

ON THE INVERSE PROBLEM OF CHEMICAL KINETICS

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Abstract:

The inverse problem of chemical kinetics is the reconstruction of the overall (time-independent) stoichiometry in a closed system, from the knowledge of the kinetics of all elementary reactions which occur in this system. This problem has no solution in the general case. Conditions under which the chemical process in the system considered can be represented by a single stoichiometric equation are determined.

Consider a closed system in which N chemical species S_1, S_2, \dots, S_N participate in M elementary chemical reactions

$$\sum_{j=1}^N v_{ij} S_j = 0 \quad (1)$$

$i = 1, 2, \dots, M$. Suppose also that these reactions obey the law of mass action, but that their rate constants are not known.

What can be said about the overall chemical change in this system? Under which conditions is possible to write down a stoichiometric equation, describing the overall chemical reaction and being independent of both time and rate constants?

In the present paper we offer answers to the above questions. As to the author's knowledge, the above problems have not been considered and solved in the general case in the chemical literature.

In chemistry is usual to present the net chemical change in the system considered by a stoichiometric equation of the form

$$\sum_{j=1}^N v_j S_j = 0 \quad (2)$$

Obviously, (2) must be a linear combination of the equations (1). Therefore

$$v_j = \sum_{i=1}^M \lambda_i v_{ij} \quad (3)$$

where the multipliers λ_i remain still to be determined.

If $n_j(t)$ is the mole number of the substance S_j in time t , then by the law of definite proportions,

$$\frac{v_j}{v_k} = \frac{n_j(t_0) - n_j(t_1)}{n_k(t_0) - n_k(t_1)} \quad . \quad (4)$$

Hence the stoichiometric coefficients of (2) depend both on the initial composition of the system (at time t_0) and on an arbitrary time interval $t_1 - t_0$. In addition, v_j is a time-dependent quantity.[†]

Two chemical reactions of the form (1), say the h -th and the i -th reaction, are said to be stoichiometrically independent^{2,3} if the vectors $(v_{h1}, v_{h2}, \dots, v_{hN})$ and $(v_{i1}, v_{i2}, \dots, v_{iN})$ are linearly independent. Now, in order to be able to determine λ_i in (3), we have first to eliminate the elementary reactions (1) which are not stoichiometrically independent. The number of mutually independent elementary reactions is m , where

[†] The ambiguity of eq. (4) can be avoided either by setting $t_1 - t_0 \rightarrow 0$ or by setting $t_1 \rightarrow \infty$. The first choice defines the stoichiometric coefficients in the moment t , i.e. $v_j = \lambda \frac{dn_j(t)}{dt}$. The second choice gives $v_j = \lambda \{n_j(t_0) - n_j(\text{eq})\}$, with $n_j(\text{eq})$ being the mole number of S_j at equilibrium and λ an arbitrary constant¹.

$$m = \text{rank} \begin{bmatrix} v_{11} & v_{12} & \cdots & v_{1N} \\ v_{21} & v_{22} & \cdots & v_{2N} \\ \cdot & \cdot & \cdots & \cdot \\ v_{M1} & v_{M2} & \cdots & v_{MN} \end{bmatrix} .$$

If $m < M$, then the choice of the independent reactions (1) is to some extent arbitrary³. Let us label the reactions (1) so that the first m of them are stoichiometrically independent:

$$\text{rank} \begin{bmatrix} v_{11} & v_{12} & \cdots & v_{1N} \\ v_{21} & v_{22} & \cdots & v_{2N} \\ \cdot & \cdot & \cdots & \cdot \\ v_{m1} & v_{m2} & \cdots & v_{mN} \end{bmatrix} = m .$$

Then one can set $\lambda_i = 0$ for $m+1 \leq i \leq M$.

In order to determine the multipliers λ_i for $i = 1, \dots, m$ we need some additional information on the chemical system considered. If the chemical species S_j is a reactant, then v_j is negative. If S_j is a product, then v_j must be positive. If, however, S_j is assumed to be an intermediate in the overall chemical reaction (2), then $v_j = 0$.

Let, by convention, the substances S_j , $j = 1, \dots, I$ ($I < N$) be considered as intermediates. Then the system of homogenous linear equations

$$\sum_{i=1}^m \lambda_i v_{ij} = 0 \quad j = 1, \dots, I \quad (5)$$

must be fulfilled. Let

$$\underline{v} = \begin{bmatrix} v_{11} & \cdots & v_{1I} \\ \vdots & \cdots & \vdots \\ v_{m1} & \cdots & v_{mI} \end{bmatrix}$$

Then according to well-known results from linear algebra, the system (5) has

- (a) no non-trivial solution if $\text{rank } \underline{v} = m$,
 - (b) one independent non-trivial solution if $\text{rank } \underline{v} = m - 1$,
- and
- (c) several independent solutions if $\text{rank } \underline{v} < m - 1$.

Note that $\text{rank } \underline{v} \leq \min \{m, N\}$.

On the basis of these arguments one immediately arrives to the following conclusions.

- (a) If $\text{rank } \underline{v} = m$, then the assumption that S_1, \dots, S_I are intermediates leads to contradictions and need to be revisited.
- (b) If $\text{rank } \underline{v} = m - 1$, then there is a unique stoichiometry for the overall chemical reaction. Namely, from \underline{v} one can determine the numbers b_i , $i = 1, \dots, m$, such that $\lambda_i = b_i \lambda_1$. Consequently, from (3),

$$v_j = \lambda_1 \sum_{i=1}^m b_i v_{ij}.$$

Without loss of generality one may set $\lambda_1 = 1$.

Hence, the stoichiometric coefficients v_j are independent of the rate constants.

- (c) If $\text{rank } \underline{v} < m - 1$, then the stoichiometry of the overall chemical reaction depends on $m - \text{rank } \underline{v} - 1$ parameters, which, in the general case are time-dependent. In other words, an equation of the form (2), being independent of time and

rate constants, does not exist for the system considered.

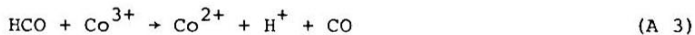
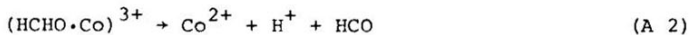
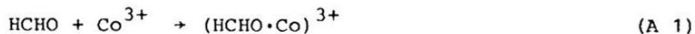
In the case $I = 0$ we have to set $\text{rank } \underline{v} = 0$. Then if $m = 1$, we reach the (trivial) conclusion (b). Otherwise, if $m > 1$, no stoichiometry independent of the rate constants can be formulated.

E x a m p l e s

In order to illustrate the above obtained general result we shall elaborate two simple examples. The net chemical reaction in the first case cannot be represented by a single equation. On the other hand, irrespective of a complicated mechanism, there is a chemical equation for the reaction of chlorine with hydrogen. More examples based on a similar reasoning can be found elsewhere⁴.

(a) Oxidation of formaldehyde with Co^{3+}

The following mechanism was proposed^{5,6} for this reaction.



Hence $M = 7$ and $N = 12$. It is easy to see that the reactions (A 1) - (A 6) are stoichiometrically independent. The reaction (A 7) is, however, just the reverse of (A 4). Hence $m = 6$.

The substances $S_1 = (\text{HCHO}\cdot\text{Co})^{3+}$, $S_2 = \text{HCO}$, $S_3 = \text{HO}$ and $S_4 = \text{H}$ are intermediates. Then

$$\underline{v} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ -1 & 1 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & -1 & 1 & 0 \\ 0 & -1 & 0 & 1 \\ 0 & 1 & 0 & -1 \end{bmatrix} \quad \text{rank } \underline{v} = 4 \quad .$$

Therefore it is not possible to present the process (A) by a single chemical equation.

If, on the other hand, we neglect the (side) reactions (A 4) - (A 7), then we have only two intermediates: $S_1 = (\text{HCHO}\cdot\text{Co})^{3+}$ and $S_2 = \text{HCO}$, and

$$\underline{v} = \begin{bmatrix} 1 & 0 \\ -1 & 1 \\ 0 & -1 \end{bmatrix} \quad \text{rank } \underline{v} = 2.$$

Since now $m = 3$, there exists indeed a time-independent stoichiometry, viz.



(b) Reaction of chlorine with hydrogen

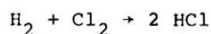
The well-known mechanism of this reaction is



In this case $M = 6$ and $N = 5$. The first three elementary reactions can be chosen as independent, $m = 3$. Really, (B 5) is the reverse of (B 1), (B 4) = (B 1) - (B 3) and (B 5) = (B 3) - (B 2) - (B 1). The intermediates are $S_1 = \text{Cl}$ and $S_2 = \text{H}$ and therefore

$$\underline{v} = \begin{bmatrix} 2 & 0 \\ -1 & 1 \\ 1 & -1 \end{bmatrix} \quad \text{rank } \underline{v}_e = 2 \quad .$$

Consequently, the reaction of chlorine with hydrogen can be presented by a unique stoichiometric equation, viz.



R E F E R E N C E S

1. P.L.Corio, *Trans. Kentucky Acad.Sci.* 32, 51 (1970);
T.M.Barbara and P.L.Corio, *J.Chem.Educ.* 57, 243 (1980).
2. R.Aris, *Introduction to the Analysis of Chemical Reactors*,
Prentice Hall, Englewood 1964.
3. A.Bander and H.H.Günthard, *Helv.Chim.Acta* 55, 2263 (1972);
S.Lengyel and T.Gyarmati, *J.Chem.Phys.* 75, 2384 (1981).
4. H. Mauser, *Z.Naturforsch.* 23b, 1021 (1968).
5. C.E.Bawn and A.G.White, *J.Chem.Soc.*, 344 (1951).
6. T.A.Turney, *Oxidation Mechanisms*, Butterworths, London 1965.