ChE classroom

WHAT IS CHEMICAL STOICHIOMETRY?

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A CONSIDERABLE AMOUNT OF literature has arisen in recent years [1-21], which, based on earlier work [22-29], has focussed on the utility of the description of the stoichiometry of closed, chemical systems in terms of linear algebra. This utility, however, does not seem to be appreciated as widely as it should be.* This may be partly because the treatments mostly involve stoichiometry as it impinges on other fields, such as kinetics and thermodynamics, with possibly some resulting confusion over terminology and the nature of the basic questions being resolved by stoichiometry itself.

Here we focus on chemical stoichiometry, *per se*, in a treatment free from kinetic or thermodynamic considerations, in order to focus on these basic questions and their answers. Specifically we provide a means for determining the following:

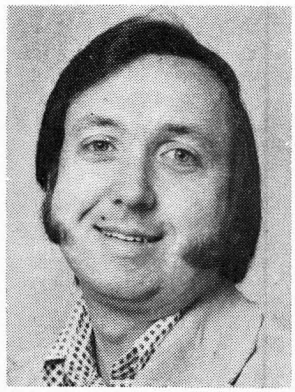
- **the number of stoichiometric degrees of freedom, which is the same as the number of independent chemical equations**
- **the number of components**
- **a permissible set of chemical equations, and**
- **a permissible set of components,**

for a closed system undergoing chemical reaction, which includes allowance for mass transfer between phases. The treatment allows for the presence of inert species and charged species.

It is first necessary to justify the questions and provide unambiguous terminology. The method is then presented and illustrated with several examples.

CHEMICAL STOICHIOMETRY

WE MAY DEFINE CHEMICAL stoichiometry as the constraints placed on the composition of a closed, chemical system by the necessity of conserving the amount of each elemental or atomic species in any physicochemical change in state occurring within the system. These constraints take the form of conservation equations. The difference between the number of variables (e.g., relative mole numbers of species in a basis amount of system) used to describe the composition and the number of such conservation equations may be called the number of stoichiometric degrees of freedom, denoted by F_s. This is then the number of pieces of information or relations among the variables required to determine completely any compositional state from a given one. These pieces of information or relations may come from analytical determinations or from kinetic rate laws or from equilibrium constraints, but, apart from the num-



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*For example, the Chemical Engineers' Handbook [30] has short sections on matrices [30a] and on solutions of linear equations [30b], but the applications mentioned for the former do not include chemical stoichiometry.

ber required, they are outside the scope of stoichiometry. The determination of F_s depends only on the basic concept of conservation of atomic species, and is independent of other concepts and descriptive features, including temperature, pressure, uniformity of a phase, whether or not a system is at equilibrium, and the nature and mechanism of reactions actually taking place.

The stoichiometric description of a chemical system may be in terms of algebraic atom-balance equations, or, more familiarly, in terms of chemical equations. Chemical stoichiometry also enables us to determine the number (R) of such chemical equations and to write a permissible set of them in terms of the reacting species involved. It is important to see the connection between the atom-balance equations and the chemical equations, and this is treated below.

Whether or not chemical equations are used, it is convenient to divide the reacting species into two groups: components and non-components (the latter are sometimes [21] referred to as key components). In terms of chemical equations, the components may be viewed as the "building blocks" for formation of the non-components, one equation being required for each non-component. The minimum number of such building blocks that must be available in order that any compositional state of the system can be realized is the number of components C. Chemical stoichiometry enables us to determine C and a permissible set of components from the species making up the system.

TERMINOLOGY

We define the following terms:

Chemical species: a chemical entity distinguishable from other such entities by (1) its molecular formula; or failing that, by (2) its molecular structure (e.g., to distinguish isomeric forms with the same molecular formula); or failing that, by (3) the phase in which it occurs (e.g., H_2O (l) is a species distinct from $H_2O(g)$); the number of species is N

Chemical substance: a chemical entity distinguishable by (1) or (2) above, but not by (3); thus H_2O (l) and $H_2O(g)$ are the same substance, water

Chemical system: a collection of chemical species and elements denoted by an ordered set of species and an ordered set of the elements contained therein as follows: $[(A_1, A_2, \ldots, A_i, \ldots, A_N), (E_1, E_2, \ldots, E_k, \ldots, E_M)]$, where A_i is the molecular formula, together with structural and phase designations, if necessary, of species i, and E_k is element k; the list of elements includes (1) each isotope involved in isotopic exchange, (2) the protonic charge, p, if ionic species are involved, and (3) a designation, such as $X_1, X_2, \ldots$, for each inert substance in the species list, an inert substance being one that is not involved in the system in the sense of physicochemical change; the number of elements is M

We may define chemical stoichiometry as the constraints placed upon the composition of a closed, chemical system by the necessity of conserving the amount of each elemental or atomic species in any physicochemical change in state occurring within the system.

Formula vector [25], $\mathbf{a}_i$: the vector of subscripts to the elements in the molecular formula of a species; e.g., for $C_6H_5NO_2$, $\mathbf{a} = (6, 5, 1, 2)^T$; in what follows, all vectors are column vectors and superscript T denotes the transpose of a vector

Formula-vector matrix, A: the M x N matrix in which column i is $\mathbf{a}_i$; $\mathbf{A} = (\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_i, \ldots, \mathbf{a}_N)$; A is also the coefficient matrix in the element-balance equations $\sum_i \mathbf{a}_{ki}\mathbf{n}_i = b_k$; $k = 1, 2, \ldots, M$ (see equ. (1), below), where $\mathbf{a}_{ki}$ is the subscript to the kth element in the molecular formula of species i

Species-abundance vector, n: the vector of non-negative real numbers representing the numbers of moles of the species in a basis amount of the chemical system; $\mathbf{n} = (n_1, n_2, \ldots, n_i, \ldots, n_N)^T$; $n_i \geq 0$

Element-abundance vector, b: the vector of non-negative real numbers representing the numbers of moles of elements in a basis amount of the chemical system; the element-balance equations may be written as $\mathbf{An} = \mathbf{b}$; **b** is often specified by the relative amounts of "reactants" for the system

Closed chemical system: one for which all possible **n** satisfy the element-balance equations for some given **b**

Species-abundance-change vector, $\delta\mathbf{n} = \mathbf{n}^{(2)} - \mathbf{n}^{(1)}$: the changes in mole numbers between two states of the closed chemical system; it must satisfy $\mathbf{A}\delta\mathbf{n} = \mathbf{0}$

Feasibility or infeasibility of a closed chemical system refers to whether or not a given **b** is compatible with the species list; e.g., for the system $[(H_2O, H_2, O_2), (H, O); \mathbf{b} = (b_H, b_O)^T]$, $\mathbf{b} = (3, 2)^T$ is feasible, but $\mathbf{b} = (3, 0)^T$ is infeasible; a necessary condition for feasibility is that the rank of the augmented matrix (**A**, **b**), obtained from the system of linear equations $\mathbf{An} = \mathbf{b}$, be equal to the rank of **A**; this is not a sufficient condition because the algebraic theorem on which it is based allows for the possibility of solutions involving negative values for some or all of the n_i; a sufficient condition for infeasibility is that the ranks be unequal; we assume in what follows that all systems are feasible

ATOM-BALANCE EQUATIONS AND CHEMICAL EQUATIONS

In a closed system, the conservation of atomic species can be expressed in a set of atom-balance equations, one for each element:

$$\sum_{i=1}^{N} a_{ki}n_i = b_k; k = 1, 2, \ldots, M. \qquad (1)$$

In vector-matrix notation, this is

$$\mathbf{An} = \mathbf{b}. \qquad (1a)$$

These equations may alternately be written so as to express the change from one compositional state to another. Thus in a closed system,

$$\sum_{i=1}^{N} a_{ki}\delta n_i = 0; k = 1, 2, \ldots, M, \qquad (2)$$

or

$$\mathbf{A}\delta\mathbf{n} = \mathbf{0}. \qquad (2a)$$

The maximum number of linearly independent atom-balance equations, which is the same as the maximum number of linearly independent rows (or columns) in the matrix **A**, is given by the rank of **A** [31].

Before giving the general description, we use an example to illustrate these relations and the connection between them and chemical equations, and also the ideas of components, non-components, and stoichiometric degrees of freedom. Consider first then a closed, reacting system made up of the given species CH_4, S_2, CS_2 and H_2S. Formally, this is represented as

$$[(CH_4, S_2, CS_2, H_2S), (C, H, S)], \qquad (A)$$

where the first set is that of the species, arbitrarily ordered as indicated, and the second set is that of the elements, also arbitrarily ordered.

The atom-balance equations (1) are, for the species and the elements in the order chosen, and with subscripts 1, 2, 3 and 4 referring to CH_4, S_2, CS_2 and H_2S, respectively.

$$\begin{aligned} 1\,n_1 + 0\,n_2 + 1\,n_3 + 0\,n_4 &= b_C, \\ 4\,n_1 + 0\,n_2 + 0\,n_3 + 2\,n_4 &= b_H, \\ \text{and } 0\,n_1 + 2\,n_2 + 2\,n_3 + 1\,n_4 &= b_S. \end{aligned}$$

For a given **b**, we have three equations in four unknowns. We expect to be able to solve for any three n's in terms of the fourth; that is, we have one degree of freedom. Suppose we have one particular solution of these equations (e.g., one corresponding to an initial state), $\mathbf{n}^* = (n_1^*, n_2^*, n_3^*, n_4^*)^T$. For a change from this state to any other state, with composition **n**, on rewriting the above equations in terms of n*, and subtracting one set from the other, we have

$$\left.\begin{aligned} 1\delta n_1 + 0\delta n_2 + 1\delta n_3 + 0\delta n_4 &= 0, \\ 4\delta n_1 + 0\delta n_2 + 0\delta n_3 + 2\delta n_4 &= 0, \\ \text{and } 0\delta n_1 + 2\delta n_2 + 2\delta n_3 + 1\delta n_4 &= 0, \end{aligned}\right\} \qquad (B)$$

where $\delta n_1 = n_1 - n_1^*$, etc.

The first of these, for example, states that the amount of carbon in the closed system is fixed ($\delta n_C = 0$), regardless of how much chemical change occurs. The second and third refer similarly to hydrogen and sulfur, respectively.

The matrix **A** for this system is

$$\mathbf{A} = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 4 & 0 & 0 & 2 \\ 0 & 2 & 2 & 1 \end{bmatrix}, \qquad (C)$$

where the columns are the formula vectors for the species in the order given in specification (A).

Equations (B) can be rearranged to solve for any three δn's in terms of the fourth, e.g., δn_1, δn_2 and δn_3 in terms of δn_4. To accomplish this we reduce **A** to unit matrix form [31a] by elementary row operations [31b]. The "unit matrix form" is represented by [31a]

$$\mathbf{A}^* = \begin{bmatrix} \mathbf{I}_C & \mathbf{Z} \\ \mathbf{0} & \mathbf{0} \end{bmatrix}, \qquad (3)$$

where $\mathbf{I}_C$ is a (C x C) unit matrix, and **Z** is a (C x (N − C)) matrix whose elements may be nonzero. The number C is the rank of **A** and of **A***. The procedure in general is similar to that used in the solution of linear algebraic equations by Gauss-Jordon reduction [31c]. In this particular case, we obtain eventually a matrix **A*** given by

$$\mathbf{A}^* = \begin{bmatrix} 1 & 0 & 0 & \frac{1}{2} \\ 0 & 1 & 0 & 1 \\ 0 & 0 & 1 & -\frac{1}{2} \end{bmatrix}. \qquad (D)$$

Here the unit matrix is (3 x 3) and the rank of **A** is then 3.

Equation (D) implies that equations (B) can be written

$$\left.\begin{aligned} \delta n_1 \qquad\quad + \tfrac{1}{2}\delta n_4 &= 0, \\ \delta n_2 \qquad + \delta n_4 &= 0, \\ \text{and } \delta n_3 - \tfrac{1}{2}\delta n_4 &= 0. \end{aligned}\right\} \qquad (E)$$

In other words the mole-number changes for reaction involving these species can all be related by stoichiometry to one mole-number change, such as that for H_2S, as indicated.

Alternatively we may write Equations (E) as

The stoichiometric description of a chemical system may be in terms of algebraic atom-balance equations, or, more familiarly, in terms of chemical equations.

$$\frac{\delta n_4}{+1} = \frac{\delta n_1}{-\frac{1}{2}} = \frac{\delta n_2}{-1} = \frac{\delta n_3}{+\frac{1}{2}}.$$

Setting these quantities equal to a parameter ξ, and substituting for δn_i, etc. in equations (B), we obtain

$$1(-\tfrac{1}{2})\xi + 0(-1)\xi + 1(\tfrac{1}{2})\xi + 0(1)\xi = 0,$$
$$4(-\tfrac{1}{2})\xi + 0(-1)\xi + 0(\tfrac{1}{2})\xi + 2(1)\xi = 0,$$
$$0(-\tfrac{1}{2})\xi + 2(-1)\xi + 2(\tfrac{1}{2})\xi + 1(1)\xi = 0,$$

and

$$\text{or} \quad -\tfrac{1}{2}\begin{bmatrix}1\\4\\0\end{bmatrix}\xi - 1\begin{bmatrix}0\\0\\2\end{bmatrix}\xi + \tfrac{1}{2}\begin{bmatrix}1\\0\\2\end{bmatrix}\xi + 1\begin{bmatrix}0\\2\\1\end{bmatrix}\xi = \begin{bmatrix}0\\0\\0\end{bmatrix}. \qquad (F)$$

And replacing each vector in (F) by the corresponding molecular formula, we have

$$-\tfrac{1}{2}\,CH_4 - 1\,S_2 + \tfrac{1}{2}\,CS_2 + 1\,H_2S = 0,$$
$$\text{or} \quad \tfrac{1}{2}\,CH_4 + 1\,S_2 - \tfrac{1}{2}\,CS_2 = 1\,H_2S, \qquad (G)$$

or, as we would usually write,

$$CH_4 + 2\,S_2 = CS_2 + 2\,H_2S. \qquad (H)$$

We thus see that a chemical equation is a shorthand way of writing equation (F). Note that the coefficients of the species on the left side of equation (G) are contained in the last column of matrix **A*** in equation (D). Equation (G) is written as though these species are the (three) components or building blocks for the formation of one mole of the non-component H_2S. The components are thus the species represented by the columns in the unit matrix of **A***, the non-component is the species represented by the remaining column apart from the unit matrix, and the coefficients in equation (G) are given in the order (down the last column) in which the components are represented in the first three columns.

(The technique described in this example leading to equations (D) and (G) can also be used to balance an oxidation-reduction equation in inorganic-analytical chemistry, as an alternative to methods such as the half-reaction method using oxidation numbers [32], and analogous ion-electron and valence-electron methods [33], which require additional concepts.)

A slightly more involved system results if we add H_2 to our species list contained in (A). We now have five δn's in the three equations corresponding to (B). An additional column is added to matrix **A**, which becomes

$$\mathbf{A} = \begin{bmatrix}1 & 0 & 1 & 0 & 0\\ 4 & 0 & 0 & 2 & 2\\ 0 & 2 & 2 & 1 & 0\end{bmatrix}. \qquad (I)$$

By means of elementary row operations, this can be reduced to

$$\mathbf{A^*} = \begin{bmatrix}1 & 0 & 0 & \frac{1}{2} & \frac{1}{2}\\ 0 & 1 & 0 & 1 & \frac{1}{2}\\ 0 & 0 & 1 & -\frac{1}{2} & -\frac{1}{2}\end{bmatrix}. \qquad (J)$$

Again the rank of the matrix is 3, which is the number of components C. The same set of components can be used, CH_4, S_2 and CS_2. The difference is that there are now two columns apart from the unit matrix, which implies two independent mole number changes, or stoichiometric degrees of freedom ($F_s = 2$), or chemical equations ($R = 2$). The matrix form (J) provides a solution for each of δn_1, δn_2 and δn_3 in terms of δn_4 and δn_5. Alternatively, it provides the stoichiometric coefficients for the two equations in which one mole of each of the two non-components is "formed" in turn from the three components. Thus from column 4 of (J) for H_2S, as before, we obtain

$$\tfrac{1}{2}\,CH_4 + 1S_2 - \tfrac{1}{2}\,CS_2 = H_2S, \qquad (K)$$
$$\text{or} \quad CH_4 + 2S_2 = CS_2 + 2H_2S, \qquad (K')$$

and from column 5 for H_2, we obtain similarly

$$\tfrac{1}{2}\,CH_4 + \tfrac{1}{2}\,S_2 - \tfrac{1}{2}\,CS_2 = H_2, \qquad (L)$$
$$\text{or} \quad CH_4 + S_2 = CS_2 + 2H_2. \qquad (L')$$

Equations (K′) and (L′) can be said to represent the stoichiometry of this (five-species) reaction system. However, they are not unique; any linear combination of them can be used to replace either one. They carry no necessary implications about the mechanism of reaction(s) occurring, or about "reactants" or "products".

In these two examples no column interchanges were required to obtain the unit matrix form (3). This is because in each case the arbitrary ordering of species was such that the first three (CH_4, S_2, CS_2) formed a permissible set of components, satisfying the necessary condition that each element be contained in at least one molecular formula. If this is not the case, it will be automatically taken care of by the requirement of column interchange(s) to arrive at the unit matrix form (3). For example, in the second case, if the species were arbitrarily ordered as H_2, S_2, H_2S, CS_2, CH_4, the

first three would not form a permissible set of components, since the element C is missing. The procedure provided here would, however, reorder the species automatically by column interchange to provide a permissible set in the unit matrix.

GENERAL TREATMENT

Equations (1) or (1a) are a set of M linear algebraic equations in N unknowns **n** for given **b**. The general solution of this set of equations may be written

$$\mathbf{n} = \mathbf{n}^* + \sum_{j=1}^{R} \nu_j \xi_j, \qquad (4)$$

where $\mathbf{n}^*$ is any particular solution of equations (1); ν_j, j = 1, 2, . . ., R, are a set of linearly independent solutions of the corresponding homogeneous equations (2); and ξ_j are a set of arbitrary real numbers. The number R is given by

$$R = N - \text{Rank } (\mathbf{A}), \qquad (5)$$

and is the maximum number of linearly independent solutions of equations (2).

The chemical significance of equation (4) is that any compositional state of the system **n**, can be written in terms of any particular state $\mathbf{n}^*$ and a linear combination of a set of R linearly independent vectors ν_j obeying equations (2) or (2a).

Equation (4) leads naturally to the concept of chemical equations. To show this, we first use the fact that the vectors ν_j in equation (4) are solutions of equations (2a) and write

$$\mathbf{A}\nu_j = 0 \; ; j = 1, 2, \ldots, R. \qquad (6)$$

A convenient way of writing all R such equations at once is by defining a matrix **N** whose columns are the vectors ν_j; that is,

$$\mathbf{N} = (\nu_1, \nu_2, \ldots, \nu_R). \qquad (7)$$

This enables us to write equations (6) as the single equation

$$\mathbf{A}\,\mathbf{N} = 0. \qquad (6a)$$

The additional vector and matrix quantities in equations (6) and (6a) are defined in general as

Stoichiometric coefficient vector, ν: any nonzero vector of N real numbers satisfying the equation $\mathbf{A}\,\nu = 0$; and

Complete stoichiometric coefficient matrix, N: a matrix whose R columns are stoichiometric vectors with the additional specification that R = N − Rank (A), equation (5).

An alternative way of writing equations (6) explicitly involving the columns of A is

$$\sum_{i=1}^{N} \mathbf{a}_i \nu_{ij} = 0 \; ; j = 1, 2, \ldots, R, \qquad (6b)$$

where ν_{ij} is the stoichiometric coefficient of the ith species in equation j. A set of chemical equations results from equations (6b) when we replace the formula vectors $\mathbf{a}_i$ by their species names, A_i:

$$\sum_{i=1}^{N} A_i \nu_{ij} = 0 \; ; j = 1, 2, \ldots, R. \qquad (8)$$

Equations (K′) and (L′) above together are an illustrative set of equations (8) for the system made up of reacting species CH_4, S_2, CS_2, H_2S and H_2. Thus such equations are a chemical shorthand way of writing the vector equations (6b). By definition a

Complete set of stoichiometric equations is the set of equations (8), where the ν_{ij} form a complete stoichiometric coefficient matrix **N**, as defined above.

In passing, we point out that the parameters ξ_j in equations (4), and the corresponding ξ's in the examples above, are the "extent of reaction" parameters introduced by De Donder [34].

If we define

$$C = \text{Rank } (\mathbf{A}), \qquad (9)$$

the significance of C is as follows: we can solve equations (1) for C n_i's given R n_i's, provided the formula vectors of those C n_i's are linearly independent. This is equivalent to partitioning the species involved into two groups, components (numbering C) and non-components (numbering R), as discussed above, where the components may be regarded as chemical "building blocks" for forming the non-components in chemical equations, one equation being required for each non-component. This leads to the definition of a

Component: one of a set of C species of the chemical system, the number of which is the least number required to make up any compositional state of the system; the formula vectors of these species must have the property that Rank $(\mathbf{a}_1, \mathbf{a}_2, \ldots, \mathbf{a}_C)$ = C, whre C = Rank (A).

GENERAL PROCEDURE

The procedure simultaneously determines rank (A) and a complete set of chemical equations. A Fortran computer program implementing it is available from the authors, and we describe the "hand-calculation" procedure below.

The steps are as follows:

1. Write the formula-vector matrix, A, for the given sys-

We wish to emphasize that the stoichiometric description of a chemical system can be obtained solely from a list of the species and elements involved. It does not require, initially, a set of chemical equations.

tem, with each column identified at the top by the chemical species represented.

2. Form a unit matrix as large as possible in the upper-left portion of A by elementary row operations, and column interchange if necessary; if columns are interchanged, the designation of the species (at the top) must be interchanged also. The final result is a matrix A*.
3. At the end of these steps, the following are established:
   - the rank of the matrix A, which is C, the number of components, is the same as the number of 1's on the principal diagonal of A*;
   - a set of components is given by the C species above the columns of the unit matrix;
   - the maximum number of linearly independent stoichiometric equations is given by R = N − C;
   - the stoichiometric coefficients of a permissible set of these equations are obtained from the columns of the part of the matrix A* to the right of the unit matrix; each column relates to the formation from the components of one mole of the species whose designation heads that column, and the entries in the column refer to the stoichiometric coefficients of the components in the order of the component columns in the unit matrix.

The following illustrations demonstrate the procedure, and also show how inert species and charged species are treated.

Illustration 1. For the system

$$[(CO_2, H_2O, H_2, CH_4, CO, N_2), (H, C, O, X_{N2})],$$

determine F_s, C and R, and a permissible set of chemical equations. Note that N_2 is inert.

Solution: Following the steps outlined above, we have

1.
$$\begin{array}{c} \\ \mathbf{A} = \end{array} \begin{array}{c} (1)\ (2)\ (3)\ (4)\ (5)\ (6) \\ \begin{bmatrix} 0 & 2 & 2 & 4 & 0 & 0 \\ 1 & 0 & 0 & 1 & 1 & 0 \\ 2 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \end{array}$$

Here the numbers at the tops of the columns correspond to the species in the order given, and the rows are in the order of the elements given.

2. The matrix **A** can be put in the following form by means of elementary row operations and column interchanges:

$$\begin{array}{c} \\ \mathbf{A}^* = \end{array} \begin{array}{c} (3)\ (1)\ (2)\ (6)\ (4)\ (5) \\ \begin{bmatrix} 1 & 0 & 0 & 0 & 4 & 1 \\ 0 & 1 & 0 & 0 & 1 & 1 \\ 0 & 0 & 1 & 0 & -2 & -1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{bmatrix} \end{array}$$

3. (i) rank (**A**) = 4 = C;
   (ii) a set of components is H_2, CO_2, H_2O, and the inert N_2;
   (iii) R = N − rank (**A**) = 6 − 4 = 2 = F_s
   (iv) the set of two equations indicated by the entries in the last two columns is

$$4H_2 + 1CO_2 - 2H_2O = CH_4,$$
$$\text{and } 1H_2 + 1CO_2 - 1H_2O = CO,$$

or, as we would usually write them,

$$4H_2 + CO_2 = 2H_2O + CH_4,$$
$$\text{and } H_2 + CO_2 = H_2O + CO.$$

Illustration 2. For the system [35],

$$[(Fe(C_2O_4)^+, Fe(C_2O_4)_2^-, Fe(C_2O_4)_3^{3-}, Fe^{3+}, SO_4^{2-}, HSO_4^-, H^+, HC_2O_4^-, H_2C_2O_4, C_2O_4^{2-}), (Fe, C, O, S, H, p)],$$

determine F_s, C, and R, and a permissible set of chemical equations.

Solution: Following the steps outlined above, we have

1.
$$\begin{array}{c} \\ \mathbf{A} = \end{array} \begin{array}{c} (1)\ (2)\ (3)\ (4)\ (5)\ (6)\ (7)\ (8)\ (9)\ (10) \\ \begin{bmatrix} 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 2 & 4 & 6 & 0 & 0 & 0 & 0 & 2 & 2 & 2 \\ 4 & 8 & 12 & 0 & 4 & 4 & 0 & 4 & 4 & 4 \\ 0 & 0 & 0 & 0 & 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 2 & 0 \\ 1 & -1 & -3 & 3 & -2 & -1 & 1 & -1 & 0 & -2 \end{bmatrix} \end{array}$$

2. The matrix **A** can be put in the following form:

$$\begin{array}{c} \\ \mathbf{A}^* = \end{array} \begin{array}{c} (1)\ (2)\ (5)\ (6)\ (3)\ (4)\ (7)\ (8)\ (9)\ (10) \\ \begin{bmatrix} 1 & 0 & 0 & 0 & -1 & 2 & 0 & -1 & -1 & -1 \\ 0 & 1 & 0 & 0 & 2 & -1 & 0 & 1 & 1 & 1 \\ 0 & 0 & 1 & 0 & 0 & 0 & -1 & -1 & -2 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 1 & 1 & 2 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \end{array}$$

3. (i) rank (**A**) = 4 = C;
   (ii) a set of components is $Fe(C_2O_4)^+(1)$, $Fe(C_2O_4)_2^-(2)$, $SO_4^{2-}(5)$ and $HSO_4^-(6)$;
   (iii) R = N − rank (**A**) = 10 − 4 = 6 = F_s
   (iv) the set of six equations indicated is

$$2Fe(C_2O_4)_2^- = Fe(C_2O_4)^+ + Fe(C_2O_4)_3^{3-}$$
$$2Fe(C_2O_4)^+ = Fe(C_2O_4)_2^- + Fe^{3+}$$
$$HSO_4^- = SO_4^{2-} + H^+$$
$$Fe(C_2O_4)_2^- + HSO_4^- = Fe(C_2O_4)^+ + SO_4^{2-} + HC_2O_4^-$$
$$Fe(C_2O_4)_2^- + 2HSO_4^- = Fe(C_2O_4)^+ + 2SO_4^{2-} + H_2C_2O_4$$
$$Fe(C_2O_4)_2^- = Fe(C_2O_4)^+ + C_2O_4^{2-}$$

In conclusion, we wish to emphasize that the stoichiometric description of a chemical system can be obtained solely from a list of the species and elements involved. It does not require initially a set of chemical equations, no matter how generated. However, if a set of chemical equations is used initially, the set can similarly be tested to determine the maximum number of independent equations [3a]. We do not recommend this approach for a stoichiometric point of view, but rather recommend the approach, as described here, that begins with the list of species and generates a permissible set of equations. □

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ROBERT PERRY DIES

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