

# CHEMICAL REACTION PATHS, I

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## Introduction

The stoichiometric constraints of the chemical reactions in closed systems exactly determine the changes of composition. If the composition is given as a point in the mole number space spanned by the mole numbers of the participant molecule species as co-ordinates, then the stoichiometric constraints determine the path of this composition point ("reaction path"). The composition can also be given not only by the mole numbers, but also by the mole fractions, as a point in the "mole fraction space". The dimension number of the mole fraction space is smaller by one than that of the mole number space.

In case of a single reaction with the analysis of the reaction paths it can be proved that they are forming a straight line set starting from a common focus point [4]. This focus lies outside the composition range. In the case of fully or partially stoichiometric compositions, the reaction lines lie in subspaces of the mole number space. The fully stoichiometric subspace is a one dimensional space, a characteristic reaction line. The points of intersection between the stoichiometric line and the boundary of the composition domain, represent two further characteristic points of the system.

In the following the general properties of the chemical reaction lines will briefly be summarized and the quite general derivation of the three main characteristic points will be given. It will be shown that the locus vectors of these points can simply be formulated with the aid of the stoichiometric coefficients of the chemical reaction.

### 1. The chemical reaction. Definition and invariants

Chemical reaction is termed a process of transformation of some molecular species into other molecular species leaving unchanged all the atoms (that is, nuclei) of the molecules. If the atoms are undergoing a change, then a nuclear reaction can be spoken of. In most cases, invariant parts can be not only single atoms, but also groups of several atoms. These invariant parts are termed the "radicals". Consequently, a radical may be a single atom. Any molecule can be considered as composed of such radicals.

In this sense the mole weight of the  $k$ -th molecule species  $M_k$  can be given as

$$M_k = \sum_{g=1}^G \lambda_{gk} \cdot M_g \quad \begin{matrix} k = 1, 2, \dots, K \\ g = 1, 2, \dots, G \end{matrix} \quad (1a)$$

where  $M_g$  is the "radical weight" of the  $g$ -th radical (for a single atom the atomic weight)

$\lambda_{gk}$  the number of the  $g$ -th radical in the  $k$ -th molecule species, a positive integer.

Considering geometrically  $M_k$  as the  $k$ -th element of the  $K$ -dimensional vector  $\mathbf{M}_k$ ,  $M_g$  as the  $g$ -th element of a  $G$ -dimensional vector  $\mathbf{M}_g$  and  $\lambda_{gk}$  as an element of the matrix  $\lambda$  having  $G$  rows and  $K$  columns, (1a) can be written in the form of a matrix equation

$$\mathbf{M}_k = \tilde{\lambda} \cdot \mathbf{M}_g \quad (1b)$$

where the matrix  $\tilde{\lambda}$  is the transposed of the matrix  $\lambda$ :

$$\lambda = \begin{pmatrix} \lambda_{11} & \dots & \lambda_{1K} \\ \vdots & & \vdots \\ \lambda_{G1} & \dots & \lambda_{GK} \end{pmatrix}; \quad \tilde{\lambda} = \begin{pmatrix} \lambda_{11} & \dots & \lambda_{1G} \\ \vdots & & \vdots \\ \lambda_{K1} & \dots & \lambda_{KG} \end{pmatrix}$$

Matrix  $\lambda$ , named "radical-number matrix" can be

lying rectangle matrix, if  $G < K$   
 quadratic matrix, if  $G = K$   
 standing rectangle matrix, if  $G > K$

The quantity of components (molecular species) will be given by the mole numbers  $n_k$ . Then the vector  $\mathbf{n}_k$  with components  $n_k$ , characterises the composition of the system as locus vector of the "composition point" in the mole-number space. In a similar manner,  $n_g$ , the  $g$ -th "radical-number" gives the quantity of the  $g$ -th radical and  $\mathbf{n}_g$  vector with components  $n_g$  characterises the "radical (or atomic) composition" of the system.

The relation between mole and radical numbers is given by the following vector equation:

$$\mathbf{n}_g = \lambda \cdot \mathbf{n}_k. \quad (2)$$

In closed system two main balances can be formulated.

The weight balance:

$$\mathbf{M}_k \cdot d\mathbf{n}_k = 0. \quad (3)$$

This equation means geometrically that the scalar product of the mole-weight and of the mole number change vector is equal to zero, the two vectors are orthogonal.

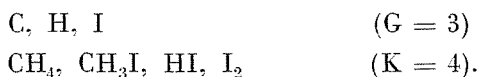
The invariance of the quantity of radicals can be formulated as follows:

$$dn_g = \lambda \cdot dn_k = 0 \quad (4)$$

what means: the displacement-vector of the composition point  $dn_k$  is orthogonal to all row vectors of the matrix  $\lambda$ .

The foregoing can be illustrated by some simple instances.

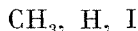
Let us have three kinds of radicals (all three being atomic species) and let them form four molecule species:



Giving indices in the above order:

$$\lambda = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 4 & 3 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix}. \quad (5)$$

The invariant radicals, however, can be chosen also in a different way:



In this case some of the invariant radicals are composed of several atoms. Matrix  $\lambda$  is in the latter case:

$$\lambda'' = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix}. \quad (6)$$

The connection between the two sets of radicals can be expressed by a transformation matrix  $\mathbf{T}$ :

$$\lambda' = \mathbf{T} \cdot \lambda'' \quad (7)$$

where

$$\mathbf{T} = \begin{pmatrix} 1 & 0 & 0 \\ 3 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}. \quad (8)$$

and (7) in a concrete form:

$$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 4 & 3 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 3 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \cdot \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix}.$$

As a matter of course, no fragment of a composed radical must be taken into consideration either separately or together with another. The choice shall not be in contradiction with Eq. (1).

A simple example for quadratic  $\lambda$ -matrix is:

Let us have four types of radicals:



Let them form four types of molecules:



These can participate in the reaction of type:



The matrix  $\lambda$  is here:

$$\lambda = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 1 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & 1 \end{pmatrix} \quad (9)$$

In the case of first order reaction (isomerisation) the matrix columns are not independent, because of the atomic composition of the participant molecules is the same:

$$\lambda_{g1} = \lambda_{g2} = \dots = \lambda_g. \quad (10)$$

Matrix  $\lambda$  can be written as a dyadic product

$$\lambda = \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \vdots \end{pmatrix} (1, 1, 1, \dots) \quad (11)$$

Be the atomes for example: C and H and the molecules: cyclopropane and propylene ( $C_3H_6$ )

$$\lambda = \begin{pmatrix} 3 & 3 \\ 6 & 6 \end{pmatrix} = \begin{pmatrix} 3 \\ 6 \end{pmatrix} (1 \quad 1)$$

The second member of this product is a vector having only unity elements.

## 2. The stoichiometric equation of chemical reaction

The relation between the changes of different mole numbers due to a chemical reaction can be given by the stoichiometric coefficients  $\nu_k$ .

Denoting the stoichiometric coefficients of the reactants by  $\nu'_k$  and the coefficients of the products by  $\nu''_k$  (for the  $k$ -th molecular species) then the weight balance equation is:

$$\sum_{k=1}^K \nu'_k \cdot M_k = \sum_{k=1}^K \nu''_k \cdot M_k \quad (12)$$

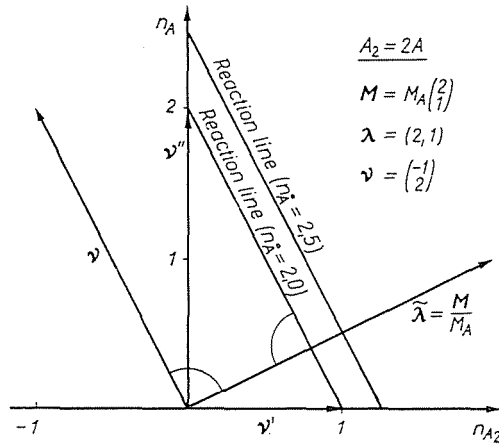


Fig. 1

Writing the chemical symbols instead of the mole weights, we have the stoichiometric equation.

In the case of a single chemical reaction the set of numbers  $\nu'_k$  or  $\nu''_k$  defines a  $K$ -dimensional vector ( $\nu'$  or  $\nu''$ , respectively).

We define the stoichiometric coefficient vector for the whole reaction:

$$\nu = \nu'' - \nu' \quad (13)$$

The mass balance (12) can then be written:

$$\tilde{\nu} \cdot \mathbf{M}_k = \mathbf{0} \quad (14)$$

i.e., the stoichiometric vector  $\nu$  is orthogonal to the mole weight vector  $\mathbf{M}_k$  (see Fig. 1).

*The reaction co-ordinate.* The stoichiometric constraints give relations between the changes of mole numbers  $dn_k$  as follows

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \dots = \frac{dn_K}{\nu_K} = d\xi \quad (15)$$

where  $\xi$  is the reaction co-ordinate, a common reaction parameter of the extent of the reaction. In the component (mole-number) space  $\xi$  is a scalar. (15) can be written more generally as follows

$$d\mathbf{n}_k = \nu \cdot d\xi \quad (16)$$

and after integration

$$\mathbf{n}_k = \mathbf{n}_k(0) + \nu \cdot \xi \quad (17)$$

where  $\mathbf{n}_k(0)$  is the locus vector of the initial composition, and

$$\xi = 0 \text{ for } t = 0.$$

(16) and (17) mean that the displacement of the composition point  $\mathbf{n}_k$  have the direction of the stoichiometric vector  $\nu$ . Because latter is a constant vector, the path of the composition point  $\mathbf{n}_k$  is a straight line parallel to  $\nu$ .

Combining (4) and (16)

$$d\mathbf{n}_g = \lambda \cdot d\mathbf{n}_k = \lambda \cdot \nu \cdot d\xi = 0.$$

Upon chemical change:

$$d\xi \neq 0$$

$$\lambda \cdot \nu = 0 \quad (18)$$

(18) expresses the invariance of radicals and represents strict constraints for values  $\nu_k$ . Geometrically: the vector  $\nu$  must be orthogonal to all row vectors of matrix  $\lambda$  (Fig. 1).

It follows from (18) that if a matrix can be written as a product with a first factor (from left) the vector  $\nu$ , then after multiplication by matrix  $\lambda$  (from left), the product vanishes.

(18) can be visualized by the following example:

Radical species (atoms): C, H, I

Molecular species:  $\text{CH}_4$ ,  $\text{CH}_3\text{I}$ , HI,  $\text{I}_2$

Chemical reaction:



The stoichiometric coefficient vector:

$$\nu = \begin{pmatrix} -1 \\ 1 \\ 1 \\ -1 \end{pmatrix}$$

One can prove the product to vanish:

$$\begin{pmatrix} 1 & 1 & 0 & 0 \\ 4 & 3 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix} \cdot \begin{pmatrix} -1 \\ 1 \\ 1 \\ -1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

In the same manner there exists an orthogonality with matrix taken from (6).

*The mole number change of a reaction*

The scalar product of vector  $\nu$  with the "summing vector"

$$(1, 1, \dots)$$

gives the mole number change of the reaction:

$$(1, 1, \dots) \begin{pmatrix} \nu_1 \\ \nu_2 \\ \vdots \end{pmatrix} = \sum_{k=1}^K \nu_k = \Delta \nu \quad (19)$$

First order reaction (18) follows from the radical number balance too. Combining (11) and (18)

$$\lambda \nu = \begin{pmatrix} \lambda_1 \\ \lambda_2 \\ \lambda_3 \\ \vdots \end{pmatrix} (1, 1) \begin{pmatrix} 1 \\ 2 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \\ \vdots \end{pmatrix} = \mathbf{0}$$

*Equivalent chemical reactions.* Two reactions will be told stoichiometrically equivalent when any of quotients

$$\frac{dn_i}{dn_k} = \frac{\nu_i}{\nu_k} = \frac{\bar{\nu}_i}{\bar{\nu}_k} \quad (20)$$

are the same in the two reactions.

For example, the multiplication of the whole reaction by a constant number  $\alpha$  leads to an equivalent reaction (The "multiplicative arbitrariness" of chemical reactions).

$$\begin{array}{l} \text{The transformation} \quad \bar{\nu} = \alpha \cdot \nu \\ \quad \quad \quad \quad \quad \alpha = -1 \end{array} \quad (21)$$

is the inversion of the reaction. Such transformations leave invariable the relations (14) and (18).

Geometrically, the multiplication of vector by a scalar results in a simple stretching of vector leaving invariable its "direction" and therefore all orthogonality relations (14, 18). This can be proved in a single manner:

$$\begin{aligned}\mathbf{M}_k \cdot \alpha \cdot \nu &= \alpha \cdot \mathbf{M}_k \cdot \nu = \alpha \cdot 0 = 0 \\ \lambda \cdot \alpha \cdot \nu &= \alpha \cdot \lambda \cdot \nu = \alpha \cdot 0 = 0\end{aligned}$$

Another equivalent transformation is the permutation of components (the change of their sequence). This transformation is equivalent to the multiplication of vector  $\nu$  by a permutation matrix  $\mathbf{P}$  [2].

$$\bar{\nu} = \mathbf{P} \cdot \nu \quad (22)$$

In this case the same transformation is to be made on matrices  $\mathbf{M}_k$  and  $\lambda$

$$\begin{aligned}\bar{\mathbf{M}}_k &= \mathbf{P} \cdot \mathbf{M}_k \\ -\bar{\lambda} &= \lambda \cdot \tilde{\mathbf{P}}\end{aligned} \quad (23)$$

The invariance of orthogonality relations (14) and (18) can be proved by making use of the relationship

$$\tilde{\mathbf{P}} \cdot \mathbf{P} = \mathbf{E} \quad (24)$$

( $\mathbf{E}$ : the unity matrix)

$$\begin{aligned}\bar{\nu} \cdot \bar{\mathbf{M}}_k &= (\overline{\mathbf{P} \nu}) \cdot \mathbf{P} \cdot \mathbf{M}_k = \tilde{\nu} \cdot \tilde{\mathbf{P}} \cdot \mathbf{P} \cdot \mathbf{M}_k = \tilde{\nu} \cdot \mathbf{M}_k \\ \bar{\lambda} \bar{\nu} &= \lambda \cdot \tilde{\mathbf{P}} \cdot \mathbf{P} \cdot \nu = \lambda \cdot \mathbf{E} \cdot \nu = \lambda \nu = 0.\end{aligned}$$

It is permitted to permute the sequence of the radical species, or to transform in agreement with 1 by multiplying matrix  $\lambda$  by a  $G$ -dimensional permutation matrix or a non-singular matrix  $\mathbf{T}$  (from left):

$$\bar{\lambda} = \mathbf{T} \cdot \lambda. \quad (25)$$

The invariance of vector  $\mathbf{M}_k$  demands then the transformation of vector  $\mathbf{M}_g$ :

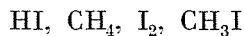
$$\bar{\mathbf{M}}_g = \tilde{\mathbf{T}}^{-1} \cdot \mathbf{M}_g \quad (26)$$

where  $\tilde{\mathbf{T}}^{-1}$  is the reciprocal matrix of  $\tilde{\mathbf{T}}$ .

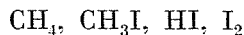


Such transformation of  $\lambda$  (any multiplication from left) does not affect orthogonalities (18).

Be, for example, the sequence of components at the reaction in the former example



instead of:



The change of sequence is equivalent to the transformation by the permutation matrix:

$$\mathbf{P} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix}$$

The new stoichiometric coefficient vector:

$$\bar{\nu} = \mathbf{P} \cdot \nu = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} -1 \\ 1 \\ 1 \\ -1 \end{pmatrix} = \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix}$$

and the transformed  $\lambda$  matrix:

$$\bar{\lambda} = \lambda \cdot \tilde{\mathbf{P}} = \begin{pmatrix} 1 & 1 & 0 & 0 \\ 4 & 3 & 1 & 0 \\ 0 & 1 & 1 & 2 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 4 & 0 & 3 \\ 1 & 0 & 2 & 1 \end{pmatrix}$$

Checking of (24):

$$\tilde{\mathbf{P}} \cdot \mathbf{P} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \mathbf{E}$$

and the orthogonality of  $\bar{\nu}$  and  $\bar{\lambda}$ :

$$\bar{\lambda} \cdot \bar{\nu} = \begin{pmatrix} 0 & 1 & 0 & 1 \\ 1 & 4 & 0 & 3 \\ 1 & 0 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 \\ -1 \\ -1 \\ 1 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} = \mathbf{0}$$

### The rank of the matrix $\lambda$

The rank of a matrix  $\lambda$  is equal to the dimension number of the space spanned by its row or column vectors. Algebraically, the rank is the number of linearly independent rows or columns. Consequently, the rank cannot be greater than the number of rows or columns. A vector has a single column, its rank is therefore one. For example

$$\text{Rank } (\nu) = 1 \quad (27)$$

Rank ( $\lambda$ ) can be maximum equal to  $G$  (lying matrix,  $G < K$ ) or to  $K$  (standing matrix,  $G > K$ ). Rank ( $\lambda$ ) can be calculated in the following manner:  $\nu$  and columns of  $\lambda$  are vectors in the  $K$ -dimensional space (composition space). According to (18), every row vector of  $\lambda$  is orthogonal to the vector  $\nu$ , they lie in a  $(K - 1)$ -dimensional subspace orthogonal to  $\nu$ . In that sense, in the case of a single reaction

$$\text{Rank } (\lambda) = K - 1. \quad (28)$$

At first order reaction

$$K = 2$$

$$\text{Rank } (\lambda) = 1.$$

This is in accordance with (11), expressing the fact that  $\lambda$  can be written as a single dyadic product. As known [2], the rank of a matrix is equal to the minimal number of dyadic products.

According to (28), the rank ( $\lambda$ ) in (9) can be proved to equal three.

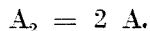
### 3. The chemical reaction lines

*Reaction lines in the mole number space.* As mentioned, the composition of a  $K$ -component system can be given as a point in the  $K$ -dimensional mole number space. The vector  $\mathbf{n}_k$  is the locus vector of this composition point.

According to (16) and (17), the path of the composition point is always a straight line parallel to the vector  $\nu$ . The reaction lines cannot cross or touch each another, two lines any close are unattainable one for another. This unattainability follows from the closeness of the system. The different lines belong to different quantities of radicals which are invariable in closed system during the chemical change (nuclear reactions excluded).

Reaction lines can be plotted in a plane only in case of a two-component system.

Let us take a reaction of the type



The molecular species are:  $A_2$  and  $A$

The single invariable radical:  $A$

The mole weight vector:

$$\mathbf{M} = M_A \begin{pmatrix} 2 \\ 1 \end{pmatrix}$$

Matrix  $\lambda$ :  $\lambda = (2, 1)$

Vector  $\nu$ :  $\nu = \begin{pmatrix} -1 \\ 2 \end{pmatrix}$

Two reaction lines belonging to different initial conditions are seen in Fig. 1.

*Reaction lines in the mole fraction space*

In the mole fraction space the situation is somewhat different.

The definition of the mole fraction ( $x_k$ ):

$$x_k = \frac{n_k}{\sum_k n_k} \quad (29a)$$

and of the mole fraction vector:

$$\mathbf{x} = \frac{1}{\sum_k n_k} \cdot \mathbf{n}_k. \quad (29b)$$

The range of mole fractions:

$$0 \leq x_k \leq 1.$$

From definition (29):

$$\sum_k x_k = (1, 1, \dots) \begin{pmatrix} x_1 \\ x_2 \\ \vdots \end{pmatrix} = 1 \quad (30)$$

what means that the mole fractions are not independent. The number of independent mole fractions is  $(K-1)$ .

The mole fraction space has therefore a dimension number less by one than the mole number space. The domain of real compositions represents a  $K-1$  dimensional simplex with vertices in the points:

$$(1, 0, 0 \dots), \\ (0, 1, 0, \dots),$$

and so on.



The vector equation of the mole fraction — reaction lines can be derived as follows:

Making a summation of (17) (scalar multiplication by the summation vector)

$$\sum_k n_k = \sum_k n_k(0) + \Delta v \cdot \xi \quad (31)$$

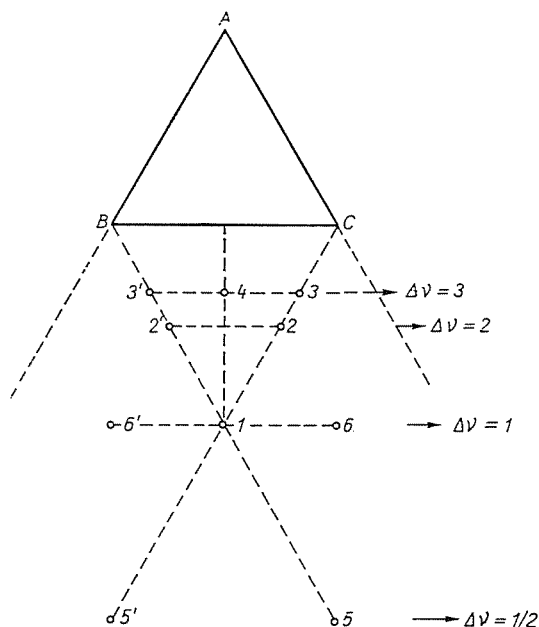


Fig. 4

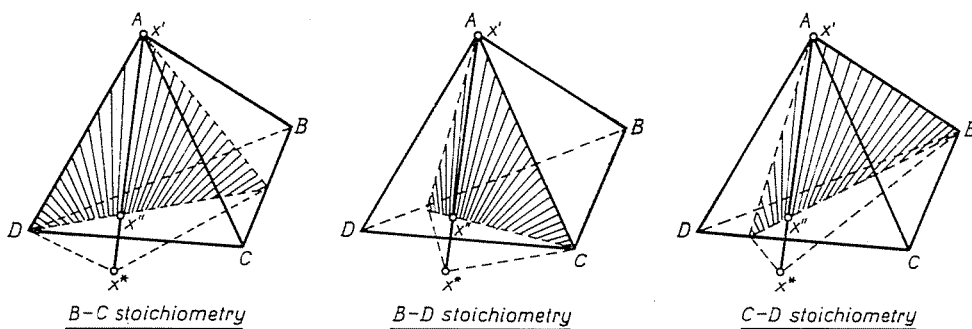


Fig. 5

and combining with (17) and (29)

$$\mathbf{x} = \frac{1}{\sum_k n_k} (\mathbf{n}_k(0) + \mathbf{v} \cdot \xi) = \frac{1}{\sum_k n_k(0) + \Delta v \cdot \xi} (\mathbf{n}_k(0) + \mathbf{v} \cdot \xi) \quad (32)$$

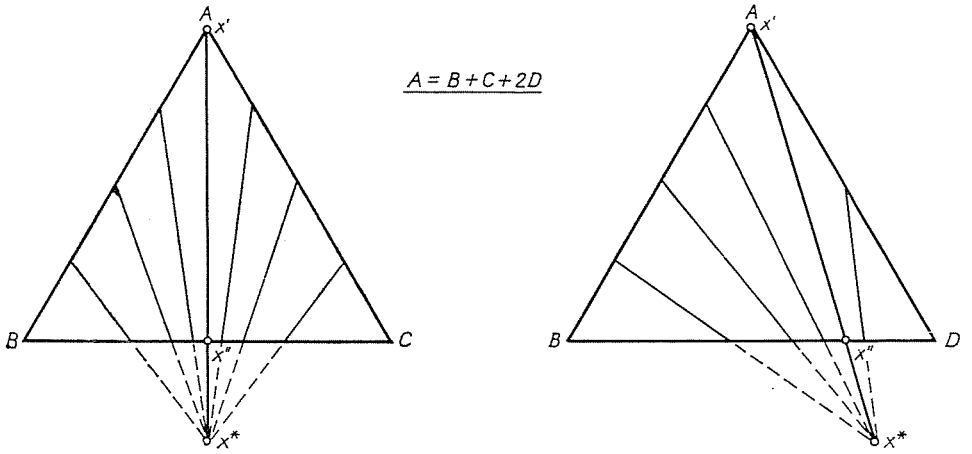


Fig. 6

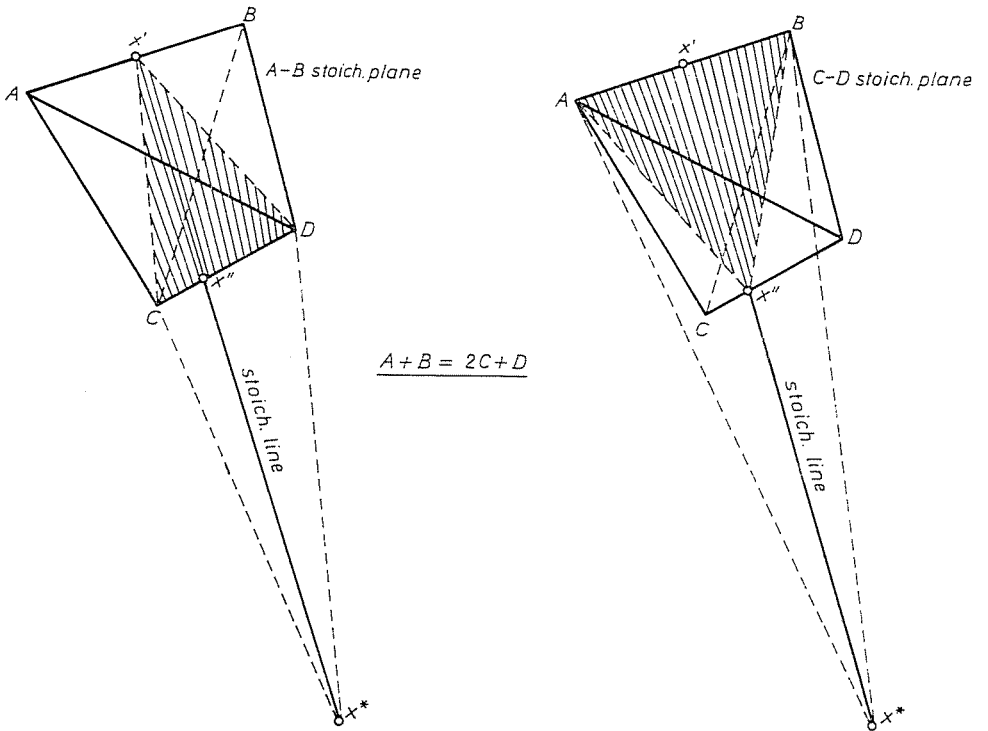


Fig. 7

and

$$\mathbf{x} + \mathbf{x} \frac{\Delta v \cdot \xi}{\sum_k n_k(0)} = \mathbf{x}(0) + \nu \cdot \frac{\xi}{\sum_k n_k(0)}$$

where

$$\mathbf{x}(0) = \frac{1}{\sum_k n_k(0)} \cdot \mathbf{n}_k(0) \quad (33)$$

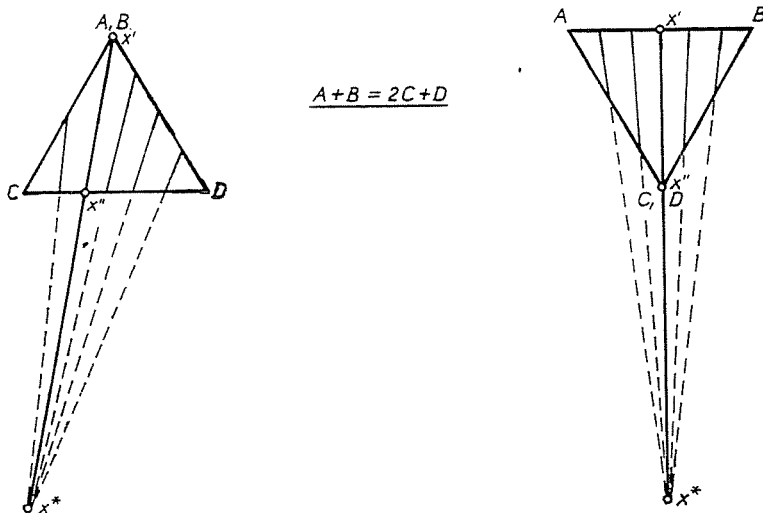


Fig. 8

represents the initial composition point.

After further rearranging

$$\mathbf{x} - \mathbf{x}(0) = \frac{\Delta v \cdot \xi}{\sum_k n_k(0)} (\mathbf{x}^* - \mathbf{x}) \quad (34)$$

where

$$\mathbf{x}^* = \frac{1}{\Delta v} \cdot \nu \quad (35)$$

(34) gives the vector equation of the reaction paths in the mole fraction space and  $\mathbf{x}^*$  is the normalized stoichiometric coefficient vector.

*The focus point*

Two main consequences can be deduced from Equation (34). At first, the reaction paths are straight lines in the mole fraction space too. Secondly,

all of these lines are diverging from a common point given by the vector  $\mathbf{x}^*$ . This characteristic point can be termed the "focus point" of the system. The components of the vector  $\mathbf{x}^*$  are the normalized stoichiometric coefficients.  $\mathbf{x}^*$  depends only on the vector  $\mathbf{v}$  and the mole number change  $\Delta\gamma$  and is independent of the initial conditions.

The focus point lies in the mole fraction space but outside of the range of realizable compositions (Fig. 3) because of vector  $\mathbf{v}$  always has at least one negative element. The focus point is therefore unattainable. So the reaction lines are unattainable for each other in the mole fraction space, as well as in the mole number space.

If the mole number change of the reaction vanishes,

$$\Delta\gamma = 0$$

from 34

$$\mathbf{x} - \mathbf{x}(0) = \frac{\xi}{\sum_k n_k(0)} \cdot \mathbf{v} \quad (36)$$

that is, the reaction lines will be parallel to each other and to the vector  $\mathbf{v}$  and the focus point will be in the infinity.

*Stoichiometric reaction lines.* A mixture is told (fully) stoichiometric when the mole numbers of the reactants or products fulfil the requirements

$$\frac{n'_1}{\nu'_1} = \frac{n'_2}{\nu'_2} = \dots = (\xi - \xi'_0) \quad (37a)$$

$$\frac{n''_1}{\nu''_1} = \frac{n''_2}{\nu''_2} = \dots = -(\xi - \xi''_0) \quad (37b)$$

where

$$\xi = \xi'_0 \text{ if } n'_1 = n'_2 = \dots = 0$$

$$\xi = \xi''_0 \text{ if } n''_1 = n''_2 = \dots = 0$$

and

$$\xi'_0 > \xi > \xi''_0.$$

A stoichiometric initial composition remains stoichiometric during the chemical change.

The vector equation of the stoichiometric reaction line can be derived as follows.

Equations (37a) and (37b) can be written as vector equations for the reactants and products

$$\begin{aligned} \mathbf{n}'_k &= \nu'_k (\xi - \xi'_0) \\ \mathbf{n}''_k &= -\nu''_k (\xi - \xi''_0) \end{aligned} \quad (38)$$



The mole number vector  $\mathbf{n}_k$  is

$$\mathbf{n}_k = \mathbf{n}'_k + \mathbf{n}''_k = \mathbf{v}' (\xi - \xi'_0) - \mathbf{v}'' (\xi - \xi''_0) \quad (39)$$

and the sum of mole numbers

$$\sum_k n_k = \left( \sum_k v'_k \right) (\xi - \xi'_0) - \left( \sum_k v''_k \right) (\xi - \xi''_0) \quad (40)$$

From (29a)

$$\mathbf{x} \left[ \left( \sum_k v'_k \right) (\xi - \xi'_0) - \left( \sum_k v''_k \right) (\xi - \xi''_0) \right] = \mathbf{v}' (\xi - \xi'_0) - \mathbf{v}'' (\xi - \xi''_0). \quad (41)$$

Rearranged:

$$\left( \mathbf{x} + \frac{\mathbf{v}'}{\sum_k v'_k} \right) \left( \sum_k v'_k \right) (\xi - \xi'_0) = \left( \mathbf{x} - \frac{\mathbf{v}''}{\sum_k v''_k} \right) \left( \sum_k v''_k \right) (\xi - \xi''_0). \quad (42)$$

Let

$$\begin{aligned} \mathbf{x} &= \mathbf{x}' \quad \text{if } \xi = \xi''_0 \\ \mathbf{x} &= \mathbf{x}'' \quad \text{if } \xi = \xi'_0 \end{aligned} \quad (43)$$

hence:

$$\mathbf{x}' = \left( \frac{1}{\sum_k v'_k} \right) \cdot \mathbf{v}' \quad (44a)$$

$$\mathbf{x}'' = \left( \frac{1}{\sum_k v''_k} \right) \cdot \mathbf{v}'' \quad (44b)$$

and the vector equation of the fully stoichiometric reaction line:

$$(\mathbf{x} - \mathbf{x}') \left( \sum_k v'_k \right) (\xi - \xi'_0) = (\mathbf{x} - \mathbf{x}'') \left( \sum_k v''_k \right) (\xi - \xi''_0). \quad (45)$$

Eqs. (44) define two further characteristic points in the composition space, namely where the stoichiometric line pierces the boundary of composition domain (Fig. 3).

According to (44), these characteristic vectors are the normalized  $\mathbf{v}'$  and  $\mathbf{v}''$  vectors, on the analogy of the focus point  $\mathbf{x}^*$  being the normalized  $\mathbf{v}$  vector. In contrary of  $\mathbf{x}^*$ ,  $\mathbf{x}'$  and  $\mathbf{x}''$  belong to realizable compositions.

Analogously, one can define further characteristic points as normalized row vectors of matrix  $\lambda$ . These vectors are orthogonal to vectors  $\mathbf{v}$  and  $\mathbf{x}^*$ .

Introducing  $\xi^n$  "normalized reaction co-ordinate" instead of  $\xi$ , defined as

$$\xi^n \equiv \frac{\xi - \xi''_0}{\xi - \xi'_0} \quad (46)$$

(45) can be written as

$$(\mathbf{x} - \mathbf{x}'') \left( \sum_k \nu_k'' \right) \xi^n = (\mathbf{x}' - \mathbf{x}) \left( \sum_k \nu_k' \right) (1 - \xi^n). \quad (47)$$

In that case

$$\begin{aligned} \xi^n &= 0, \text{ if } \mathbf{x} = \mathbf{x}' \\ \xi^n &= 1, \text{ if } \mathbf{x} = \mathbf{x}'' \\ \xi^n &= \infty, \text{ if } \mathbf{x} = \mathbf{x}^*. \end{aligned}$$

From (35) and (44)

$$(\mathbf{x}^* - \mathbf{x}') \left( \sum_k \nu_k' \right) = (\mathbf{x}^* - \mathbf{x}'') \left( \sum_k \nu_k'' \right) \quad (48)$$

and the proportion of the two distances:

$$\frac{|\mathbf{x}^* - \mathbf{x}'|}{|\mathbf{x}^* - \mathbf{x}''|} = \frac{\sum_k \nu_k''}{\sum_k \nu_k'} = \frac{\Delta v}{\left( \sum_k \nu_k' \right)} + 1. \quad (49)$$

The number of relationships in (37) is

$$K - 2.$$

The dimension number of the mole fraction space being

$$K - 1$$

consequently, the dimension number of the (fully) stoichiometric system is

$$K - 1 - K + 2 = 1$$

that is, a straight line section. The fully stoichiometric system behaves therefore as a simple first order reaction, having as "reactant" a mixture of the reactants in a composition given by  $\nu'$  and as single "product" the mixture of the product components in a composition given by  $\nu''$ .

#### *Partially stoichiometric systems*

If the number  $S$  of the constraints in (37) is smaller than  $(K - 2)$ ,

$$0 > S > K - 2$$

then the reaction lines lie in a subspace having a dimension number

$$K - S - 1$$

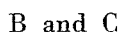
#### 4. Examples

##### a) Reaction lines in a three-component system

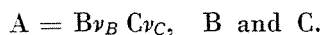
A chemical reaction between three molecular species can always be written in the form



with radicals



molecules



In that case

$$\lambda = \begin{pmatrix} \nu_B & 1 & 0 \\ \nu_C & 0 & 1 \end{pmatrix}$$

and

$$\nu = \begin{pmatrix} -1 \\ \nu_B \\ \nu_C \end{pmatrix} \quad (49)$$

(48) can be regarded as canonical form for the reaction of three molecular species.

The characteristic points in the mole fraction space

$$\mathbf{x}' = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix}; \quad \mathbf{x}'' = \begin{pmatrix} 0 \\ \nu_B \\ \nu_C \end{pmatrix} \frac{1}{\nu_B + \nu_C} \quad (50)$$

$$\mathbf{x}^* = \begin{pmatrix} -1 \\ \nu_B \\ \nu_C \end{pmatrix} \cdot \frac{1}{\nu_B + \nu_C - 1}. \quad (51)$$

The reaction lines can be plotted on a triangular diagram (Fig. 3),  $\mathbf{x}'$  composition point being the vertex A,  $\mathbf{x}''$  lying on the base line B—C.

Point  $\mathbf{x}^*$  lies in the range

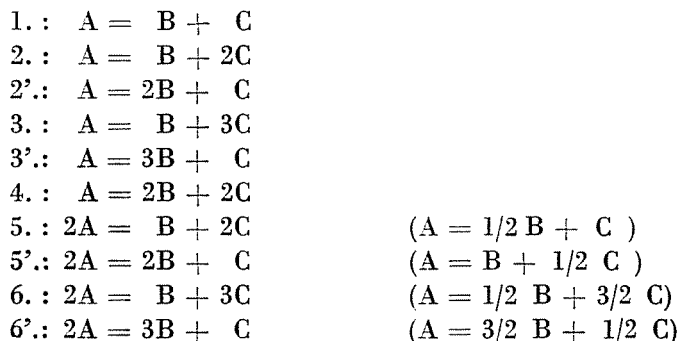
$$\begin{aligned} x_A &< 0 \\ x_B &> 0 \\ x_C &> 0 \end{aligned}$$

The focus points belonging to the same mole number change  $\Delta\nu$  lie on the common straight line parallel to B—C, the spacings being inversely proportional to the mole number change.

The focus points belonging to the same  $\nu_A/\nu_B$  ratio lie on the straight line passing through point A.

The reaction lines of reactions without mole number change form a parallel line set. These lines are easy to construct with the aid of the characteristic points  $x'$  and  $x''$ , former being point A, and latter the point dividing the base line B—C in a ratio  $v_A/v_B$ .

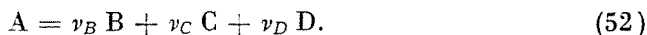
In Fig. 4 some types of reactions are plotted. The reactions are as follows:



#### b) Reaction lines in a four-component system

In that case the mole number space has four, the mole fraction space three dimensions. The composition range of the mole fraction space is a tetrahedron having vertices in distances of unity from the opposite planes.

With four components there are two canonical reaction types. The first:

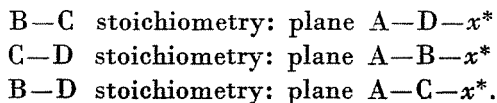


Reaction lines can be plotted by means of two projection planes, for example planes A—B—C and A—B—D. These projections are typical triangular diagrams (Fig. 6).

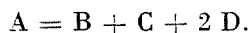
The focus point lies in the range

$$\begin{aligned} x_A &< 0 \\ x_B &> 0 \\ x_C &> 0 \\ x_D &> 0 \end{aligned}$$

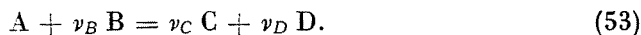
outside of the tetrahedron, but inside the three-dimensional space. The fully stoichiometric line passes through the focus and vertex A. The partially stoichiometric lines lie in planes. There are three such planes (Fig. 5):



The stoichiometric planes intersect one another in the stoichiometric line. In Fig. 5 the reaction lines of the reaction are plotted:



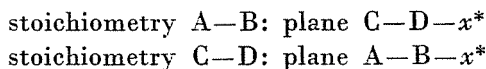
The second reaction type:



The focus lies in the range

$$\begin{aligned} x_A &< 0 \\ x_B &< 0 \\ x_C &> 0 \\ x_D &> 0 \end{aligned}$$

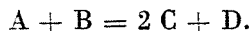
outside the tetrahedron. The fully stoichiometric reaction line connects the base lines A—B and C—D. The two stoichiometric planes are: (Fig. 7)



The characteristic points  $x'$  and  $x''$  are on the lines A—B and C—D dividing them in the ratios  $\nu_A/\nu_B$  and  $\nu_C/\nu_D$ , respectively.

The visualisation of the reaction lines can be made with the aid of two projection planes orthogonal to the lines A—B and C—D. The projections can be plotted on triangular diagrams.

Figs 7 and 8 show the lines of the reaction



### Summary

The geometry of reaction paths is analysed in the composition space in the case of a single chemical reaction. The reaction lines form a straight line set. In the case of stoichiometric composition, the reaction lines lie in subspaces of the composition space. The fully stoichiometric subspace is a single line. The set of reaction lines have in the mole fraction space three main characteristic points, all lying on the stoichiometric line. These are: the "focus point" and the two piercing points with the boundary of composition domain.

It is shown that the locus vectors of the characteristic points can be simply formulated with the aid of the stoichiometric coefficients of the chemical reaction.

In some examples the reaction lines, stoichiometric subspaces and characteristic points are visualized in the cases of two, three and four component systems.

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