Cohen, M. H., and G. Lucovsky, (eds.), "Amorphous and Liquid Semiconductors," *J. Non-Crystal. Sol.*, **8-10** (1972).
Kadoi, H., Y. Tabata, and K. Oshima, "Studies of Transition Phenomena of Some Organic Solids by Electrical Conductivity Measurement at Low Temperature," *J. Phys. Chem.*, **76**, 115 (1972).
Maxwell, J. Clerk, "A Treatise on Electricity and Magnetism," 1st ed., Vol. 1, p. 365, Clarendon, Oxford (1873).
Newby, R. A., R. R. Rothfus, and Kun Li, "Effective Conductivity of Randomly Dispersed Homogeneous Systems," *Chem. Engr. Comm.* (submitted).
Prigogine, I., and R. Dufay, "Chemical Thermodynamics," D. H. Everett, (trans.), p. 254-260, Longmans Green, London (1954).
Robinson, R. A., and R. H. Stokes, "Electrolyte Solutions," 2nd ed., p. 41-42, Butterworths, London (1959).

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Independent Reactions in the Presence of Isomers

In reacting systems, the number of independent chemical reactions, the number of components, and the number of chemical species are generally assumed to be so related that the sum of the first two equals the third. Standard methods of obtaining the number of independent reactions (that is, formation equations or rank of the element-by-species matrix) may fail when chemical isomers appear in reactant streams, product streams, or both. The errors encountered with various types of isomers are delineated in this paper along with corrective measures. The element-by-species matrix is judged to be more suitable as a starting point than formation equations when matrix size and number of manipulations are considered.

J. C. WHITWELL
and
S. R. DARTT

Department of Chemical Engineering
Princeton University
Princeton, New Jersey 08540

SCOPE

Process design requires initial completion of all material and energy balances. The designer must be able to enumerate the numbers of independent material balances, independent reactions, and degrees of freedom. When chemical isomers are present in the reactant and/or product streams, the usual techniques for establishing the quantities may, and frequently will, fail to produce correct results. The objectives of this paper are to provide corrective action to one of the standard techniques so as to eliminate such failures, to incorporate these corrections into a few simple statements which may be added to an existing rank-determining computer program, and to plan the program for use as a subroutine in a more extensive program to calculate the degrees of freedom for any configuration of elements in a process specification.

CONCLUSIONS AND SIGNIFICANCE

When isomers appear in the product and/or reactant streams of a processing unit, the usual methods of relating numbers of species, numbers of components, and numbers of independent reactions may be inapplicable. Two common methods are the establishment of the numbers of independent reactions by the method of formation equations or, alternately, the determination of the number of components as the rank of the element-by-species matrix. In either instance, the total number of chemical species can readily be counted. Then, using the generally accepted relationship that the number of species is equal to the sum of the numbers of components and independent reactions, either method allows the calculation of the missing element in this relationship.

When isomers are present neither one of these methods can be counted upon to give correct results. It is therefore impossible either to establish the number of independent material balances which can be drawn around the unit or to calculate the enthalpy change attributable to the reactions. Since these calculations relating quantities in the external streams of the unit must precede all calculations of internals (that is, design considerations), no systematic analysis of material balances, energy balances, or numbers of independent specifications can be established.

This paper presents a method and a computer program for obtaining correct numbers of independent material balances and chemical reactions, thereby allowing preliminary design calculations to proceed. It is shown that either the element-by-species matrix or the formation equations matrix may constitute a starting point. The former is chosen and emphasized here since it provides a much smaller matrix and a greatly reduced number of matrix manipulations.

Using the computer program developed here, a more extensive program can be written providing the degrees of freedom available to the designer for any processing elements or unit. This latter program, which is the ultimate objective motivating the present work, will be presented at a subsequent date.

S. R. Dartt is with BASF Wyandotte Company, Detroit, Michigan.

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It is often necessary, when a mixture of reactants produces a mixture of products, to specify simultaneously the number of independent reactions and the numbers of species and independent components present. One reason is a need for provision of a definite number of independent material balances for purposes of inventory, control, and design.

This paper is concerned with the calculation of these quantities under any conditions of feeds and products. In most situations, little difficulty is encountered. A number of authors (for example, Smith and Van Ness, 1959; Amundson, 1966; Aris, 1965a, 1965b; Denbigh, 1964) have proposed systematic procedures for accomplishing these enumerations. Aris (1968) has recognized that occasions will arise when the standard procedures are not viable due to the presence of chemical compounds whose empirical formulas are indistinguishable; that is, isomers differing only in stereo or molecular arrangement. He has proposed a method for treating these cases. While his work is beautifully precise, his mathematical nomenclature and sophistication may discourage many readers. A less esoteric solution to the general problem of relating numbers of species, independent material balances, and independent reactions is presented here with a number of illustrations. The adaptation of any standard computer program for determining matrix rank by adding a few conditional statements is a major objective. When the matrices are small (for example, about 5×10 or even slightly larger), the solutions can easily be obtained by hand or with standard calculators.

APPLICATION

For material and energy balances the number of reactions is important, but the mechanistic forms are unimportant. At this stage in design calculations or analysis of performance, interest centers on the externals without regard for internals or mechanism. Since enthalpy changes are independent of the path, it is unimportant in heat balances to know whether the equations written to accomplish the changes between feed and product species are thermodynamically sound—or even possible. All that is required is that a correct number of equations (NRX) be known and that some reactions in this number be postulated to convert all the existing feed species to all the product species.

Amundson (1966), Aris (1965), Denbigh (1971), and Smith and Van Ness (1959) agree that the number of independent reactions is equal to the difference between the number of chemical species present and the number of components. The relationship is usually written

$$NSP - NC = NRX \tag{1}$$

where

NSP is the number of chemical species present,
NC is the number of components, and
NRX is the number of independent chemical reactions required.

The number of components, as defined by various authorities, but quoted directly from Denbigh (1971) is "the minimum number of substances which must be available from the laboratory in order to make up any chosen equilibrium mixture of the system in question." When special constraints are removed (for example, $CaCO_3$ is decomposing in a system originally devoid of CaO and CO_2), the definition is consistent with the maximum number of material balances (NMB) applicable to the system.

The main thrust of this work is as forerunner to a computer program calculating degrees of freedom for any processing element (for example, separations column, reactor, condenser) or any processing unit combining any number of such elements (Dartt, 1972). A consistent system for calculating degrees of freedom in physical and/or chemical systems has been described (Whitwell and Toner, 1969). The first prerequisite in reacting systems is a knowledge of the maximum number of material balances. When the system is devoid of isomers, the number of independent material balances is fairly obviously equal to the unconstrained number of components. It is in this sense that the symbol NC has been used throughout this paper. As noted later, this number cannot change with the introduction of isomeric forms and, under these circumstances, NC is not the number of components in the true thermodynamic sense. As used in this paper, it always means maximum number of independent material balances applicable to the system in question, that is, $NC = NMB$.

When isomeric forms of reactants and/or products exist, Equation (1) will on occasion give incorrect results if either of the following standard procedures is followed:

a. The number of independent reactions (NRX) is obtained by the method of formation reactions (Denbigh 1971; or Smith and Van Ness, 1959); the number of independent material balances (NMB) is then obtained by rearranging Equation (1) to read

$$NC = NSP - NRX \tag{1a}$$

or

b. The number of material balances is equated to the rank of the element-by-species matrix and the number of independent reactions is calculated directly by Equation (1).

When isomeric compounds exist, method a will sometimes fail and method b will always fail. Despite this implied inferiority, method b has been chosen as the basis for the modified procedure. The element-by-species matrix is much smaller than that required by the formation equation matrix and programming is somewhat simplified. The proposed program, in Fortran IV, is included in the appendix.

NUMBERS OF INDEPENDENT EQUATIONS—STANDARD METHODS

As an illustration of the standard rank-determining method (Amundson, 1966), let CO be hydrogenated with the intention of producing methanol (CH_3OH). This primary product is accompanied by a side reaction producing water vapor and methane (CH_4). To determine the number of independent reactions, formulate an element-by-species matrix in which the rows are designated by all the chemical elements in both reactant and product species, while the columns are designated by all species. The matrix for the case stated will then appear as

	CO	H_2	H_2O	CH_4	CH_3OH
C	1	0	0	1	1
H	0	2	2	4	4
O	1	0	1	0	1

If this matrix is reduced to echelon form (that is, the a_{ii} elements in the first three rows are unity or zero and the $a_{ij} = 0$, for $j < i$), the rank will be the sum of the a_{ii}. Rearrangement of rows and/or columns is permissible in the reduction. After the reduction the rank R is equal to NC and

$$NRX = NSP - NC \tag{1}$$

as previously noted.

The echelon form of the matrix in question becomes

	CO	H_2	H_2O	CH_4	CH_3OH
C	1	0	0	1	1
H	0	1	1	2	2
O	0	0	1	−1	0

In this matrix all the a_{ii} elements up to $i = 3$ have values of unity. Consequently the matrix is of maximum rank, three, and the number of components is then 3. Since the number of species is 5, the number of independent equations is 2 [Equation (1)]. The reactions are, of course,

$$CO + 2H_2 = CH_3OH$$

and

$$CO + 3H_2 = CH_4 + H_2O$$

In the formation equations matrix, columns are labeled corresponding to each product, each reactant, and each chemical element involved in any of these compounds. Then each row contains the algebraic coefficients in the chemical equation representing the formation of one of these compounds from its elements. In the simple example just stated:

C	H_2	O_2	CO	CH_3OH	CH_4	H_2O
1	0	½	−1			
1	2	½		−1		
1	2	0			−1	
0	1	½				−1

This matrix is reduced to produce rows which contain zero elements in all columns designated by elements which do not appear as a reactant or product. Reducing the matrix by ordinary Gaussian elimination:

C	O_2	H_2	CO	CH_3OH	CH_4	H_2O
1	½	0	−1			
0	½	1				−1
0	0	3	1		−1	−1
0	0	2	1	−1		

The numbers of reactions and species, as well as the coefficients in the algebraic equations, are represented by the 2×5 matrix on the lower right and located by the 2×2 null matrix on the left; the latter involves zero coefficients on carbon and oxygen since these elements are neither reactants nor products. Thus there are correctly defined 5 species, 3 components, and 2 independent reactions.

This illustration is so simple that all the facts ascertained by the manipulations were obvious from the start. It is included to define the two basic methods when isomeric complications are absent.

PRESENCE OF ISOMERS

The element-by-species method requires modification in situations where isomeric forms are present, are consequently indistinguishable in their empirical formulas, and cannot therefore provide unique column identification (for example, C_2H_6O represents both ethyl alcohol and dimethyl ether; C_7H_8O represents ortho-, meta-, or paracresol).

Three types of isomeric species should be considered:

a. Isomeric species exist on either or both sides of the equation, but their relative concentrations are not goverened by the stoichiometry nor by their proportions in the reactant stream.

2. Isomeric forms react in parallel in identical fashion to form sets of new products whose types are established by, and are parallel in form to, those of the reactants. The original concentrations of reacting isomers may, or may not, govern the relative proportions of the corresponding isomeric product forms.

3. Isomeric forms appear in a reaction and their proportions are governed solely by stoichiometry.

Examples of systems meeting these classifications are presented first. The form of each is then generalized. Finally, rules for applying the method of rank-determining matrix and correcting initial values of *NSP* and *NRX* will be presented. In each case, formation equations will also be discussed.

Class a

1. Benzene (C_6H_6) and H_2 are combined to form a mixture of cyclohexane (C_6H_{12}) and methylcyclopentane (C_6H_{12}).

2. The three isomers of pentane—*n*-pentane (C_5H_{12}), 2-methylbutane (C_5H_{12}), and tetramethylmethane (C_5H_{12})—are each formed from carbon and hydrogen.

In 1, the required two independent reactions can be represented generally as

$$A + B \rightarrow M_0$$
$$A + B \rightarrow M_0'$$

where M_0 designates a substance of specific empirical formula and M_0' represents an isomer of M_0.

In 2, one more independent reaction is required:

$$A + B \rightarrow M_0''$$

where M_0'' is another isomer of M_0.

The relative quantities of M_0, M_0', and M_0'' are determined by the reaction conditions, not by stoichiometry.

This category can be further generalized by supposing that k forms of a compound M_0 were isomerized into n new forms. The number of independent reactions required to represent the $(k + n)$ isomers of the same compound is $(k + n - 1)$, k to change all the isomers fed into one product form and $(n - 1)$ to convert this single product form into the remaining $(n - 1)$ isomeric product species.

Class b

1. Cyclohexane (C_6H_{12}) and methyl cyclopentane (C_6H_{12}) are each chlorinated to a monochlor product.

2. Ortho-, meta-, and paracresols are each sulfonated to the corresponding sulfonates.

In the first, with both reactions complete, the ratio between reactants is maintained in the chlorinated products. In the second, the ratio of the ortho-, meta-, and paraspecies may remain unchanged or may differ in reactant and product mixtures, regardless of completion.

In general, reactions of this sort may be written

$$M_0 + A \rightarrow M_1 + B$$
$$M_0' + A \rightarrow M_1' + B$$
$$\vdots$$
$$M_0^{(n)} + A \rightarrow M_1^{(n)} + B$$

where each M_1 is related to the corresponding M_0 by the stoichiometry of the reaction, and A and B are additional reactants and products. Thus n reactions are performed although the element-by-species matrix will be found to

be capable of representing only one uniquely.

If the ratios M_0/M_0', M_0/M'', ..., $M_0/M_0^{(n)}$ are identical to M_1/M_1', M_1/M_1'', ..., $M_1/M_1^{(n)}$, only n reactions are involved. If the ratios change (for example, the ratio of ortho-to para-species is not the same in product and reactant streams), one can express the interchanges of isomer types either in the reactants or the products, as

$$\begin{array}{lcl} M_0 \rightarrow M_0' & & M_1 \rightarrow M_1' \\ \cdot & & \cdot \\ \cdot & \text{or} & \cdot \\ \cdot & & \cdot \\ M_0 \rightarrow M_0^{(n)} & & M_1 \rightarrow M_1^{(n)} \end{array}$$

Class c

1. Sucrose ($C_{12}H_{22}O_{11}$) hydrolyzes to glucose ($C_6H_{12}O_6$) and fructose ($C_6H_{12}O_6$).
2. A mixture of 1-butene (C_4H_8) and 2-butene (C_4H_8) is hydrogenated to an octane (C_8H_{18}).
3. The same mixture of butenes is isomerized to an octene (C_8H_{16}).

In this situation the ratio of isomers is dependent upon the stoichiometry, not kinetics. The general form is

$$A + B \rightarrow M_0 + M_0' + \ldots + M_0^{(n)}$$

or the reverse. Obviously only one independent reaction is required to produce (or consume) the n isomeric forms.

NUMBER OF SPECIES

In the element-by-species rank-determining matrix only one column should be used for each isomeric form. The inclusion of an additional column for another isomeric or polymeric form will produce a column identical or proportional to one already existing. The rank of the matrix obviously cannot be affected by such additional columns. Clearly, all species will not be uniquely represented and the number of columns understates the true number of species. Consequently the number of unrepresented isomeric or polymeric species must be added to the number with chemically unique formulas, hereafter called the basic number. This basic number will be designated *BNSP* and the corrected total number will be designated *NSP*.

Class a. The total number of species with formula identity is represented by the symbol *IDEMP*; only one of these isomers already appears and therefore (*IDEMP* − 1) must be added to the number of species in the original matrix.

Class b. The total number of isomeric forms existing on both sides of the equations is represented by *ISOMR*. Each isomer exists in several forms, hereafter designated as *TYPES* (for example, ortho-, meta-, etc.) and only one of these *TYPES* is already represented in a column of the matrix. Additional species involved but not represented in the matrix are numerically equal to (*ISOMR*) (*TYPES* − 1). This expression can be derived by hypothesizing a few reactions involving this class of polymers; then the expression (*ISOMR*) (*TYPES* − 1) representing the number of species not represented in the original rank-determining matrix can be obtained by induction.

Class c. The total number of isomeric forms produced by (or consumed in) the single reaction is represented by the value of *SPLIT*; therefore (*SPLIT* − 1) must be added to the number of species in the original matrix.

The rules for obtaining the total number of species (*NSP*) from the basic number (*BNSP*) appearing in the rank-determining matrix program can be summarized algebraically as

$$NSP = BNSP + (IDEMP - 1) + (ISOMR)\,(TYPES - 1) + (SPLIT - 1) \quad (2)$$

In the application of Equation (2), the values of the variables *IDEMP*, *ISOMR*, *TYPES*, and *SPLIT* are each assumed to be unity unless isomers exist, in which case the appropriate numbers of the affected variables are entered. The computer program (Appendix II)* operates differently; it tests for the value of each variable and uses the modifications incorporated into Equation (2) one at a time as it discovers nonzero values.

INDEPENDENT REACTIONS

Now that the number of species has been corrected, it might be thought that Equation (1) could be routinely applied to calculate the number of independent reactions (*NRX*). A few simple examples will prove that such is not always true. In the sulfonation of two isomers of cresol, with no change in the ratio of the two from feed to product streams, the rank is 3 (that is, $NC = 3$), *NSP* has been found to be 6, so that application of Equation (1) would produce

$$NRX = NSP - NC = 6 - 3 = 3,$$

a figure which is incorrect. Further, if three isomers had been involved also with no change in ratios from reactants to products, $NSP = 8$; *NC* remains equal to 3 so that *NRX* is predicted to be 5 when obviously it must be 3. As an additional example, if two isomeric forms exist and if the ratio of the isomers present is changed during the reaction, Equation (1) predicts the correct number of 3 independent reactions, the third reaction accounting for conversion of one isomeric product species to the other.

Rules for the number of independent reactions in each specific case must therefore be formulated. Equation (1) will be used only to establish, from the rank-determining matrix, the number which would exist if, and only if, no isomeric forms exist. This value will be the initial value, *BNRX*, as *BNSP* represents only the number of species with unique empirical formulas.

Class a. Each new isomeric form must require one new independent reaction. For example, if three forms of pentane are synthesized from carbon and hydrogen, 3 independent reactions are required. The rank-determining matrix will define the need for one. In the extreme as previously noted, if k forms of A are reformed into n new forms, $(n + k - 1)$ independent reactions are required, k to change all feed forms into one product form and $(n - 1)$ additional reactions to produce all the other product species from the original hypothetical one. In this extreme case where only one unique formula exists, the rank-determining matrix says that there are no reactions for there is only one unique species, and rank of the matrix (truly a column vector) is one. Thus the initial value of *NRX* as obtained from the rank-determining matrix is zero and must be increased by one less than the number of isomers.

Class b. The correction factor needed to determine the number of independent reactions depends on three variables, the numbers of isomers, the number of types of this isomer (for example, ortho-, meta-, etc.), and the ratio in which the isomeric forms exist in feed and product streams. As was true with NSP, induction, based on a few simple cases, will provide the general form for this factor. With no change in the ratio of isomers from reactants to any of

* See footnote on page 1114.

the product forms, it is necessary to add to the previously determined number of reactions one less than the number of isomer forms multiplied by one less than the number of types. Expressed symbolically, this number is

$$(\text{ISOMR} - 1)\,(\text{TYPES} - 1)$$

If, in addition, the ratios of isomers are different in product and reactant species, another correction must be made. The number of product forms in which the original ratio is not maintained (designated *XCHNG*) multiplied by one less than the number of types present must be added. Symbolically, this number is

$$(\text{XCHNG})\,(\text{TYPES} - 1)$$

Class c. In this case the number of species is increased, as previously detailed, but the number of reactions is unchanged and no corrections to *NRX* are required.

To summarize the corrections, designate the number of reactions obtained from the rank-determining matrix as *BNRX*. Then for the classes of isomers discussed:

$$NRX = BNRX + IDEMP - 1 + (ISOMR - 1)\,(TYPES - 1) + (XCHNG)\,(TYPES - 1) \quad (3)$$

where all symbols have the same meaning as in Equation (2) and *XCHNG* has just been defined in the preceding remarks on Class b isomers.

The remarks on Equation (2) regarding values of unity for *IDEMP*, *ISOMR*, and *TYPES* when no isomers of these classes occur, apply also to Equation (3). The computer program handles each term individually and successively here also.

MORE COMPLICATED SITUATIONS

It is quite apparent that more than one of each isomeric class might be encountered in one process reactor. To provide for these situations, all the correction terms in Equations (2) and (3) can be repeated. For example, one can repeat all the *IDEMP* corrections, labeling them *IDEMP*1, *IDEMP*2, ..., *IDEMPk*; similarly for *ISOMR*, *SPLIT*, *TYPES*, and *XCHNG*. Then statements analogous to *NRX*-0880 through *NRX*-0930 must be repeated in the computer program* for each of these new variables.

SUMMARY

The number of independent reactions occurring in a system free of isomers can be obtained using the rank of a chemical element-by-species matrix and the relationship

$$NRX = NSP - R = NSP - NC.$$

In cases where isomers appear, it is simple to add Equations (2) and (3) so as to arrive at the correct numbers of components, species, and independent reactions. Several examples have been included to illustrate the technique.

The correct value of the number of components (*NC*) can also be obtained from the formation-equation matrix (Denbigh, 1964; Smith and Van Ness, 1959) but only at the expense of considerably greater computer storage, reduction manipulations, and programming complexity.

A number of examples are discussed in detail in Appendix I. The Fortran IV computer program is listed in Appendix II.* Three examples are included in Appendix II, illustrating requisite data decks and resulting output.

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NOTATION

- *BNRX* = number of independent reactions before correcting for the presence of isomeric forms in product and/or reactant streams
- *BNSP* = number of chemical species with unique empirical formulas
- i = 0, 1, 2, ..., as subscript indicating specific isomeric forms
- *IDEMP* = number of isomers in class a (that is, proportions not governed by stoichiometry nor proportions in reactant stream)
- *ISOMR* = number of isomers in class b (that is, reacting identically and in parallel to give parallel forms of products)
- $M_i, M_i', M_i'', \ldots$ = each M_i is related to a corresponding M_j ($j \neq i$) by the stoichiometry of the reaction; each M_i related to each M_i', M_i'', etc., as another isomeric form of the same chemical species
- *NMB* = maximum number of independent material balances
- *NC* = $NMB = R$
- *NRX* = final number of independent chemical reactions
- *NSP* = final number of chemical species present
- *SPLIT* = the number of isomers produced or consumed in a single reaction whose ratio is controlled by the stoichiometry
- *TYPES* = number of types of isomeric forms reacting in parallel
- *XCHNG* = number of parallel product forms in which the original reacting ratio is not maintained

LITERATURE CITED

Amundson, N. R., *Mathematical Methods in Chemical Engineering*, pp. 50-54, Prentice-Hall, Englewood Cliffs, N. J. (1966).

Aris, R., *Introduction to the Analysis of Chemical Reactors*, pp. 10-14, Prentice-Hall, Englewood Cliffs, N. J. (1965).

———., "Prolegomena to the Rational Analysis of Systems," *Arch. Rational Mech. Anal.*, **19**, 81-99 (1965).

———., "Prolegomena to the Rational Analysis of Systems. II. Some Addenda," *ibid.*, **27**, #5, 356-64 (1968).

Dartt, S. R., "Degrees of Freedom in Process Specification," B.S.E. thesis, Princeton Univ., pp. 7-16, 63, 64, 71-94 (1972).

Denbigh, K., *Principles of Chemical Equilibrium*, pp. 171, 187-94, Cambridge Univ. Press, London, England (1971).

Smith, J. M., and H. C. Van Ness, "Introduction to Chemical Engineering Thermodynamics," pp. 42-46, McGraw-Hill, N. Y. (1959).

Whitwell, J. C., and R. K. Toner, *Conservation of Mass and Energy*, pp. 183-209, 455-67, McGraw-Hill, N. Y. (1969).

* See footnote on page 1114.

APPENDIX I

Examples

1. Reaction of ethylene and water.
2. Formation of three isomers of C_5H_{12}.
3. Sulfonation of ortho- and meta-cresol.
4. Sulfonation and butylation of ortho-, meta-, and para-cresol.
5. Same as Example 4 but with the polymer of butylene as an added product.
6. Same as Example 5 with ratios of ortho- and meta-forms changing from reactants to products.
7. Hydrolysis of sucrose to glucose and fructose.

Case 1—Identical Empirical Formulas

Feed species: C_2H_4, H_2O.
Product species: ethyl alcohol and dimethyl ether, both C_2H_6O

Basic matrix:

	H_2O	C_2H_4	C_2H_6O	
O	1	0	1	$NSP = 3$
H	2	4	6	NC = Rank = 2
C	0	2	2	

The last column is obviously the sum of the first two and consequently full rank of three is impossible. Since rank is 2, so is the number of components, and, according to Equation (1), the preliminary estimate ($BNRX$) of the number of independent reactions is one. However, in this case the number of species is not represented fully by the column headings. The true number is 4, and there are 2 independent reactions:

$$C_2H_4 + H_2O = C_2H_5OH$$

$$C_2H_4 + H_2O = CH_3—O—CH_3$$

Here $IDEMP = 2$, one each for C_2H_5OH and $(CH_3)_2O$. Consequently, if one applies Equations (2) and (3),

$$NSP = 3 + IDEMP - 1 = 3 + 2 - 1 = 4$$

$$NRX = 1 + IDEMP - 1 = 2$$

These values, which are correct, would also be obtained by applying the standard method of formation equations (Denbigh, 1964; Smith and Van Ness, 1959). The applicable matrices are

C	H_2	O_2	C_2H_4	H_2O	C_2H_5OH	$(CH_3)_2O$
2	2	0	−1	0	0	0
0	1	1/2	0	−1	0	0
2	3	1/2	0	0	−1	0
2	3	1/2	0	0	0	−1

By Gaussian elimination:

2	2	0	−1	0	0	0
0	1	1/2	0	−1	0	0
0	0	0	1	1	−1	
0	0	0	1	1	0	−1

The 2 × 4 lower, right-hand partition is applicable since none of the elements are present and all their coefficients in these two rows are zero (that is, the lower left 2 × 3 matrix is null). The two equations previously noted are postulated by the coefficients of the 2 × 4, the number of species is 4 and

$$NSP - NRX = NC = 2.$$

The matrix manipulations are obviously somewhat more complex and the size of the matrix is greater than the method proposed in this paper.

Case 2—Identical Empirical Formulas

Feed species: carbon and hydrogen.
Product species: three forms of C_5H_{12}, n-pentane, 2-methylbutane, and tetramethyl methane.

$IDEMP = 3$
Basic matrix:

	C	H_2	C_5H_{12}	
C	1	0	5	Rank = 2
H	0	2	12	

Again the rank is obvious, indicating two components and one reaction.

Now recognizing that pentane existed in three forms ($IDEMP = 3$), and applying Equations (2) and (3), the number of species is really 5 and the number of independent reactions is 3, each being 2 greater than when only one product species was recognized. The formation equations will also give correct values in this relatively trivial case.

Case 3—Chemical Isomers in Both Feed and Product Streams

Feed species: ortho- and meta-cresol, sulfuric acid, water.
Product species: ortho- and meta-cresol sulfonates, water.
$ISOMR = 2$; $TYPES = 2$; $IDEMP = 0$; $XCHNG = 0$.
Basic matrix:

	cresol	acid	sulfonate	water				
O	1	4	4	1	→	1	4	4	4
S	0	1	1	0		0	1	1	0
H	8	2	8	2		0	0	1	−1
C	7	0	7	0		0	0	0	0

Rank and number of components both obviously equal 3, so that, with the four unique species, the number of independent reactions is 4 − 3 = 1. In this instance, one of the cresol forms is disregarded. Thus there should be two reactions, one for each isomer of cresol, and the number of species increases by 2. Applying Equations (2) and (3);

$$NSP = 4 + (ISOMR)\,(TYPES - 1) = 4 + (2)\,(1) = 6$$

$$NRX = 1 + (ISOMR - 1)\,(TYPES - 1) = 2.$$

The method of formation equations requires one equation for the formation from its elements of each reactant and product. Labeling ortho-cresol as OC and its sulfonate as OCS with MC and MCS being the designation for the corresponding meta compounds, the formation reaction matrix is

C	H_2	O_2	S	OC	MC	OCS	MCS	H_2O	Acid
7	4	1/2	0	−1	0	0	0	0	0
7	4	1/2	0	0	−1	0	0	0	0
7	4	2	1	0	0	−1	0	0	0
7	4	2	1	0	0	0	−1	0	0
0	1	1/2	0	0	0	0	0	−1	0
0	1	2	1	0	0	0	0	0	−1

In reduced form, with column designations unchanged:

7	4	1/2	0	−1	0	0	0	0	0
0	1	1/2	0	0	0	0	0	−1	0
0	0	−3/2	−1	0	0	0	0	−1	1
0	0	0	0	1	0	−1	0	−1	1
0	0	0	0	−1	1	0	0	0	0
0	0	0	0	0	1	0	−1	−1	1

Partitioning now shows the lower left 3 × 4 null matrix of elemental forms and the lower right 3 × 6 matrix then implies the three equations:

$$OC + \text{acid} = OCS + H_2O$$

$$MC + \text{acid} = MCS + H_2O$$

$$OC = MC$$

But the last equation is not allowed in this instance and the method consequently predicts an incorrect reaction system. It does however, by Equation (1), predict

$$NC = 6 - 3 = 3,$$

which is correct.

The calculations are again obviously more extensive than the element-by-species method, and some special instructions are required to tell the computer that the equation relating OC and MC is not allowed. The same special instruction was required in the simpler element-by-species procedure.

It is worth noting that the formation matrix equation can be reduced in a number of different ways, producing a different set of chemical equations. For example, in this case the final reduced matrix might be

C	H_2	O_2	S	OC	MC	OCS	MCS	H_2O	Acid
7	4	1/2	0	−1	0	0	0	0	0
0	1	1/2	0	0	0	0	0	−1	0
0	0	3/2	1	1	0	1	0	0	0
0	0	0	0	0	0	1	−1	0	0
0	0	0	0	1	−1	0	0	0	0
0	0	0	0	−1	0	1	0	1	−1

The equations suggested in this lower right hand 3 × 6 matrix are

$$OCS = MCS$$

$$OC = MC$$

$$OCS + H_2O = OC + \text{acid}$$

These equations obviously produce all the desired products and, as indicated earlier, the mechanism is unimportant for heat balances. However, this set of equations is less obviously related to the constraint that ortho- and meta-isomers be reretained in the same ratio in reactants and products.

Case 4—Chemical Isomers in Both Feed and Product Streams (Continued)

Feed species: as in Case 3 but with isobutylene (C_4H_8) added, and all three forms of cresol present, ortho-, meta-, and para-.

Product species: as in Case 3, but with ortho-, meta-, and para-butyl-cresols ($C_{11}H_{16}O$) added.

ISOMR = 3; *TYPES* = 3.

Since the same isomers (for example, the 3 cresols) enter into another reaction producing other isomeric forms, their presence as reactants has already been counted. Thus the value of *ISOMR* is set to 3, the number of chemical species with the same isomeric forms.

Basic matrix:

	cresol	water	acid	sulfonate	butyl cresols	C_4H_8
O	1	1	4	4	1	0
S	0	0	1	1	0	0
H	8	2	2	8	16	8
C	7	0	0	7	11	4

which gives, with some rearrangement of columns,

$$\begin{bmatrix} 1 & 4 & 1 & 1 & 4 & 0 \\ 0 & 1 & 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & -1 & -1 & -1 \\ 0 & 0 & 0 & 1 & 0 & 1 \end{bmatrix} \quad \text{Rank} = NC = 4$$

Applying Equations (2) and (3), where *TYPES* = 3, *ISOMR* = 3, the numbers of species are

$$6 + (3 \times 2) = 12$$

and the independent reactions are

$$2 + (2)\,(2) = 6.$$

Both of these calculations can readily be checked and shown to be correct. Three isomers of cresol are sulfonated and the same three react with butylene, giving 6 reactions. Six species were not listed in the rank matrix, the second two forms of cresol, sulfonate, and butyl cresol.

The formation equation matrix will eventually reduce to give a 6 × 4 null lower left matrix and, obviously, a 6 × 12 lower right hand matrix. The number of species, 12, cannot fail to be correct, but the 8 reactions is incorrect. The 8 reactions might include 6 interchanges between ortho- and meta- and para-forms of cresols, cresol sulfonate and butyl cresols, one equation for action of acid on *one* isomer of cresol, and a final one for the reaction of butene with *one* isomer of cresol. (As previously indicated, other reductions might suggest another consistent set of six reactions.)

Regardless of the reactions indicated,

$$12 - 8 = 4 = NC,$$

which is correct, Apparently the only consistently successful calculation from the formation equation matrix is the number of components. This number is obviously more easily obtained from the element-by-species matrix.

Case 5—Chemical Isomers in Both Feed and Product Streams

Feed species: same as in 4, but only ortho- and meta-forms of cresol.

Product species: same as in 4, but, in addition, the butylene polymerizes and the product can be considered to be a single polymer species (for example, the trimer).

There is no point in listing the element-species matrix, for it must be same as that in Case 4. The polymer column is proportional to the monomer column and cannot change the rank. Thus *NC* remains equal to 4. However, we now have, in addition to *TYPES* = 2, *ISOMR* = 3, an additional complication, *IDEMP* = 2, to account for the polymeric form. Thus, after applying Equations (2) and (3) for both types of isomers, *NSP* = 10 and *NRX* = 5. These numbers may be shown to be correct in the same manner used in previous examples.

These examples could be extended. For instance, the case where dibutyl cresols are also formed is pertinent in this mixture. Then *ISOMR* = 4 while *TYPES* and *IDEMP* remain the same. The answers are obvious and give the correct information from standard use of Equations (2) and (3).

Case 6

Identical conditions as in Case 5 except that we now predict that both isomeric products will be in a ratio different from that pertaining to the ratio in the feed. Then *XCHNG* = 2 and

$$XCHNG\,(\text{TYPES} - 1) = 2.$$

The number of species is unchanged and *NSP* = 10 as before. The number of independent reactions is, however, increased by 2 and *NRX* = 7 instead of the 5 noted in Case 5.

Case 7—Splitting or the Reverse

Only one additional case needs consideration. Here the products contain the same species forms as was true in Case 2, but their origin is obviously, from knowledge of product and reactant species, due to a single, not multiple reaction. An example would be the formation of glucose and fructose from sucrose:

$$C_{12}H_{22}O_{11} + H_2O = C_6H_{12}O_6 + C_6H_{12}O_6$$

sucrose — glucose — fructose

According to previous procedures, only one of the products would appear in the rank matrix.

Basic matrix:

	Water	$C_6H_{12}O_6$	Sucrose
O	1	6	11
C	0	6	12
H	2	12	22

$$\rightarrow \begin{bmatrix} 1 & 6 & 11 \\ 0 & 1 & 2 \\ 0 & 0 & 0 \end{bmatrix}$$

Since rank is 2 and species are 3, the number of independent reactions is 1, which is correct. Since *SPLIT* does not appear in Equation (3), the single reaction predicted by the rank-determining matrix is correct. Also by Equation (2), *NSP* = *BNSP* + 1 = 4, an obviously correct number.

The formation equation method gives the correct values of *NC* and *NSP* but, as so often in previous cases, an incorrect value of *NRX*.

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