \mathbf{b}_1 = (\mathbf{b}_2 + \mathbf{b}_3 + \mathbf{b}_4 + \mathbf{b}_5)$. The graph contains three basic elements with parallel paths of linearly dependent stoichiometry. Those are

 (101)
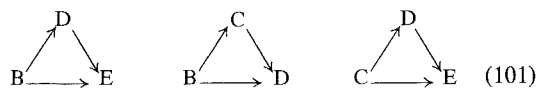
As shown by Asbjørnsen[10], an asymptotic reaction invariant may be found also in this case, by the procedure of partitioning the material balance equations, as well as the linearly dependent reactions:

$$\dot{\mathbf{x}}_1 = \frac{1}{\tau}(\mathbf{x}_{1f} - \mathbf{x}_1) - [A_{11} \mid A_{12}]\begin{bmatrix} \mathbf{r}_1 \\ \hline \mathbf{r}_2 \end{bmatrix}$$

$$A = N^T$$

$$\dot{\mathbf{x}}_2 = \frac{1}{\tau}(\mathbf{x}_{2f} - \mathbf{x}_1) - [A_{21} \mid A_{22}]\begin{bmatrix} \mathbf{r}_1 \\ \hline \mathbf{r}_2 \end{bmatrix}. \tag{102}$$

Here, A_{11} is a square $p \times p$ matrix of rank p, which is also the rank of A. Since all rows in the matrix $[A_{21} \quad A_{22}]$ are linear combinations of the rows in the matrix $[A_{11} \quad A_{12}]$, it follows that

$$A_{21}A_{11}^{-1}A_{12} - A_{22} = 0. \qquad (103)$$

Hence, the asymptotic reaction invariant $\mathbf{z}$ is as before in Eq. (6)

$$\mathbf{z} = \mathbf{x}_2 - A_{21}A_{11}^{-1}\mathbf{x}_1. \qquad (104)$$

The projection matrix P_1 is then:

$$P_1 = \left[\begin{array}{c|c} 0 & 0 \\ \hline -A_{21}A_{11}^{-1} & I \end{array}\right]. \qquad (105)$$

For the hydrogenation model, let the matrix A be partitioned:

$$A = \left[\begin{array}{cccccc|c} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ \hline -1 & 1 & 1 & 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 1 & 1 & 0 \\ 0 & 0 & -1 & 0 & -1 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & -1 & -1 \end{array}\right]$$

$$= \left[\begin{array}{c|c} A_{21} & A_{22} \\ \hline A_{11} & A_{12} \end{array}\right]. \qquad (106)$$

Then the reaction invariant z is seen to be a scalar and expressed through

$$z = x_1 - [-1 \ -1 \ -1 \ -1] \begin{bmatrix} x_2 \\ x_3 \\ x_4 \\ x_5 \end{bmatrix}$$

$$= x_1 + x_2 + x_3 + x_4 + x_5 \qquad (107)$$

This equation expresses z as the sum of all the mole numbers, which naturally has to be reaction invariant in the elementary first order reactions suggested. The projection operator P_1 is:

$$P_1 = \left[\begin{array}{c} 0 \\ \hline 1 \ 1 \ 1 \ 1 \ 1 \end{array}\right]. \qquad (108)$$

For the projection operator P_2, the procedures in the previous Section 4.2 may still be applied, with some minor modifications in the computation of the pseudoinverse. Of course, the matrix A_1^{-1} in Sections 3–4.1 does not exist now, since rank $(A_1) < n$, with $n < n_r$.

Suppose that A has rank $p < n$. Suppose that we know a real $n \times p$ matrix B and a real $p \times n_c$ matrix C, both of rank p, having the property

$$A = BC. \qquad (109)$$

Then the pseudoinverse of A may be expressed as[5],

$$A\dagger = C^T(CC^T)^{-1}(B^TB)^{-1}B^T \qquad (110)$$

The pseudoinverse $A\dagger$ is unique.

Considering now $\mathbf{x}(t)$ as given by Eq. (25), the projection from E_n onto $\mathcal{N}(A^T)\ [= \mathcal{R}(A)^{\perp}]$ is

$$P_2\dot{\mathbf{x}}(t) = (I - AA\dagger)\dot{\mathbf{x}}(t) = -A\mathbf{r} + AA\dagger A\mathbf{r}. \qquad (111)$$

A general property of the pseudo-inverse is that[5]:

$$AA\dagger A = A \qquad (112)$$

such that for a batch reaction, we still have

$$\dot{\mathbf{w}}(t) \triangleq P_2\dot{\mathbf{x}}(t) = \mathbf{0} \qquad (113)$$

where $\mathbf{w} \in \mathcal{N}(A^T)$.

The orthogonal projection on $\mathcal{R}(A)$ is still

$$(I - P_2)\dot{\mathbf{x}}(t) = A\dot{\mathbf{v}}(t) = AA\dagger\dot{\mathbf{x}}(t) = -AA\dagger A\mathbf{r} \qquad (114)$$

i.e.

$$A\dot{\mathbf{v}}(t) = -A\mathbf{r}. \qquad (115)$$

Projecting again on $\mathcal{R}(A^T)\ [= \mathcal{N}(A)^{\perp}]$,

$$\dot{\mathbf{v}} = -\mathbf{r}(\mathbf{w} + A\mathbf{v}). \qquad (116)$$

This procedure may be illustrated by the hydrogenation model, as introduced above. Let the matrix B be the first 5×4 part of matrix A. Then the rank of B is four (p), and the matrix C follows such that $A = BC$:

$$B = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -1 & 1 & 1 & 1 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$$C = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & -1 & -1 & 0 \\ 0 & 0 & 1 & 0 & 1 & 0 & -1 \\ 0 & 0 & 0 & 1 & 0 & 1 & -1 \end{bmatrix} \qquad (117)$$

The pseudo-inverse of A is computed from Eq. (30), and found to be:

$$A\dagger = \frac{1}{20} \begin{bmatrix} 16 & -4 & -4 & -4 & -4 \\ 4 & 4 & -6 & -1 & -1 \\ 4 & 4 & -1 & -6 & -1 \\ 4 & 4 & -1 & -1 & -6 \\ 0 & 0 & 5 & -5 & 0 \\ 0 & 0 & 5 & 0 & -5 \\ 0 & 0 & 0 & 5 & -5 \end{bmatrix} \qquad (118)$$

Furthermore:

$$AA\dagger = \frac{1}{5}\begin{bmatrix} 4 & -1 & -1 & -1 & -1 \\ -1 & 4 & -1 & -1 & -1 \\ -1 & -1 & 4 & -1 & -1 \\ -1 & -1 & -1 & 4 & -1 \\ -1 & -1 & -1 & -1 & 4 \end{bmatrix} \quad (119)$$

giving the projection operator P_2

$$P_2 = \frac{1}{5}\begin{bmatrix} 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 \end{bmatrix} \quad (120)$$

which has rank one. As shown before, the rank of P_2 corresponds to the dimension of the reaction invariant z, which in this case is one. Hence, it is shown by this simple illustration how the concepts of reaction rate invariants apply equally well to systems where the stoichiometric matrix does not have full rank. If too many parallel reactions occur with linearly related stoichiometry, a reaction invariant subset may still be found by the two projection methods suggested.

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