Advanced Data Analysis and Modelling in Chemical Engineering

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CHAPTER 2

Chemical Composition and Structure: Linear Algebra

2.1 Introduction

The following questions often arise in the practice of chemical engineering:

- Given a set of components of known atomic composition, establish which of them are key to determine, together with the element balances, the amounts of all others. Furthermore, find a way of generating all possible reactions involving these components. This will be addressed by the augmented molecular matrix, introduced in Section 2.2.
- Given a set of reactions, determine which of these are key to describing all other reactions as combinations of this set and how to do this. Also determine which additional balances appear and which thermodynamic characteristics (enthalpy change, equilibrium coefficient) are dependent. This will be addressed by the augmented stoichiometric matrix, introduced in Section 2.3.
- For a set of reactions involving intermediates, which typically cannot be measured, determine the overall reactions, that is, the ones not involving such intermediates, and find the numbers by which these can be written as combinations of the given reactions (the so-called Horiuti numbers). This will be addressed by augmenting a specially crafted stoichiometric matrix, as explained in Section 2.4.

What is a *matrix?* It is a square or rectangular array of numbers or expressions, placed between parentheses, for example:

$$\begin{bmatrix} 1 & 3 & -7 \\ 2 & -4 & 3 \end{bmatrix} \tag{2.1}$$

In this case there are two rows and three columns, and we call this a 2×3 matrix, mentioning first the number of rows and then the number of columns. There can be no empty spaces left in the matrix. Matrices are widely used in engineering to represent a variety of mathematical objects and relationships. We will gradually introduce them, in close connection with the requirements from chemistry and engineering that justify their use.

Let us start with chemical reactions. A statement such as

$$2H_2 + O_2 \rightarrow 2H_2O \tag{2.2}$$

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describes a chemical process, a reaction, that consumes two molecules of hydrogen gas, H_2, and one molecule of oxygen gas, O_2, to produce two molecules of water, H_2O. Such a reaction does not actually occur as the collision of the three gas molecules involved, but rather as a complicated, not yet fully elucidated set of reaction steps. Nevertheless, Eq. (2.2) describes the overall reaction and can readily be tested experimentally: two moles of hydrogen and one mole of oxygen are transformed into two moles of water. The statement in Eq. (2.2) implies that all H_2 and O_2 should be completely transformed into H_2O so that no H_2 or O_2 should be left. Thus, Eq. (2.2) is a falsifiable statement, and therefore scientific.

If we ignore the direction of the arrow in Eq. (2.2), it can be viewed as an equality of sorts:

$$2H_2 + O_2 \triangleq 2H_2O \tag{2.3}$$

where "$\triangleq$"denotes the equality of all atom counts on both sides. This is not an absolute equality: O_2 and $2H_2$ together are not the same as $2H_2O$, but they are amenable to transformation into each other. Eq. (2.3) can be rewritten as

$$-2H_2 - O_2 + 2H_2O \triangleq \text{zero} \tag{2.4}$$

By convention, the terms that originate from the left-hand side, the reactants, are assigned a negative sign, and the products are assigned a positive sign. Maybe we could associate this equation to a (1×3) matrix? The matrix

$$\begin{bmatrix} -2 & -1 & 2 \end{bmatrix} \tag{2.5}$$

would be the most natural choice, but since the meaning of the columns (H_2, O_2, and H_2O) would be lost, we introduce a typographical convention for indicating the meaning of the columns:

$$\begin{matrix} H_2 & O_2 & H_2O \\ \begin{bmatrix} -2 & -1 & 2 \end{bmatrix} \end{matrix} \tag{2.6}$$

Note that the chemical symbols in Eq. (2.6) are hints, *not* part of the matrix!

Another reaction might occur between the same reactants, namely the synthesis of hydrogen peroxide:

$$H_2 + O_2 \rightarrow H_2O_2 \tag{2.7}$$

This reaction can be represented by the matrix:

$$\begin{matrix} H_2 & O_2 & H_2O_2 \\ \begin{bmatrix} -1 & -1 & 1 \end{bmatrix} \end{matrix} \tag{2.8}$$

and it is logical to represent the system of both reactions, Eqs. (2.2), (2.7), by the 2×4 matrix:

$$\begin{matrix} & \mathrm{H_2} & \mathrm{O_2} & \mathrm{H_2O} & \mathrm{H_2O_2} \\ \begin{bmatrix} \\ \\ \end{bmatrix} & \begin{matrix} -2 \\ -1 \end{matrix} & \begin{matrix} -1 \\ -1 \end{matrix} & \begin{matrix} 2 \\ 0 \end{matrix} & \begin{matrix} 0 \\ 1 \end{matrix} \end{matrix} \tag{2.9}$$

Note that for this matrix the rows are not labeled. We could add more hints by adding the names of the reaction products to the left of the matrix, as in

$$\begin{matrix} & \mathrm{H_2} & \mathrm{O_2} & \mathrm{H_2O} & \mathrm{H_2O_2} \\ \mathrm{H_2O} \\ \mathrm{H_2O_2} \end{matrix} \begin{bmatrix} -2 & -1 & 2 & 0 \\ -1 & -1 & 0 & 1 \end{bmatrix} \tag{2.10}$$

but initially we will consider the rows of this stoichiometric matrix as merely stoichiometric information: how many molecules of reactants (negative entries) produce how many molecules of products (positive entries)? Components that do not occur in a particular reaction have a zero entry in that row. Reactions are the building blocks of a chemical description, but before we can handle them more formally, we must also express how each component combines its constituent elements. This is done in the molecular matrix.

2.2 The Molecular Matrix and Augmented Molecular Matrix

2.2.1 The Molecular Matrix

For every component present in the reaction mixture under consideration, its elemental composition must be specified in order to verify that all elements are properly preserved. The most convenient and complete way of specifying the elemental composition is by a matrix in which the columns correspond to the elements, with possibly one column reserved for electric charge, and the rows signify the different molecules, ions, radicals, and so forth, that are being considered. This is called the *molecular matrix* $\mathbf{M}$. For instance, for a mixture consisting of H_2, CH_4, C_2H_6, and C_2H_4, the molecular matrix is given by

$$\mathbf{M} = \begin{matrix} & \mathrm{C} & \mathrm{H} \\ \mathrm{H_2} \\ \mathrm{CH_4} \\ \mathrm{C_2H_6} \\ \mathrm{C_2H_4} \end{matrix} \begin{bmatrix} 0 & 2 \\ 1 & 4 \\ 2 & 6 \\ 2 & 4 \end{bmatrix} \tag{2.11}$$

Based on this molecular matrix, the molar masses of the components can be determined from the atomic masses of the elements. For instance, the molar mass of C_2H_6 is two times the atomic mass of C plus six times that of H. To express such relationships in a very compact manner, mathematicians have devised a special way of multiplying matrices: the

atomic masses of the elements can be grouped in a column vector $\mathbf{m_A}$ (in this case consisting of two rows),

$$\mathbf{m_A} = \begin{matrix} \text{H} \\ \text{C} \end{matrix} \begin{bmatrix} 1.008 \\ 12 \end{bmatrix} \tag{2.12}$$

and the molar masses of the components can go in a 4×1 column vector $\mathbf{m_M}$:

$$\mathbf{m_M} = \begin{matrix} \text{H}_2 \\ \text{CH}_4 \\ \text{C}_2\text{H}_6 \\ \text{C}_2\text{H}_4 \end{matrix} \begin{bmatrix} 2.016 \\ 16.032 \\ 30.048 \\ 28.032 \end{bmatrix} \tag{2.13}$$

Then in compact form, $\mathbf{m_M} = \mathbf{M}\mathbf{m_A}$. In general, a product of two matrices $\mathbf{B}$ and $\mathbf{C}$ is defined only if the number of columns of $\mathbf{B}$ equals the number of rows of $\mathbf{C}$, and the product $\mathbf{P} = \mathbf{BC}$ will have the number of rows of $\mathbf{B}$ and the number of columns of $\mathbf{C}$. A general entry P_{ij} of $\mathbf{P}$ is then given by definition as a sum of products of entries of row i of $\mathbf{B}$ and entries of column j of $\mathbf{C}$:

$$P_{ij} = \mathbf{B}_{i1}\mathbf{C}_{1j} + \mathbf{B}_{i2}\mathbf{C}_{2j} + \cdots + \mathbf{B}_{ip}\mathbf{C}_{pj} \tag{2.14}$$

where p is the number of columns of $\mathbf{B}$ (and rows of $\mathbf{C}$).

Furthermore, when a set of mathematical objects $\nu_1, \nu_2, \ldots, \nu_n$ can be multiplied by real numbers a_i and the sum of the products satisfies the equation $a_1\nu_1 + a_2\nu_2 + \cdots + a_n\nu_n = 0$, where not all real numbers $a_1, a_2, \ldots, a_n$ are zero, they are said to be *linearly dependent*, otherwise they are called *linearly independent*. For instance, the equations $x + y = 5$ and $x - y = 9$ are linearly independent, but if we add the equation $x = 7$, they become dependent, since $x + y = 5$ plus $x - y = 9$ minus twice $x = 7$ yields $0 = 0$. A set of linearly independent objects that is maximal, that is, to which no object can be added without losing linear independence, is called a *basis*. In the previous example, $x + y = 5$ by itself is not a basis since $x - y = 9$ can be added to it without losing linear independence, but the set of these two equations does form a basis since no third equation can be added to this set independently.

2.2.2 Application of the Molecular Matrix to Element Balances

In practice, it is often crucial to calculate the balance for each of the elements present in the components of a mixture. Now the questions arise how many of these balances are independent and which amounts can be deduced from other ones given the element balance values. To solve this problem in a systematic way, a certain ordering of the components must be chosen; typically, the best known or most easily measured components should be listed first. Then the molecular matrix can be augmented by adding a unit matrix,

that is, a matrix with ones on the main diagonal and zeros elsewhere, to its right. For the molecular matrix represented by Eq. (2.11), we obtain

$$\begin{array}{c} \\ H_2 \\ CH_4 \\ C_2H_6 \\ C_2H_4 \end{array} \begin{array}{c} \begin{array}{cccccc} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{array} \\ \begin{bmatrix} 0 & 2 & 1 & 0 & 0 & 0 \\ 1 & 4 & 0 & 1 & 0 & 0 \\ 2 & 6 & 0 & 0 & 1 & 0 \\ 2 & 4 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.15}$$

This matrix is best interpreted as a form of double bookkeeping as used in accounting: in the first two columns, the counts of the elements C and H, now called C_t and H_t, for total C and H, are tallied (debit); in the next four columns, the components are figured (credit).

An augmented molecular matrix can be transformed to a *Reduced Row Echelon Form* or *RREF*. This method is essential to all matrix transformations in this chapter. The idea behind the RREF is that we work from the first column all the way to the rightmost one. For each column we determine whether it is possible to eliminate it by finding a nonzero entry, or *pivot,* in a row that has not been considered before. If not, we skip to the next column. If a pivot is found, we use it to eliminate all other entries in that row. We also move the pivot row up as far as possible. We cannot tell in advance where all the pivots will be found; we must find them one by one since the elimination procedure can change zero entries into nonzero ones and vice versa. In general, we also do not know in advance how many pivots will be found. However, in the special case of a matrix augmented with a unit matrix, we do know that their number will be equal to the number of rows.

As an example, consider the augmented matrix for a mixture consisting of H_2, CH_4, C_2H_6, and C_2H_4 given by Eq. (2.15). In order to find the RREF, we start with the first column and find a nonzero entry in the second row. We move this second row up to the first position:

$$\begin{array}{c} \begin{array}{cccccc} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{array} \\ \begin{bmatrix} \mathbf{1} & 4 & 0 & 1 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 & 0 \\ 2 & 6 & 0 & 0 & 1 & 0 \\ 2 & 4 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.16}$$

The pivot is in bold. Note that the hints labeling the rows are absent, since their identity will not be preserved during the reduction of the matrix.

Next, we use the first row to eliminate all other entries of the first column. The second row requires no action since the value there is already zero. We subtract twice the first row from the third row, changing the matrix to

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 4 & 0 & 1 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & -2 & 1 & 0 \\ 2 & 4 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.17}$$

Similarly, we subtract twice the first row from the fourth row, resulting in

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 4 & 0 & 1 & 0 & 0 \\ 0 & 2 & 1 & 0 & 0 & 0 \\ 0 & -2 & 0 & -2 & 1 & 0 \\ 0 & -4 & 0 & -2 & 0 & 1 \end{bmatrix} \end{array} \tag{2.18}$$

Now we tackle the second column. The first row has already been assigned a pivot, so we do not consider it for elimination purposes. In the second row, we find a nonzero value, 2, by which we divide the entries in this row:

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 4 & 0 & 1 & 0 & 0 \\ 0 & \mathbf{1} & 1/2 & 0 & 0 & 0 \\ 0 & -2 & 0 & -2 & 1 & 0 \\ 0 & -4 & 0 & -2 & 0 & 1 \end{bmatrix} \end{array} \tag{2.19}$$

Now we use this second row for the elimination of the entries in the other rows of the second column, including the first row. So we subtract four times the second row from the first, add twice the second row to the third, and add four times the second row to the fourth. The result of these operations is

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & -2 & 1 & 0 & 0 \\ 0 & \mathbf{1} & 1/2 & 0 & 0 & 0 \\ 0 & 0 & 1 & -2 & 1 & 0 \\ 0 & 0 & 2 & -2 & 0 & 1 \end{bmatrix} \end{array} \tag{2.20}$$

When looking at the third column to find a pivot, we do not consider the first and second rows because they have already been assigned pivots. We do, however, find a suitable entry, 1, in the third row and use this as a pivot. We add twice the third row to the first, subtract half of it from the second, and subtract twice the third row from the fourth.

This results in

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & 0 & -3 & 2 & 0 \\ 0 & \mathbf{1} & 0 & 1 & -1/2 & 0 \\ 0 & 0 & \mathbf{1} & -2 & 1 & 0 \\ 0 & 0 & 0 & 2 & -2 & 1 \end{bmatrix} \end{array} \tag{2.21}$$

Finally, in the fourth column we do not consider the first three rows, because they already have pivots, but find a nonzero value in the fourth row, 2, and choose it as a pivot. First we divide the entries in the fourth row by this value,

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & 0 & -3 & 2 & 0 \\ 0 & \mathbf{1} & 0 & 1 & -1/2 & 0 \\ 0 & 0 & \mathbf{1} & -2 & 1 & 0 \\ 0 & 0 & 0 & \mathbf{1} & -1 & 1/2 \end{bmatrix} \end{array} \tag{2.22}$$

and then add three times the fourth row to the first, subtract it once from the second, and add it twice to the third:

$$\begin{array}{c} \begin{matrix} C_t & H_t & H_2 & CH_4 & C_2H_6 & C_2H_4 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & 0 & 0 & -1 & 3/2 \\ 0 & \mathbf{1} & 0 & 0 & 1/2 & -1/2 \\ 0 & 0 & \mathbf{1} & 0 & -1 & 1 \\ 0 & 0 & 0 & \mathbf{1} & -1 & 1/2 \end{bmatrix} \end{array} \tag{2.23}$$

We have now obtained the RREF. Fig. 2.1 shows a map of this matrix indicating the subareas.

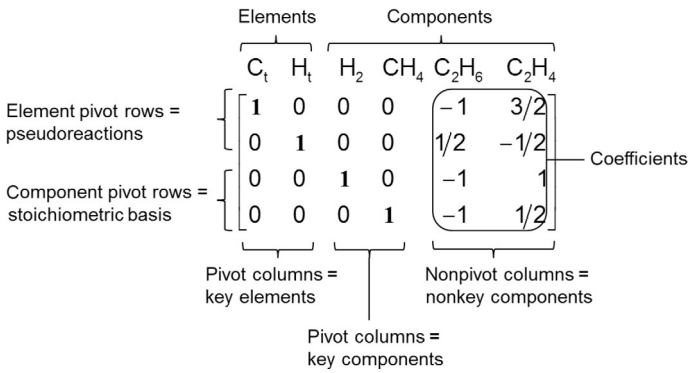

Fig. 2.1
Map of subareas in the RREF of Eq. (2.23).

Because the molecular matrix was augmented with a unit matrix, the pivot columns together form a unit submatrix indicating the *key elements* and *key components*. Key elements of a certain chemical mixture are those the amounts of which cannot be determined from the amounts of other elements; key components are those the amounts of which, together with the amounts of the key elements, uniquely determine the amounts of the other, nonkey components.

Every row has a pivot; the first two rows have pivots in element columns and are related to pseudoreactions in which precisely one atom of the element is "created" as the result of a transformation of components. Contrary to ordinary chemical reactions, there is no balance of the pivotal element in these pseudoreactions, but instead an excess of a single atom in the products. For instance, the first row in Eq. (2.23) represents the pseudoreaction $C_2H_6 \rightleftarrows 3/2\ C_2H_4$ with an excess of one C atom in the product: reactants and products contain two and three C atoms, respectively. Similarly, the pseudoreaction in the second row, $1/2\ C_2H_4 \rightleftarrows 1/2\ C_2H_6$, has an excess of one H atom (two H atoms in reactants, three in products).

The pivots of the third and fourth rows are not elements but the components H_2 and CH_4. They represent the reactions $C_2H_6 \rightleftarrows H_2 + C_2H_4$, in which a single unit of H_2 is formed, and $C_2H_6 \rightleftarrows CH_4 + 1/2\,C_2H_4$, in which a single unit of CH_4 is formed. These rows corresponding to reactions form a stoichiometric basis for all reactions involving the components considered.

The first four columns are pivot columns, in which only entries 1 occur as pivots and all other entries are zero. The fifth and sixth columns have no pivot, and correspond to components that are not key. Their amounts can be deduced from the element balances and the key components. The coefficients can be read off at once in the columns, which were obtained from the pseudoreactions and reactions. In the fifth column, the amount of C_2H_6 equals

$$n_{C_2H_6} = -n_{C_t} + 1/2 n_{H_t} - n_{H_2} - n_{CH_4} \tag{2.24}$$

and in the sixth, the amount of C_2H_4 equals

$$n_{C_2H_4} = 3/2 n_{C_t} - 1/2 n_{H_t} + n_{H_2} + 1/2 n_{CH_4} \tag{2.25}$$

In this example, if we assume that $n_{C_2H_4}$ can be written as a linear combination:

$$n_{C_2H_4} = \alpha n_{C_t} + \beta n_{H_t} + \gamma n_{H_2} + \delta n_{CH_4} \tag{2.26}$$

and consider the effect of the first pseudoreaction, $C_2H_6 \rightleftarrows 3/2\,C_2H_4$, in which C is "created" and H_2 and CH_4 do not participate, n_{C_t} increases by 1, $n_{C_2H_4}$ by 3/2, and n_{H_t}, n_{H_2}, and n_{CH_4} are not affected.

Consequently, α must equal 3/2. In the same way, β, γ, and δ are determined uniquely by the second, third, and fourth pseudoreactions and reactions.

Summarizing, to analyze the element balances

(1) list the elements and components present in the order of decreasing ease of measurement.
(2) form the molecular matrix by entering the number of atoms of an element for each component in its own row.
(3) augment this matrix by adding a unit matrix to its right.
(4) perform the operations resulting in the RREF.

Then, in the result:

(1) every row is still stoichiometrically valid.
(2) every pivot column corresponds to a value that must be known, either that of an element balance or of a key component.
(3) every nonpivot column corresponds to an unknown value that can be deduced from the pivots using the matrix coefficients in that column.
(4) the rows for which all elemental entries are zero form the basis of stoichiometrically possible reactions.

Because the matrix is augmented with a unit matrix, the total number of pivot columns always equals the number of rows, which is also the number of components. It also equals the number of key elements plus the number of key components. The number of key elements can be less than the total number of elements, when some element columns have no pivot.

Example 2.1 Fixed Ratio of Elements

Consider a mixture consisting of the isomers *c*-C_4H_8, *t*-C_4H_8, and the dimer C_8H_{16}. In order to determine which are the key elements, and the key and nonkey components, we first construct the molecular matrix as

$$\begin{array}{c} \\ c\text{-}C_4H_8 \\ t\text{-}C_4H_8 \\ C_8H_{16} \end{array} \begin{array}{c} \begin{array}{cc} C & H \end{array} \\ \begin{bmatrix} 4 & 8 \\ 4 & 8 \\ 8 & 16 \end{bmatrix} \end{array} \tag{2.27}$$

We augment it to the matrix:

$$\begin{array}{ccccc} C_t & H_t & c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \\ \begin{bmatrix} 4 & 8 & 1 & 0 & 0 \\ 4 & 8 & 0 & 1 & 0 \\ 8 & 16 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.28}$$

with RREF

$$\begin{array}{c} \begin{matrix} C_t & H_t & c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 2 & 0 & 0 & 1/8 \\ 0 & 0 & \mathbf{1} & 0 & -1/2 \\ 0 & 0 & 0 & \mathbf{1} & -1/2 \end{bmatrix} \end{array} \tag{2.29}$$

An unusual event occurs here: the second column, even though elemental, has no pivot. It therefore contains a nonkey element, and we can read from it that H_t is twice C_t in all components of the mixture. Next, *c*-C_4H_8 and *t*-C_4H_8 are the two key components, and the amount of C_8H_{16} is always given by

$$n_{C_8H_{16}} = 1/8 n_{C_t} - 1/2 n_{c\text{-}C_4H_8} - 1/2 n_{t\text{-}C_4H_8} \tag{2.30}$$

The general result that can be derived from this example is the fundamental equation:

$$\text{Number of key components} = \text{number of components} - \text{number of key elements} \tag{2.31}$$

The number of key components is thus a property of the reaction mixture, but the key components actually chosen depend on the ordering: the components listed first will be chosen to be key components. This is why it is useful to order the components by decreasing ease of measurement, so that the components whose values can be measured more easily will be selected as key components.

The RREF method is completely mechanical, so it requires no insight and when performed correctly will always give the same result: even though different nonzero entries might be chosen as pivots in its course, the final result will always be the same. Conceptually, the RREF means that given an ordering of variables, we try and eliminate all possible (pivot) variables when they can be expressed in terms of other variables that come later in the ordering.

Verifying that the element balances hold is an essential way of making sure that no components were overlooked. Then the determination of the key components is not arbitrary, since it only depends on knowing the composition of the mixture of all participating components.

Example 2.2 Different Order of Components

Rework the example with the molecular matrix given by Eq. (2.11), but now with the reverse order of components.

Solution:

The new molecular matrix is

$$\begin{array}{c} \begin{matrix} & C & H \end{matrix} \\ \begin{matrix} C_2H_4 \\ C_2H_6 \\ CH_4 \\ H_2 \end{matrix} \begin{bmatrix} 2 & 4 \\ 2 & 6 \\ 1 & 4 \\ 0 & 2 \end{bmatrix} \end{array} \tag{2.32}$$

After augmentation with a unit matrix, this matrix becomes

$$\begin{array}{c} \begin{matrix} C_t & H_t & C_2H_4 & C_2H_6 & CH_4 & H_2 \end{matrix} \\ \begin{bmatrix} 2 & 4 & 1 & 0 & 0 & 0 \\ 2 & 6 & 0 & 1 & 0 & 0 \\ 1 & 4 & 0 & 0 & 1 & 0 \\ 0 & 2 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.33}$$

Its RREF is readily computed to be

$$\begin{array}{c} \begin{matrix} C_t & H_t & C_2H_4 & C_2H_6 & CH_4 & H_2 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & 0 & 0 & 1 & -2 \\ 0 & \mathbf{1} & 0 & 0 & 0 & 1/2 \\ 0 & 0 & \mathbf{1} & 0 & -2 & 2 \\ 0 & 0 & 0 & \mathbf{1} & -2 & 1 \end{bmatrix} \end{array} \tag{2.34}$$

so that now the key components are C_2H_4 and C_2H_6 (because they come earlier in the ordering). The basic reactions are $C_2H_4 + 2H_2 \rightleftarrows 2CH_4$ and $C_2H_6 + H_2 \rightleftarrows 2CH_4$. The amounts of the nonkey components work out to

$$n_{CH_4} = n_{C_t} - 2n_{C_2H_4} - 2n_{C_2H_6} \tag{2.35}$$

and

$$n_{H_2} = -2n_{C_t} + 1/2n_{H_t} + 2n_{C_2H_4} + n_{C_2H_6} \tag{2.36}$$

Example 2.3 Mixture Containing a One-Atom Molecule

Calculate the balances for a mixture containing the molecules C (atomic carbon), CO, CO_2, and O_2.

Solution:

The fact that atomic carbon also occurs among the components does not require any special treatment; only the usual care must be taken to distinguish the C_t elemental column from the C atomic carbon column. The molecular matrix is

$$\begin{array}{c} \begin{matrix} & C & O \end{matrix} \\ \begin{matrix} C \\ CO \\ CO_2 \\ O_2 \end{matrix} \begin{bmatrix} 1 & 0 \\ 1 & 1 \\ 1 & 2 \\ 0 & 2 \end{bmatrix} \end{array} \tag{2.37}$$

and after augmentation,

$$\begin{array}{c} \begin{matrix} C_t & O_t & C & CO & CO_2 & O_2 \end{matrix} \\ \begin{bmatrix} 1 & 0 & 1 & 0 & 0 & 0 \\ 1 & 1 & 0 & 1 & 0 & 0 \\ 1 & 2 & 0 & 0 & 1 & 0 \\ 0 & 2 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.38}$$

Its RREF is then

$$\begin{array}{c} \begin{matrix} C_t & O_t & C & CO & CO_2 & O_2 \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & 0 & 0 & 1 & -1 \\ 0 & \mathbf{1} & 0 & 0 & 0 & 1/2 \\ 0 & 0 & \mathbf{1} & 0 & -1 & 1 \\ 0 & 0 & 0 & \mathbf{1} & -1 & 1/2 \end{bmatrix} \end{array} \tag{2.39}$$

The key components are C and CO (as dictated by the order of components) and the amount of the nonkey components can be calculated from

$$n_{CO_2} = n_{C_t} - n_C - n_{CO} \tag{2.40}$$

and

$$n_{O_2} = -n_{C_t} + 1/2 n_{O_t} + n_C + 1/2 n_{CO} \tag{2.41}$$

Example 2.4 Combination of Two Groups of Elements

Consider the components acetylene (C_2H_2), hydrochloric acid (HCl), and vinyl chloride (C_2H_3Cl). Determine the key components and balances.

Solution:

The augmented molecular matrix is

$$\begin{array}{c} \begin{matrix} C_t & H_t & Cl_t & C_2H_2 & HCl & C_2H_3Cl \end{matrix} \\ \begin{bmatrix} 2 & 2 & 0 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 1 & 0 \\ 2 & 3 & 1 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.42}$$

with RREF

$$\begin{array}{c} \begin{matrix} C_t & H_t & Cl_t & C_2H_2 & HCl & C_2H_3Cl \end{matrix} \\ \begin{bmatrix} \mathbf{1} & 0 & -1 & 0 & -3/2 & 1/2 \\ 0 & \mathbf{1} & 1 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 1 & -1 \end{bmatrix} \end{array} \tag{2.43}$$

so that C and H are the independent elements and Cl is dependent according to

$$n_{Cl_t} = -n_{C_t} + n_{H_t} \tag{2.44}$$

In this case, C_2H_2 is the only key component because C_2H_3Cl is a combination of the two groups of elements C_2H_2 and HCl.

The amounts of the nonkey components are

$$n_{HCl} = -3/2n_{C_t} + n_{H_t} + n_{C_2H_2} \tag{2.45}$$

and

$$n_{C_2H_3Cl} = 1/2n_{C_t} - n_{C_2H_2} \tag{2.46}$$

2.2.3 Remarks

The method indicated in this section works equally well for ions and radicals, ionic or not. In the case of negative ions, the excess electrons must be specified as well, since electrons are distinct from all elements; similarly, in the case of positive ions, the deficit in electrons must be indicated. This will ensure that charge is always properly preserved. When different isotopes of an element occur, they must be counted separately along with the different components they occur in. Sometimes unconventional "elements" such as active catalyst sites are used. Sometimes subcomponents can be used as pseudoelements (water in hydrates, building blocks of polymers, amino acids).

2.3 The Stoichiometric Matrix

In general, a *stoichiometric matrix* represents a set of reactions involving given components. The columns of this matrix correspond to the different components, the rows correspond to the different reactions, and the entries are stoichiometric coefficients, which by convention are negative for the reactants and positive for the products.

In Section 2.2, we have shown how the molecular matrix, when augmented with a unit matrix and converted to the corresponding RREF, yields a basis for all stoichiometrically acceptable reactions. In reality, however, many of these reactions may be chemically impossible. Therefore, a special stoichiometric matrix can be considered, in which only selected reactions occur.

2.3.1 Application of the Stoichiometric Matrix to Reactions

Consider the set of reactions

$$2H_2 + O_2 \rightleftarrows 2H_2O \tag{2.47}$$

$$H_2 + O_2 \rightleftarrows H_2O_2 \tag{2.48}$$

which is represented by the stoichiometric matrix **S**

$$\begin{matrix} \mathrm{H_2} & \mathrm{O_2} & \mathrm{H_2O} & \mathrm{H_2O_2} \end{matrix} \\ \begin{bmatrix} -2 & -1 & 2 & 0 \\ -1 & -1 & 0 & 1 \end{bmatrix} \tag{2.49}$$

while the molecular matrix **M** of the components that participate in these reactions is

$$\begin{matrix} & \mathrm{H} & \mathrm{O} \end{matrix} \\ \begin{matrix} \mathrm{H_2} \\ \mathrm{O_2} \\ \mathrm{H_2O} \\ \mathrm{H_2O_2} \end{matrix} \begin{bmatrix} 2 & 0 \\ 0 & 2 \\ 2 & 1 \\ 2 & 2 \end{bmatrix} \tag{2.50}$$

If we wish to verify, for instance, that hydrogen atoms are conserved by the first reaction, Eq. (2.47), we must count them in every term on either side, and then subtract these values: there are four hydrogen atoms on both sides and subtraction yields zero. An equivalent but mathematically more elegant method is to use the entries of the stoichiometric matrix and the molecular matrix as follows: we read -2 for the coefficient of H_2 in the first row of the stoichiometric matrix and multiply by 2, the number of H atoms in H_2 as indicated by the molecular matrix, and so on. The result is then $(-2)(2)+(-1)(0)+(2)(2)+(0)(2)=0$, which by definition is precisely the entry (1,1) of the product of the stoichiometric and molecular matrices **SM**. Similarly, the entry (ij) of that product expresses the difference in atom counts of element j in reaction i. Consequently, we can express the balance of all reactions for all elements compactly as the zero matrix with all entries zero:

$$\mathbf{SM} = 0 \tag{2.51}$$

It is useful to compute the RREF of a stoichiometric matrix because the pivots will reveal the key components, and the nonpivot columns will reveal the balances obeyed by the nonkey components. In this example, the RREF equals

$$\begin{matrix} \mathrm{H_2} & \mathrm{O_2} & \mathrm{H_2O} & \mathrm{H_2O_2} \end{matrix} \\ \begin{bmatrix} 1 & 0 & -2 & 1 \\ 0 & 1 & 2 & -2 \end{bmatrix} \tag{2.52}$$

so that the key components are H_2 and O_2, and the relationships are read off in the nonpivot columns, 3 and 4, as

$$\Delta n_{\mathrm{H_2O}} = -2\Delta n_{\mathrm{H_2}} + 2\Delta n_{\mathrm{O_2}} \tag{2.53}$$

and

$$\Delta n_{\mathrm{H_2O_2}} = \Delta n_{\mathrm{H_2}} - 2\Delta n_{\mathrm{O_2}} \tag{2.54}$$

where Δ indicates that we are expressing the changes in amounts that are caused by these reactions.

Example 2.5 Effect of the Reactions Chosen

Returning to the molecules *c*-C_4H_8, *t*-C_4H_8, and the dimer C_8H_{16} of Example 2.2, we can propose the reactions

$$c\text{-}C_4H_8 + t\text{-}C_4H_8 \rightleftarrows C_8H_{16} \tag{2.55}$$

and

$$c\text{-}C_4H_8 \rightleftarrows t\text{-}C_4H_8 \tag{2.56}$$

which are represented by the stoichiometric matrix

$$\begin{matrix} c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \end{matrix}$$
$$\begin{bmatrix} -1 & -1 & 1 \\ -1 & 1 & 0 \end{bmatrix} \tag{2.57}$$

with RREF

$$\begin{matrix} c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \end{matrix}$$
$$\begin{bmatrix} \mathbf{1} & 0 & -1/2 \\ 0 & \mathbf{1} & -1/2 \end{bmatrix} \tag{2.58}$$

so that *c*-C_4H_8 and *t*-C_4H_8 are key components, and the balance in the nonpivot column reads

$$\Delta n_{C_8H_{16}} = -1/2\Delta n_{c\text{-}C_4H_8} - 1/2\Delta n_{t\text{-}C_4H_8} \tag{2.59}$$

If, however, we retain only the first reaction, overlooking the second, isomerization reaction, the stoichiometric matrix is

$$\begin{matrix} c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \end{matrix}$$
$$\begin{bmatrix} -1 & -1 & 1 \end{bmatrix} \tag{2.60}$$

with RREF

$$\begin{matrix} c\text{-}C_4H_8 & t\text{-}C_4H_8 & C_8H_{16} \end{matrix}$$
$$\begin{bmatrix} \mathbf{1} & 1 & -1 \end{bmatrix} \tag{2.61}$$

Then there is only one key component, *c*-C_4H_8, and the nonpivot columns indicate the balances

$$\Delta n_{t\text{-}C_4H_8} = \Delta n_{c\text{-}C_4H_8} \tag{2.62}$$

and

$$\Delta n_{C_8H_{16}} = -\Delta n_{c\text{-}C_4H_8} \tag{2.63}$$

Comparing this use of the stoichiometric matrix to that of the molecular matrix (Section 2.2), we observe the following:

- When considering the molecular matrix, the element balances (C_t, H_t, etc.) provide us with absolute values. In the current setting of reactions, we can state facts only about changes in the number of molecules of the components, not about their total amounts.

- Because the stoichiometric matrix may contain fewer reactions than the ones generated by the molecular matrix, there may be more balances and fewer key components in the stoichiometric matrix than in the molecular matrix.
- The determination of key components from the stoichiometric matrix depends on more choices than in the case of the molecular matrix, since it involves selecting specific reactions. Therefore, the result of this procedure may be different.
- Again, since the components listed later tend to be expressed in terms of the ones listed earlier, the order of listing should be according to decreasing ease of measurement.

In this application, the stoichiometric matrix was not augmented, and we cannot tell by which linear combination of the original reactions the final result was obtained. Sometimes it is useful to keep track of the original reactions, for example when thermodynamic data such as enthalpy changes are required or for the calculation of equilibrium coefficients.

2.3.2 The Augmented Stoichiometric Matrix

Adding the hypothetical reaction

$$2H_2O + O_2 \rightleftarrows 2H_2O_2 \tag{2.64}$$

to the previous system, Eqs. (2.47), (2.48), results in the stoichiometric matrix

$$\mathbf{S} = \begin{array}{c} \\ \\ \\ \end{array} \begin{array}{c} \begin{array}{cccc} H_2 & O_2 & H_2O & H_2O_2 \end{array} \\ \begin{bmatrix} -2 & -1 & 2 & 0 \\ -1 & -1 & 0 & 1 \\ 0 & -1 & -2 & 2 \end{bmatrix} \end{array} \tag{2.65}$$

Augmenting this matrix with a unit matrix

$$\begin{array}{c} \begin{array}{ccccccc} H_2 & O_2 & H_2O & H_2O_2 & R_1 & R_2 & R_3 \end{array} \\ \begin{bmatrix} -2 & -1 & 2 & 0 & 1 & 0 & 0 \\ -1 & -1 & 0 & 1 & 0 & 1 & 0 \\ 0 & -1 & -2 & 2 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.66}$$

eventually results in the following RREF:

$$\begin{array}{c} \begin{array}{ccccccc} H_2 & O_2 & H_2O & H_2O_2 & R_1 & R_2 & R_3 \end{array} \\ \begin{array}{c} R_1' \\ R_2' \\ R_3' \end{array} \begin{bmatrix} \mathbf{1} & 0 & -2 & 1 & 0 & -1 & 1 \\ 0 & \mathbf{1} & 2 & -2 & 0 & 0 & -1 \\ 0 & 0 & 0 & 0 & \mathbf{1} & -2 & 1 \end{bmatrix} \end{array} \tag{2.67}$$

Fig. 2.2 shows a map of this matrix indicating the subareas. Every row represents a reaction, possibly a zero reaction, in which there are no reactants or products. Here this is the case for R_3', for which the coefficients are read off the third row in the columns representing the reactions: $(1)R_1 + (-2)R_2 + (1)R_3$, where R_1, R_2, and R_3 represent the reactions in, respectively, Eqs. (2.47), (2.48), (2.64). This produces the zero reaction R_3'. The first row in the

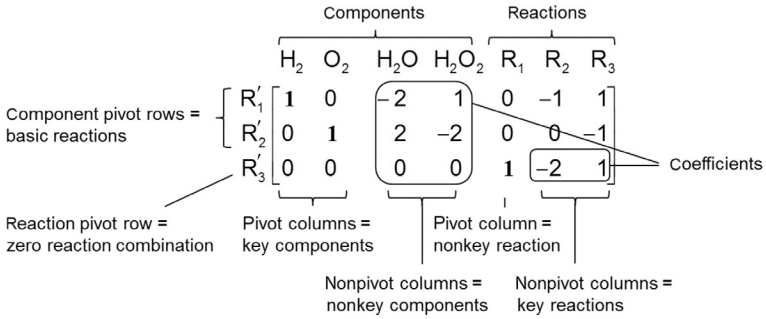

Fig. 2.2
Map of subareas in the RREF of Eq. (2.67).

reaction columns of the RREF corresponds to the reaction R_1', $2H_2O \rightleftarrows H_2 + H_2O_2$, obtained by the combination $(0)R_1 + (-1)R_2 + (1)R_3$. The second row corresponds to the reaction R_2', $2H_2O_2 \rightleftarrows O_2 + 2H_2O$, obtained by the combination $(0)R_1 + (0)R_2 + (-1)R_3$.

The reaction columns in the RREF can be interpreted as follows. If we assign a rate to each of the original reactions, r_1 for R_1, etc., and similarly rates r_1' for R_1', etc., for the new set of reactions, the problem solved by these reaction columns is how to express the original rates r_i in terms of the new ones, r_i'; for instance, the column R_2 indicates that $r_2 = (-1)r_1' + (0)r_2' + (-2)r_3'$.

2.3.2.1 How to find the key and nonkey reactions

The RREF of the augmented stoichiometric matrix indicates that every reaction with a pivot in its column can be written as a linear combination of nonpivot reactions. All entries to the left of the pivot are necessarily zero, so that the row containing the pivot must represent a zero reaction, that is, the pivot reaction added to the reactions to its right multiplied by their entries, yields zero. Hence, the pivot reaction itself is minus the sum of these multiplied reactions, and dependent on them. In this example, since R_3' is the zero reaction and R_1 is the corresponding pivot column, from $(1)R_1 + (-2)R_2 + (1)R_3 = R_3' = 0$, it follows that $R_1 = (2)R_2 + (-1)R_3$.

Contrary to the key components, which occur in pivot columns, the reactions in pivot columns are the nonkey ones. In the present example, the second and third reactions are key (nonpivot) and the first is nonkey (pivot). As before, the ordering of the reactions will influence the choice of key and nonkey reactions, and the earlier a reaction occurs in the ordering, the more likely it is not to be a key reaction. Again, we can count the number of pivot columns in two ways: on the one hand, because the matrix was augmented with a unit matrix, it equals the number of reactions. On the other hand, each pivot column either corresponds to a key component or to a nonkey reaction. Consequently,

$$\text{Number of key components} + \text{number of nonkey reactions} = \text{number of reactions} \qquad (2.68)$$

Subtracting the number of nonkey reactions from both sides yields the fundamental equality

$$\text{Number of key components} = \text{number of key reactions} \tag{2.69}$$

In this example, these numbers are both equal to two; H_2 and O_2 are the key components, and R_2 and R_3 are the key reactions.

The number of balances equals the number of nonkey components as indicated before. They are caused by the reactions, not by element balances. The coefficients by which to multiply the change of the amounts of the key components are read off on the column as before.

2.3.2.2 Enthalpy change and equilibrium coefficients

The RREF can also be used to find the enthalpy change of the reactions given in the rows: if $\Delta_r H_1$ is the enthalpy change of reaction R_1, etc., then the enthalpy change of the reaction in the first row of the RREF, $2H_2O \rightleftarrows H_2 + 2H_2O_2$, is $-\Delta_r H_2 + \Delta_r H_3$ and that of the reaction in the second row, $2H_2O_2 \rightleftarrows O_2 + 2H_2O$, is $-\Delta_r H_3$. The last row, which represents a zero reaction, must have an enthalpy change of zero, so that $0 = \Delta_r H_1 - 2\Delta_r H_2 + \Delta_r H_3$. The latter is an example of how the value of the enthalpy change of a reaction in a pivot column can be written in terms of the values of subsequent columns, in this case $\Delta_r H_1 = 2\Delta_r H_2 - \Delta_r H_3$. This example also illustrates that it is useful to list the reactions with lesser-known thermodynamic properties first.

A similar reasoning can be applied to the logarithms of the equilibrium coefficients $K_{eq,1}$, etc. The equilibrium coefficient of the first reduced reaction must equal $K_{eq,3}/K_{eq,2}$, that of the second $1/K_{eq,3}$, and that of the third, zero reaction leads to $1 = K_{eq,1}K_{eq,3}/K_{eq,2}^2$, or in solved-for form, $K_{eq,1} = K_{eq,2}^2/K_{eq,3}$. In general, the entries in a nonpivot reaction row are (with changed sign) the exponents in the product expression for the corresponding equilibrium coefficient.

2.4 Horiuti Numbers

During modeling of catalytic reactions, often unmeasured quantities enter the equations, for example when surface intermediates are considered. In such cases, one would like to know which are the overall reactions and how many of these reactions are independent.

The overall reaction is obtained by multiplying the reactions with certain coefficients, the so-called Horiuti numbers σ, and then adding the results.

Consider the following set of reactions:

$$Z + H_2O \rightleftarrows ZO + H_2 \tag{2.70}$$

$$ZO + CO \rightleftarrows Z + CO_2 \tag{2.71}$$

where Z is a symbolic element denoting an active catalyst site. What is/are the overall reaction(s)? Again, this problem can be readily solved by using the RREF. Until now, we have stressed that in choosing the order of components occurring in the molecular matrix and in the stoichiometric matrix, it is advisable to list them in order of decreasing ease of measure, so that the components that are difficult to measure can then be expressed in terms of those that are easier to measure.

However, in the Horiuti setting, the purpose is not to express the short-lived intermediates (in this case ZO and Z), which are difficult or even impossible to measure, in terms of the long-lived components (H_2, H_2O, CO, and CO_2), but to find relations between the long-lived components that do not involve the intermediates at all. That is why, in this setting, in order to eliminate the intermediates using an RREF of the stoichiometric matrix, the intermediates must be listed *first*, not last:

$$\begin{matrix} Z & ZO & H_2 & H_2O & CO & CO_2 \end{matrix}$$
$$\begin{bmatrix} -1 & 1 & 1 & -1 & 0 & 0 \\ 1 & -1 & 0 & 0 & -1 & 1 \end{bmatrix} \tag{2.72}$$

Again we augment this matrix with a unit matrix to keep track of the original reactions:

$$\begin{matrix} Z & ZO & H_2 & H_2O & CO & CO_2 & R_1 & R_2 \end{matrix}$$
$$\begin{bmatrix} -1 & 1 & 1 & -1 & 0 & 0 & 1 & 0 \\ 1 & -1 & 0 & 0 & -1 & 1 & 0 & 1 \end{bmatrix} \tag{2.73}$$

The RREF of this matrix is

$$\begin{matrix} Z & ZO & H_2 & H_2O & CO & CO_2 & R_1 & R_2 \end{matrix}$$
$$\begin{bmatrix} \mathbf{1} & -1 & 0 & 0 & -1 & 1 & 0 & 1 \\ 0 & 0 & \mathbf{1} & -1 & -1 & 1 & 1 & 1 \end{bmatrix} \tag{2.74}$$

The rows in which all intermediates have zero entries provide a basis of the overall reactions. Note that if no such rows occur, there is no overall reaction because intermediates are always involved. There can be several different overall reactions; and the same overall reaction may be found by two different sets of Horiuti numbers, but in that case their difference will produce a zero overall reaction $0 \rightleftarrows 0$, which will show up as such in the RREF.

In the present case, we ignore the first row but consider the second: $H_2O + CO \rightleftarrows H_2 + CO_2$, which is the overall reaction. its Horiuti numbers are the coefficients affecting the original reactions R_1 and R_2 in that row, that is, 1 and 1. If we bundle these numbers in a so-called Horiuti matrix, $\boldsymbol{\sigma}$, and consider only the intermediate part $\mathbf{S}_{int}$ of the stoichiometric matrix $\mathbf{S}$,

$$\boldsymbol{\sigma} = \begin{matrix} \\ \mathrm{R}_1 \\ \mathrm{R}_2 \end{matrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix}; \quad \mathbf{S}_{\mathrm{int}} = \begin{matrix} \mathrm{Z} & \mathrm{ZO} \\ \mathrm{R}_1 \\ \mathrm{R}_2 \end{matrix} \begin{bmatrix} -1 & 1 \\ 1 & -1 \end{bmatrix} \tag{2.75}$$

then we have the remarkable matrix product property that $\boldsymbol{\sigma}^{\mathrm{T}}\,\mathbf{S}_{\mathrm{int}} = 0$. Here $\boldsymbol{\sigma}^{\mathrm{T}}$ denotes the transpose of $\boldsymbol{\sigma}$, that is, the matrix obtained by interchanging the rows and columns of $\boldsymbol{\sigma}$, so that here

$$\boldsymbol{\sigma}^{\mathrm{T}} = \begin{matrix} \mathrm{R}_1 & \mathrm{R}_2 \\ \end{matrix} \begin{bmatrix} 1 & 1 \end{bmatrix} \tag{2.76}$$

Example 2.6 Reaction With Three Intermediates

Consider the set of reactions:

$$2\mathrm{Z} + \mathrm{O}_2 \rightleftarrows 2\mathrm{ZO} \tag{2.77}$$

$$\mathrm{Z} + \mathrm{CO} \rightleftarrows \mathrm{ZCO} \tag{2.78}$$

$$\mathrm{ZO} + \mathrm{CO} \rightleftarrows \mathrm{Z} + \mathrm{CO}_2 \tag{2.79}$$

$$\mathrm{ZO} + \mathrm{ZCO} \rightleftarrows 2\mathrm{Z} + \mathrm{CO}_2 \tag{2.80}$$

Determine the overall reaction(s) and Horiuti numbers.

Solution:

The augmented matrix is

$$\begin{matrix} \mathrm{Z} & \mathrm{ZO} & \mathrm{ZCO} & \mathrm{O}_2 & \mathrm{CO} & \mathrm{CO}_2 & \mathrm{R}_1 & \mathrm{R}_2 & \mathrm{R}_3 & \mathrm{R}_4 \end{matrix} \begin{bmatrix} -2 & 2 & 0 & -1 & 0 & 0 & 1 & 0 & 0 & 0 \\ -1 & 0 & 1 & 0 & -1 & 0 & 0 & 1 & 0 & 0 \\ 1 & -1 & 0 & 0 & -1 & 1 & 0 & 0 & 1 & 0 \\ 2 & -1 & -1 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{2.81}$$

with RREF

$$\begin{matrix} \mathrm{Z} & \mathrm{ZO} & \mathrm{ZCO} & \mathrm{O}_2 & \mathrm{CO} & \mathrm{CO}_2 & \mathrm{R}_1 & \mathrm{R}_2 & \mathrm{R}_3 & \mathrm{R}_4 \end{matrix} \begin{bmatrix} \mathbf{1} & 0 & -1 & 0 & 1 & 0 & 0 & 0 & -1 & 1 \\ 0 & \mathbf{1} & -1 & 0 & 2 & -1 & 0 & 0 & -2 & 1 \\ 0 & 0 & 0 & \mathbf{1} & 2 & -2 & -1 & 0 & -2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \mathbf{1} & -1 & 1 \end{bmatrix} \tag{2.82}$$

The first two rows are discarded, since the intermediates occur in these rows, but the third and fourth are kept. The overall reactions are $2\mathrm{CO}_2 \rightleftarrows 2\mathrm{CO} + \mathrm{O}_2$ and the zero reaction; the respective Horiuti numbers are $-1, 0, -2, 0$ and $0, 1, -1, 1$, and the Horiuti matrix is given by

$$\boldsymbol{\sigma} = \begin{matrix} \mathrm{R}_1 \\ \mathrm{R}_2 \\ \mathrm{R}_3 \\ \mathrm{R}_4 \end{matrix} \begin{bmatrix} -1 & 0 \\ 0 & 1 \\ -2 & -1 \\ 0 & 1 \end{bmatrix} \tag{2.83}$$

Fig. 2.3 shows a map of the RREF represented by Eq. (2.82) indicating the subareas.

In practice, the Horiuti numbers of the zero overall reaction are not considered as such, but indicate the freedom that remains in choosing a set of Horiuti numbers: any linear combination of zero-reaction Horiuti numbers can be added to or subtracted from those of any overall reaction. For instance, subtracting them from the overall ones in this case yields −1, −1, −1, −1, or, equivalently, 1, 1, 1, 1 for the reverse overall reaction. Such a set of values is visually more pleasing but cannot be expected to be favored by a mechanical procedure such as the RREF procedure, which instead tries to eliminate as many entries as possible (in all pivot columns corresponding to reactions).

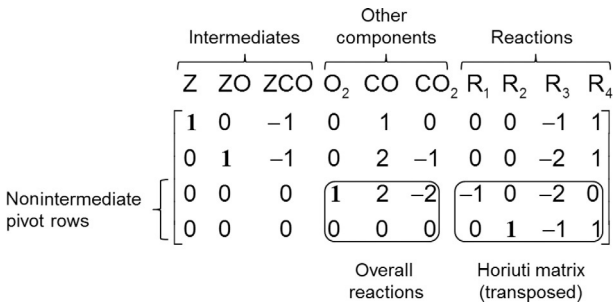

Fig. 2.3
Map of subareas in the RREF of Eq. (2.83).

Example 2.7 Two Types of Active Sites

Consider the set of reactions:

$$A + Z_1 \rightleftarrows AZ_1 \tag{2.84}$$

$$B + Z_2 \rightleftarrows BZ_2 \tag{2.85}$$

$$AZ_1 + BZ_2 \rightleftarrows AB + Z_1 + Z_2 \tag{2.86}$$

Determine the overall reaction(s) and Horiuti numbers.

Solution: The augmented matrix is

$$\begin{array}{c} \begin{array}{cccccccccc} Z_1 & Z_2 & AZ_1 & BZ_2 & A & B & AB & R_1 & R_2 & R_3 \end{array} \\ \begin{bmatrix} -1 & 0 & 1 & 0 & -1 & 0 & 0 & 1 & 0 & 0 \\ 0 & -1 & 0 & 1 & 0 & -1 & 0 & 0 & 1 & 0 \\ 1 & 1 & -1 & -1 & 0 & 0 & 1 & 0 & 0 & 1 \end{bmatrix} \end{array} \tag{2.87}$$

The RREF of this matrix is

$$\begin{array}{c} \begin{array}{cccccccccc} Z_1 & Z_2 & AZ_1 & BZ_2 & A & B & AB & R_1 & R_2 & R_3 \end{array} \\ \begin{bmatrix} \mathbf{1} & 0 & -1 & 0 & 0 & -1 & 1 & 0 & 1 & 1 \\ 0 & \mathbf{1} & 0 & -1 & 0 & 1 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & \mathbf{1} & 1 & -1 & -1 & -1 & -1 \end{bmatrix} \end{array} \tag{2.88}$$

We consider only the third row, and read out the overall reaction as AB⇄A + B with Horiuti numbers −1, −1, −1. In practice, these numbers would be more likely reported equivalently as 1, 1, 1 for the reverse reaction, A + B⇄AB. This is also the form that would have been obtained if the component AB had been listed before A and B instead of after them.

2.5 Summary

Tables 2.1 and 2.2 summarize the characteristic features of the RREFs of the augmented molecular matrix and the augmented stoichiometric matrix.

In any case, the number of key components equals the number of key reactions. If fewer reactions are retained, there will be fewer key components due to surplus balances. The following relations hold

$$\text{Number of key components of molecular matrix} = \text{number of components} - \text{number of key elements}$$

$$\text{Number of key components of stoichiometric matrix} \leq \text{number of key components of molecular matrix}$$

$$\text{Number of key components of stoichiometric matrix} = \text{number of key reactions of stoichiometric matrix}$$

Table 2.1 Characteristics of the RREF of the augmented molecular matrix

Column/Row	Entry	Comment
	Column	
Pivot element Nonpivot element Pivot component Nonpivot component	Key (or independent) element Nonkey (or dependent) element Key component Nonkey component	Read column for coefficients Read column for coefficients expressing amounts
	Row	
With element pivot With component pivot	Pseudoreaction using nonkey components to create a single atom of that element Pseudoreaction producing that component and nonkey components from nonkey components	By retaining only the rows with component pivots and discarding the element columns, the most general stoichiometric matrix for the given set of components is obtained

Table 2.2 Characteristics of the RREF of the augmented stoichiometric matrix

Column/Row	Entry	Comment
Column		
Pivot component	Key component	
Nonpivot component	Nonkey component	Read column for coefficients
Pivot reaction	Nonkey reaction	Read rest of row for coefficients, changing the sign
Nonpivot reaction	Key reaction	
Row		
With component pivot	Basic reaction to create one unit of that component without participation of any other component	
With reaction pivot	Zero reaction combination of the reactions given	

The construction of the augmented stoichiometric matrix to determine the Horiuti numbers has the same general properties in the RREF. Furthermore, the rows not involving any intermediates are of special interest, since they correspond to the overall reactions and exhibit the Horiuti numbers in the augmented columns. In addition, a Horiuti matrix can be constructed as part of the general analysis of the augmented stoichiometric matrix. The equilibrium coefficient of each overall reaction is then given by the product of the equilibrium coefficients of the elementary reactions raised to powers given by the Horiuti numbers.

Appendix. The RREF in Python

Software for computing the RREF of a matrix is readily available in computer algebra packages. For completeness, here we list a script that offers the same functionality, but works in the popular open-source package Python:

```
#!/usr/bin/python
# -*- coding: utf-8 -*-
# These ^^first two lines are comments geared towards Unix implementations
# We need the fractions package for its fast greatest common divisor implementation
import fractions
# rref(a) where a is a matrix represented as a Python list of lists of integers
# will return the RREF of a
def rref(a):
```

```
# The number of rows m is the number of lists in the list
  m = len(a)
# The number of columns n is obtained from the first list; we assume but do not check
# that all lists in a have this same length
  n = len(a[1])
# Initially, no rows have been completed in the sense of having a pivot
  rowsdone = 0
# And no columns have been done either; but we traverse the n columns to work on them
# in this for loop
  for columnsdone in range(n):
# Ignoring the rows that were done, we look for a nonzero entry in column i
      i = rowsdone
      while i < m and a[i][columnsdone] == 0:
          i = i + 1
# Did we find one?
      if i < m:
# Yes, we found a nonzero entry; if it is not yet in uppermost position…
          if i ! = rowsdone:
# … we move it up to there
              for j in range(n):
                  t = a[i][j]
                  a[i][j] = a[rowsdone][j]
                  a[rowsdone][j] = t
# Now the nonzero entry is in pivot position we use it to zero all other entries in its column:
          for i in range(m):
# … we do not zero the pivot itself
              if i ! = rowsdone:
# … but all other entries in its column by multiplying with these coefficients f and g
```

```
            f = a[rowsdone][columnsdone]
            g = a[i][columnsdone]
# … this loop handles the linear combination
            for j in range(n):
                a[i][j] = a[i][j] * f - a[rowsdone][j] * g
# … now we normalize the results by calculating their greatest common divisor, h
        h = 0
        for j in range(n):
            h = fractions.gcd(h, a[i][j])
# … and if it is nonzero, divide by it
        if h != 0:
            for j in range(n):
                a[i][j] = a[i][j] / h
# … this completes the work and we register the new row as being completed
        rowsdone = rowsdone + 1
```

Summarizing: the matrix is assumed to be given as a list of lists of integers. Its dimensions m and n are obtained from this representation, and then the code successively inspects each of the columns to see if it contains a pivot. Because all arithmetic is exact using the built-in unlimited precision integers of Python, the greatest common divisor of every new row is eliminated along the way. Whenever a pivot is found in a column, a new pivot row has been found and the number of rows done is increased accordingly. Finally, the matrix a has been modified to be in RREF form.

Nomenclature

Symbols

a_i	real number
$\Delta_r H_i$	enthalpy change of reaction i (J mol^{-1})
$K_{eq,i}$	equilibrium coefficient of reaction i
$\mathbf{M}$	molecular matrix
$\mathbf{m_A}$	column vector of atomic masses (kg mol^{-1})
$\mathbf{m_M}$	column of molar masses (kg mol^{-1})
n_i	amount of component i (mol)

$P_{i,j}$ entry of matrix **P**
R_i referring to reaction i
R'_i referring to "new" reaction i
r_i rate of reaction i (depends)
r'_i rate of "new" reaction i (depends)
S stoichiometric matrix
$\mathbf{S}_{\text{int}}$ stoichiometric matrix of intermediates
x variable
y variable

Greek symbols

Δ change
ν_i mathematical object
$\boldsymbol{\sigma}$ Horiuti matrix
σ Horiuti number

Subscripts

t total

Superscripts

T transpose

Further Reading

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