

# A General Theorem for Complex Chemical Systems Amenable to the Horiuti Approach

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This paper deals with complex chemical systems for which Horiuti's theory of stoichiometric numbers may be applied. A general theorem is proved, linking the mechanistic and overall representations: the number of linearly dependent overall reactions equals the number of linearly dependent steps.

**Key words:** Complex chemical systems, Horiuti-Temkin theory, Reaction routes, Linearly dependent reactions.

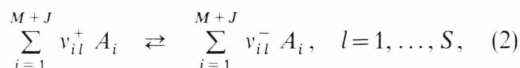
The Horiuti-Temkin theory [1]–[4] of the stoichiometric number is a fundamental tool in dealing with complex chemical systems (reaction networks). Within its framework, the number of overall stoichiometric equations corresponding to the linearly dependent reaction routes may not be linearly independent (only physically independent) [1]–[4]. The problem of determining the number  $Q$  of linearly independent overall reactions was dealt with by Horiuti [3] and by Temkin [2], [4]. The first approach leads to an inequality for  $Q$  [3], whereas the second one made use of the classical results of Gibbs [5] and Jouguet [6], linking  $Q$  to the number  $M$  of participants to the overall reactions, and the number  $C$  of independent compounds ( $Q = M - C$ ).

The examination of many particular reaction mechanisms suggested us that the number  $W$  of *linearly dependent* overall reactions equals to the number  $V$  of *linearly dependent* steps.

$$V = W. \quad (1)$$

We succeeded in giving a general demonstration of the above fact, which will be presented in the following. In fact, the law (1) is a straightforward consequence of the Temkin approach [2], [4].

Let us consider a chemical system involving  $S$  steps



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where  $A_i$ ,  $i = 1, \dots, M$  are stable species,  $A_{M+\alpha}$ ,  $\alpha = 1, \dots, J$  are active intermediates and  $\nu_{il}^\pm$  are the corresponding stoichiometric coefficients. We can assign to each step a stoichiometric vector

$$f_{M+J}^{(l)} = (f_{il})_{i=1, \dots, M+J}, \quad l = 1, \dots, S, \quad (3)$$

where

$$f_{il} = \nu_{il}^- - \nu_{il}^+. \quad (4)$$

The stoichiometric vectors are not necessarily linearly independent. Let  $K$  be the number of linearly independent stoichiometric vectors. The remaining  $V = S - K$  are linear combinations of the former.

Horiuti's method to get the reaction routes (that is, the overall reactions) consists in the finding of linear combinations of the steps that lead to the vanishing of the active intermediate stoichiometric coefficients, i.e.,

$$\sum_{z=1}^S f_{M+\alpha; z} \sigma_z = 0, \quad \alpha = 1, \dots, J, \quad (5)$$

where  $\sigma_z$  are the so-called stoichiometric numbers. We shall assume that the homogeneous system (5) has  $P$  nontrivial independent solutions, that is, there are  $P$  sets of stoichiometric numbers  $\sigma_{1l}, \sigma_{2l}, \dots, \sigma_{Sl}$ ,  $l = 1, \dots, P$  forming  $P$  vectors

$$\sigma_S^{(l)} = (\sigma_{zl})_{z=1, \dots, S}, \quad l = 1, \dots, P. \quad (6)$$

The vectors (6) form a so-called route basis [2]. This basis is not unique, as one can get, through non-singular linear transformations, other sets of vectors satisfy-

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ing the conditions (5). The vectors (6) define  $P$  independent reaction routes, resulting in  $P$  overall reactions

$$\sum_{i=1}^M \psi_{il} A_i = 0, \quad l = 1, \dots, P. \quad (7)$$

The overall stoichiometric coefficients,  $\psi_{il}$ , are determined from

$$\boldsymbol{\varphi}_{M+J}^{(l)} = \begin{pmatrix} \boldsymbol{\psi}_M^{(l)} \\ \mathbf{O}_J \end{pmatrix} = \sum_{z=1}^S \mathbf{f}_{M+J}^{(z)} \sigma_{zl}, \quad l = 1, \dots, P, \quad (8)$$

where

$$\boldsymbol{\psi}_M^{(l)} = (\psi_{il})_{i=1, \dots, M}, \quad l = 1, \dots, P \quad (9)$$

The overall stoichiometric equations (7) and the corresponding stoichiometric vectors (8)–(9) need not be linearly independent. We denote by  $Q \leq P$  the number of independent overall reactions and by  $W = P - Q$  the number of linearly dependent overall reactions.

Our demonstration comprises two sections consisting in proving the inequalities

$$W \geq V \quad \text{and} \quad V \geq W, \quad (10), (11)$$

leading to (1).

**Lemma 1** ( $W \geq V$ ). To prove (10), we are looking for sets of stoichiometric numbers,  $q_z$ , resulting in the cancellation of both stable species and active intermediates overall stoichiometric coefficients, thus coming to what Temkin called empty routes [2]:

$$\sum_{z=1}^S f_{iz} q_z = 0, \quad i = 1, \dots, M+J. \quad (12)$$

As  $V$  of the stoichiometric vectors  $\mathbf{f}_{M+J}^{(l)}$ ,  $l = 1, \dots, S$  are linearly dependent, it turns out that the system (12) has  $V$  sets of nontrivial linearly independent solutions

$$\boldsymbol{q}_S^{(z)} = (q_{iz})_{i=1, \dots, S}, \quad z = 1, \dots, V. \quad (13)$$

From (12) we notice that the vectors  $\boldsymbol{q}_S^{(z)}$  fulfill the conditions defining the vectors  $\boldsymbol{\sigma}_S^{(z)}$  [(5)]. Evidently, as  $\boldsymbol{q}_S^{(z)}$  resulted from some additional constraints [(12) for  $i = 1, \dots, M$ ] their route basis dimension,  $V$ , must be smaller, or at most equal to the  $\boldsymbol{\sigma}_S^{(z)}$  route basis dimension  $P$  ( $V \leq P$ ). It follows that we can get the vectors  $\boldsymbol{q}_S^{(z)}$  as linear combinations of  $\boldsymbol{\sigma}_S^{(z)}$ . Therefore, performing a linear transformation of  $\boldsymbol{\sigma}_S^{(z)}$ ,  $z = 1, \dots, P$ , one can always construct a route basis  $\boldsymbol{\sigma}_S'^{(z)}$ ,  $z = 1, \dots, P$ , containing the  $V$  independent vectors  $\boldsymbol{q}_S^{(z)}$ ,  $z = 1, \dots, P$ . Such a basis leads obviously to at least  $V$  empty routes, i.e.,  $P - Q = W \geq V$ . q.e.d.

**Lemma 2** ( $W \leq V$ ). To prove (11), we are looking for a linear transformation of the overall stoichiometric equations, resulting in empty routes. Multiplying the overall equations (7) by the numbers  $\varepsilon_1, \dots, \varepsilon_P$ , making use of (8) and imposing the cancellation of the resulting stoichiometric coefficients, we get

$$\left[ \sum_{l=1}^P \varepsilon_l \boldsymbol{\varphi}_{M+J}^{(l)} \right]_i = \sum_{z=1}^S \eta_z f_{iz} = 0, \quad i = 1, \dots, M+J, \quad (14)$$

where  $\eta_z$  are the components of a linear combination of the vectors  $\boldsymbol{\sigma}_S^{(l)}$ ,  $l = 1, \dots, P$ :

$$\boldsymbol{\eta}_S = (\eta_z)_{z=1, \dots, S} = \sum_{l=1}^P \varepsilon_l \boldsymbol{\sigma}_S^{(l)}. \quad (15)$$

As  $V$  of the vectors  $\mathbf{f}_{M+J}^{(l)}$  are linearly dependent, it turns out that the equations (14) form a subdetermined homogeneous linear system of  $M+J$  equations and  $S$  unknowns  $\eta_z$  admitting  $V = S - K$  sets of linearly independent nontrivial solutions

$$\boldsymbol{\eta}_S^{(q)} = (\eta_{zq})_{z=1, \dots, S}, \quad q = 1, \dots, V. \quad (16)$$

Thus, (15) leads to  $V$  linear systems of  $P$  unknowns  $(\varepsilon_{1q}, \dots, \varepsilon_{Pq})$ ,  $q = 1, \dots, V$  and  $S$  equations

$$\left( \eta_{zq} = \sum_{l=1}^P \sigma_{zl} \varepsilon_{lq}, \quad z = 1, \dots, S \right), \quad q = 1, \dots, V. \quad (17)$$

As the vectors  $\boldsymbol{\sigma}_S^{(l)}$ ,  $l = 1, \dots, P$  are linearly independent, it follows that each of the systems (17) has at most one solution, and then the whole set of  $V$  systems comprises at most  $V$  solutions. So we have at most  $V$  independent sets of numbers  $\varepsilon_l$ , leading to linearly dependent overall stoichiometric equations. Thus  $W \leq V$ . q.e.d.

*Particular case* ( $V=0$ ). In this case the steps are linearly independent, and by means of (1) we get  $W=0$ , so that the overall reactions are also linearly independent. For  $V=0$  the demonstration of the above theorem is straightforward. Now, all the stoichiometric vectors  $\mathbf{f}_{M+J}^{(l)}$  are linearly independent and the system (14) has only the trivial solution  $\boldsymbol{\eta}_S = \mathbf{O}_S$ . Therefore (15) is a linear homogeneous system of  $S$  equations and  $P$  unknowns  $\left( \sum_{l=1}^P \varepsilon_l \sigma_{zl} = 0, \quad z = 1, \dots, S \right)$  admitting only the trivial solution  $\varepsilon_l = 0$ . So linearly dependent overall equations are not allowed,  $W=0$ . q.e.d.

The physical meaning of the above theorem is clear: whether a chemical process is described by means of steps or overall reactions, the number of linearly dependent stoichiometric equations is invariant. The existence of linearly dependent overall reactions is a consequence of the linear dependence between the

steps. In particular, if the steps are linearly independent, the same is true for the overall reactions.

This paper has been reviewed by Professor Temkin. His comments suggested us a simple proof of the theorem. We are grateful for his constructive criticism.

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