Chemical Reaction Engineering - Part 12-A - stoichiometry of multiple reactions

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The purpose

Show how the number of moles of molecular species can vary...
    while keeping the mass of each element constant...
      in simple reactors such as...
        batch, plug flow, and continuous-flow stirred tank reactors,
          and show how to write the minimum number of species balances for reactor design.

Introduction

A set of Independent Stoichiometric Equations (ISE) can be determined solely from a list of the species present. ISE are used in writing necessary and sufficient sets of (a) equilibrium relations and (b) species balances in reactor design. The ISE are purely mathematical expressions, in chemical notation, that represent conservation of elements in simple reactors. They do not show how the species react with each other. Experimental measurements are required in order to identify the "reactions" (also, "reaction pathways"), the physical processes in which the species interconvert, and to write the rate expressions which appear in the species balances. It is important to distinguish between the ISE and the stoichiometric equations that represent reaction pathways.

"Single reaction systems" have only one ISE. The stoichiometric equation that represents the single reaction pathway also serves as the one ISE. The single reaction pathway is reversible and a rate equation for each of the forward and backward reactions can be written. "Multiple reaction systems" have two or more ISE and two or more reaction pathways. The set of stoichiometric equations that represents the reaction pathways often does not equal a set of ISE, and the numbers of equations in the two sets often differ. The mathematical development below applies to both single and multiple reaction systems.

THE LIST OF SPECIES USED AS AN EXAMPLE: N_2, O_2, H_2O, NH_3, NO, NO_2

For the six species in this example, there are three ISE, so this is a multiple reaction system. The determination of a set of ISE for these species is explained below.

For "simple" reactors, the necessary and sufficient number of species balances that need to be written is equal to the number of ISE. Simple reactors are defined here as those in which the relative amounts of species change only by chemical reaction. The "ideal" batch, plug flow, and continuous-flow stirred tank reactors are simple reactors. "Complex" reactors are defined as those in which the relative amounts of reactive species change by an additional mode. One example of a complex reactor is a semi-batch reactor. Another example is a membrane reactor in which H_2 is removed through permeable walls by diffusion. For complex reactors, a greater number of species balances is required.

Brief explanation of the theory

This explanation uses the given list of 6 species used as an example. With the exception of the reactor species balance section and the examples shown, this development follows that of W. R. Smith and

R.W. Missen, "Chemical Reaction Equilibrium Analysis: Theory and Algorithms," John Wiley & Sons, New York, 1982.

The column vector $\mathbf{n} = [\, n_1\ n_2\ n_3\ n_4\ n_5\ n_6\,]'$ represents the number of moles of each species present, where n_1 is the number of moles of N_2, n_2 is moles of O_2, n_3 is moles of H_2O, n_4 is moles of NH_3, n_5 is moles of NO, and n_6 is moles of NO_2. Note the Matlab transpose operator ('). We call $\mathbf{n}$ the "composition vector." For example,

$$\mathbf{n} = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}$$

In general, the same chemical species present in two different phases or two different isomers in a system is counted as two different species. For flow reactors, the numbers of moles can be replaced by molar flow rates (mol/time).

The column vector $\mathbf{b} = [\, b_1\ b_2\ b_3\,]'$ represents the number of moles of each element present. For example,

$$\mathbf{b} = \begin{bmatrix} 5 \\ 6 \\ 5 \end{bmatrix}$$

Here, b_1 is the number of moles of N, b_2 is the number of moles of O, and b_3 is the number of moles of H. For a given closed system, the numbers of moles of the elements remains constant. A "simple reactor" such as a batch, plug flow, or continuous-flow stirred tank reactor can be considered a closed system for this purpose. For flow reactors, the units are moles/time (molar flow rate) rather than moles.

The formula matrix $\mathbf{A}$ is a 3 row (corresponding to the three elements) by 6 column (corresponding to the 6 species) matrix for this example list of species. Each element of matrix $\mathbf{A}$ is the subscript of the corresponding chemical element in the corresponding species.

$$\mathbf{A} = \begin{bmatrix} 2 & 0 & 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 0 & 1 & 2 \\ 0 & 0 & 2 & 3 & 0 & 0 \end{bmatrix}$$

For these example species, the rows of formula matrix $\mathbf{A}$ correspond to the elements N, O, H in that order, top to bottom. The columns of $\mathbf{A}$ correspond to the list of species in this order from left to right: N_2, O_2, H_2O, NH_3, NO, NO_2. The order of species in the columns of $\mathbf{A}$ is arbitrary but must correspond to the order in the rows of vector $\mathbf{n}$, and the order of elements in the rows in $\mathbf{A}$ must agree with the order in the rows of vector $\mathbf{b}$. The species chosen to be on the right side of $\mathbf{A}$ will become the "unique" species in the first set of ISE, as discussed below.

For a given initial composition vector $\mathbf{n}^0$, there will be a fixed number of elements given by the values of the vector $\mathbf{b}$:

$\mathbf{A\,n}^0 = \mathbf{b}$

$$\begin{bmatrix} 2 & 0 & 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 0 & 1 & 2 \\ 0 & 0 & 2 & 3 & 0 & 0 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{bmatrix} = \begin{bmatrix} 5 \\ 6 \\ 5 \end{bmatrix}$$

If the species react and the composition vector changes from the initial $\mathbf{n}^0$, all other values of the vector $\mathbf{n}$ must also contain the same number of elements, so:

$\mathbf{A\,n} = \mathbf{b}$

$$\begin{bmatrix} 2 & 0 & 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 0 & 1 & 2 \\ 0 & 0 & 2 & 3 & 0 & 0 \end{bmatrix} \begin{bmatrix} 0.95 \\ 1.025 \\ 0.85 \\ 1.10 \\ 0.90 \\ 1.10 \end{bmatrix} = \begin{bmatrix} 5 \\ 6 \\ 5 \end{bmatrix}$$

The change in composition, $(\mathbf{n} - \mathbf{n^0})$, can be called the change vector $\Delta\mathbf{n}$.

$$\Delta\mathbf{n} = \begin{bmatrix} -0.05 \\ 0.025 \\ -0.15 \\ 0.10 \\ -0.10 \\ 0.10 \end{bmatrix}$$

The change in the moles of elements associated with $\Delta\mathbf{n}$ must be zero:

$\mathbf{A\,n} - \mathbf{A\,n^0} = \mathbf{A\,(n - n^0)} = \mathbf{A\,\Delta n} = \mathbf{(b - b)} = \mathbf{0}$ (where $\mathbf{0}$ is a null vector)

$$\begin{bmatrix} 2 & 0 & 0 & 1 & 1 & 1 \\ 0 & 2 & 1 & 0 & 1 & 2 \\ 0 & 0 & 2 & 3 & 0 & 0 \end{bmatrix} \begin{bmatrix} -0.05 \\ 0.025 \\ -0.15 \\ 0.10 \\ -0.10 \\ 0.10 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

There can be a semi-infinite number of changes in composition, $\Delta \mathbf{n}$, but all valid ones must maintain conservation of elements and obey the equation $\mathbf{A}\, \Delta \mathbf{n} = \mathbf{0}$. The general solution for this equation is:

$$\mathbf{A}\, (\mathbf{Y}\, \boldsymbol{\xi}) = \mathbf{0}$$

where $\mathbf{Y}$ is called the "complete stoichiometric matrix" and $\boldsymbol{\xi}$ is a column vector whose elements $[\xi_1\ \xi_2\ \xi_3]'$ we call "stoichiometric extents". They are scalar parameters that describe the change in composition of the system. The columns of $\mathbf{Y}$ represent a set of Independent Stoichiometric Equations (ISE) for the system. For this example list of species, $\mathbf{Y}$ has 6 rows corresponding to the 6 species and 3 columns corresponding to the number of degrees of stoichiometric freedom in the system and, thus, the number of ISE (NOT to the 3 elements).

$\mathbf{Y}$ may be obtained with Matlab by using the standard Matlab function "null" with the 'r' option set:

```
Y = null(A,'r')
```

In mathematical terms, $\mathbf{Y}$ is a "rational basis for the null space" of $\mathbf{A}$. A rational basis is provided when the 'r' option is set, vs. the default orthonormal basis.

$$\mathbf{Y} = \begin{bmatrix} -0.5 & -0.5 & -0.5 \\ 0.75 & -0.5 & -1.0 \\ -1.5 & 0.0 & 0.0 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

A method for obtaining $\mathbf{Y}$ with Mathematica is given by Missen, Mims and Saville, "Introduction to Chemical Reaction Engineering and Kinetics," Wiley, 1999. A method for obtaining $\mathbf{Y}$ "by hand" is given in Smith and Missen, 1982 (briefly, row reduction of $\mathbf{A}$, negative of right submatrix becomes top of $\mathbf{Y}$, bottom of $\mathbf{Y}$ is identity submatrix).

For example, a possible set of stoichiometric extents is

$$\boldsymbol{\xi} = \begin{bmatrix} 0.1 \\ -0.1 \\ 0.1 \end{bmatrix}$$

The columns of $\mathbf{Y}$ represent one set of ISE for the system. In a column, the element in a row represents the stoichiometric coefficient corresponding to the species that row represents. Species that increase in amount with an increase in the stoichiometric extent corresponding to that column (stoichiometric equation) have positive stoichiometric coefficients. Species that decrease in amount with an increase in the stoichiometric extent corresponding to that column (stoichiometric equation) have negative stoichiometric coefficients.

Y ξ = Δn

$$
\begin{bmatrix}
-0.5 & -0.5 & -0.5 \\
0.75 & -0.5 & -1.0 \\
-1.5 & 0.0 & 0.0 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
0.1 \\
-0.1 \\
0.1
\end{bmatrix}
=
\begin{bmatrix}
-0.05 \\
0.025 \\
-0.15 \\
0.10 \\
-0.10 \\
0.10
\end{bmatrix}
$$

A (Y ξ) = A Δn = 0

$$
\begin{bmatrix}
2 & 0 & 0 & 1 & 1 & 1 \\
0 & 2 & 1 & 0 & 1 & 2 \\
0 & 0 & 2 & 3 & 0 & 0
\end{bmatrix}
\begin{bmatrix}
-0.05 \\
0.025 \\
-0.15 \\
0.10 \\
-0.10 \\
0.10
\end{bmatrix}
=
\begin{bmatrix}
0 \\
0 \\
0
\end{bmatrix}
$$

A set of ISE is called "Independent" because none of its columns, each of which is an ISE, can be eliminated by elementary linear column operations (e.g., multiplying any column by a constant and adding the result to another column). The set is not unique because other valid sets can be obtained by performing elementary linear column operations on the members of the set.

Often, the number of ISE, i.e., number of degrees of stoichiometric freedom, equals the number of species, S, minus the number of elements, E. This is the case for our example list of 6 species with 3 elements and 6 - 3 = 3 ISE. The exception is when some elements always occur in fixed ratios with other elements. A simple example is the system of butene isomers: n-1-butene, cis-2-butene, and trans-2-butene. There are 3 species and 2 elements: C and H. Since C and H are always in the ratio C_4H_8, there are 2 ISE, since, mathematically, C_4H_8 acts as one "element". The general mathematical result is that the number of ISE, M, equals the number of species minus the rank of the formula matrix **A**, that is M = (S - rank(**A**)) >= (S - E).

This **Y** can be used "as is," or elementary linear column operations can be performed to get another **Y**.

Since,

  Y ξ = Δn = n - n⁰

the final composition in the lab for a given initial composition $\mathbf{n}^0$ and set of stoichiometric extents $[\xi_1\ \xi_2\ \xi_3]'$ can be determined from

$$\mathbf{n} = \mathbf{n}^0 + \mathbf{Y}\, \xi$$

$$
\begin{array}{c}
N_2 \\
O_2 \\
H_2O \\
NH_3 \\
NO \\
NO_2
\end{array}
\begin{bmatrix}
0.95 \\
1.025 \\
0.85 \\
1.10 \\
0.90 \\
1.10
\end{bmatrix}
=
\begin{bmatrix}
1 \\
1 \\
1 \\
1 \\
1 \\
1
\end{bmatrix}
+
\begin{bmatrix}
-0.5 & -0.5 & -0.5 \\
0.75 & -0.5 & -1.0 \\
-1.5 & 0.0 & 0.0 \\
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\begin{bmatrix}
0.1 \\
-0.1 \\
0.1
\end{bmatrix}
$$

When expanded, this gives an equation for the number of moles of each species as a function of the initial moles of that species present, the stoichiometric coefficients for that species in $\mathbf{Y}$, and the stoichiometric extents. Such an expanded set of equations can be called a "stoichiometric table" which is useful when writing species balances. For flow reactors, the numbers of moles can be replaced by molar flow rates (mol/time).

The order of rows in $\mathbf{Y}$ corresponds to the species in the same order as in the columns of A in this example. Each column of $\mathbf{Y}$ defines an ISE:

ISE 1: $0 = -0.5\ N_2 + 0.75\ O_2 - 1.5\ H_2O + NH_3$ % corresponds to column 1 of Y
ISE 2: $0 = -0.5\ N_2 - 0.5\ O_2 + NO$ % corresponds to column 2 of Y
ISE 3: $0 = -0.5\ N_2 - O_2 + NO_2$ % corresponds to column 3 of Y

Rearranging to standard form:

ISE 1: $0.5\ N_2 + 1.5\ H_2O = NH_3 + 0.75\ O_2$
ISE 2: $0.5\ N_2 + 0.5\ O_2 = NO$
ISE 3: $0.5\ N_2 + O_2 = NO_2$

In this set of ISE, NH_3 only appears in ISE 1 (is unique to ISE 1), NO is unique to ISE 2, and NO_2 is unique to ISE 3. Such a set of "unique" species will be obtained when $\mathbf{Y}$ is first derived because of the identity submatrix at the bottom of $\mathbf{Y}$. The unique species will be the M species that were placed on the right side of the formula matrix $\mathbf{A}$ when it was written.

The stoichiometric table for this set of ISE is written by expanding $\mathbf{n} = \mathbf{n}^0 + \mathbf{Y}\, \xi$

$$
\begin{aligned}
n_{N2} &= n^0_{N2} &&- 0.5\ \xi_1 &&- 0.5\ \xi_2 &&- 0.5\ \xi_3 \\
n_{O2} &= n^0_{O2} &&+ 0.75\ \xi_1 &&- 0.5\ \xi_2 &&- \xi_3 \\
n_{H2O} &= n^0_{H2O} &&- 1.5\ \xi_1 \\
n_{NH3} &= n^0_{NH3} &&+ \xi_1 \\
n_{NO} &= n^0_{NO} &&&&+ \xi_2 \\
n_{NO2} &= n^0_{NO2} &&&&&&+ \xi_3 \\
n_{inert} &= n^0_{inert}
\end{aligned}
$$

_____

$n_{total} = n^0_{total}\ - 0.25\ \xi_1 \qquad\qquad - 0.5\ \xi_3$

Note that any _inert species_ must be considered when determining the _total moles_ present.

Writing component balances for reactor design

Since there are three degrees of stoichiometric freedom in this system, we need three independent species balances: three independent equations in the three unknowns ξ_1, ξ_2, ξ_3. The shortest mathematical route to these equations starts by writing a species balance for each of the "unique" species. For a batch reactor:

$dn_{NH3}/dt = d\xi_1/dt = r_{NH3}V$
$dn_{NO}/dt\ = d\xi_2/dt = r_{NO}V$
$dn_{NO2}/dt = d\xi_3/dt = r_{NO2}V$

where V is the volume of the batch reactor.

Next, express the rates in terms of concentrations (mol volume^{-1}) using experimentally determined kinetic information about the reaction pathways. The rate of generation for any species s, r_s, equals the sum of the net rates of generation of that species in all reaction pathways. The dimensions of the rates r_s in the equations shown are (mol time^{-1} volume^{-1}). The reaction pathways are not the same as the ISE, although, in some systems, stoichiometric equations that represent reaction pathways may also serve, in a different function, as ISE.

Now use the stoichiometric table to express the mole terms in the rate expressions in terms of initial composition and the three stoichiometric extents. The equations may be made dimensionless. Finally, the three ordinary differential equations can be integrated. For a nonisothermal batch reactor, they must be integrated along with a coupled energy balance equation. At any time t, the values of the stoichiometric extents can be substituted into the stoichiometric table to determine the amount of each species at that time.

For the 6 species in this example, there are 3 ISE. For "simple" reactors, the necessary and sufficient number of species balances that need to be written is equal to the number of ISE. Simple reactors are defined as those in which the relative amounts of reactive species change only by chemical reaction.

A set of ISE can always be written such that each equation has at least one species that only appears in that equation, i.e., that is "unique" to that equation. Obtaining the matrix **Y** for a system results in a set of ISE with what we term "unique" species. Such a set of "unique" species will be obtained when **Y** is first derived because of the identity submatrix at the bottom of **Y.** The unique species will be the M species that were placed on the right side of the formula matrix **A** when it was written. Different sets of unique species can be obtained by changing the order of the columns in **A** when it is first written. After a stoichiometric matrix **Y** is derived, different sets of ISE for the same list of species can be obtained by linear operations: multiplying one ISE by a constant and adding to another.

Write the species balances for those "unique" species, with the number required equal to M, the number of ISE. Use experimental information about the reaction pathways to write expressions for the rates that appear in the species balances. Then use the stoichiometric table to express the concentrations of each species in terms of the initial composition and the stoichiometric extents. The stoichiometric extents are the unknowns to be found. Note that stoichiometric extents may have negative values. A

solution for the values of the extents can be substituted back into the stoichiometric table to get the amounts of all species present.

Alternatives to writing M species balances for simple reactors are:

(a) write a balance for each species (see p. 298 in H.S. Fogler, "Elements of Chemical Reaction Engineering," 3rd ed., Prentice-Hall, 1999),

(b) write P species balances, where P is the number of reaction pathways and where an "extent" variable has been defined for each of the pathways and a stoichiometric table has been written using those variables (see p. 152 in L.D. Schmidt, "The Engineering of Chemical Reactions, Oxford, 1998, where P here = Schmidt's R).

Summary of steps

1. Write the list of chemical components (species) present in the reactor
2. Write the formula matrix $\mathbf{A}$
3. Get the complete stoichiometric matrix $\mathbf{Y}$, e.g., with Matlab: `Y = null(A,'r')`
4. Write the initial composition vector $\mathbf{n}^0$
5. Write the stoichiometric table
6. For a "simple" reactor, write a balance equation for each of the "unique" species in $\mathbf{Y}$
7. For batch reactors, plug flow reactors, and unsteady-state continuous stirred tank reactors, step 6 produces coupled ordinary differential equations (ODEs)
8. For steady-state continuous stirred tank reactors, step 6 produces coupled algebraic equations
9. Solve the balance equations
10. For ODE integration, at each step, use the current values of the extents and the stoichiometric table to compute reactant and product concentrations for use in the rate equations

Different ISE by linear combination

Different sets of ISE for the same list of species can be obtained by linear operations: multiplying one ISE by a constant and adding to another. This is the set we obtained above:

ISE 1: $0 = -0.5\ N_2 + 0.75\ O_2 - 1.5\ H_2O + NH_3$
ISE 2: $0 = -0.5\ N_2 - 0.5\ O_2 + NO$
ISE 3: $0 = -0.5\ N_2 - O_2 + NO_2$

This is another valid set of ISE, which is obtained by linear operations on the first set:

ISE 1: $0 = N_2 - 1.5\ O_2 + 3\ H_2O - 2\ NH_3$
ISE 2: $0 = -O_2 - 2NO + 2\ NO_2$
ISE 3: $0 = 1.25\ N_2 + 1.5\ H_2O - NH_3 - 1.5\ NO$

This second set does not have a unique species for each equation, since 5 of the 6 species appear in two equations each. Writing the minimum number of component balance equations for a reactor would be more complicated using the second set that it would be using the first set.

The examples on the following two figures are screenshots from the ReactorLab software in Division 5, Lab 1. In the Lab, the initial compositions and the stoichiometric extents can be varied by the user, with the lab automatically computing the final compositions. The first figure uses the first set of ISE and the second figure uses the second set.

Stoichiometry

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on line: -   new msg: -

Div 5 Lab 1   Data Set 1

The species - N_2, O_2, H_2O, NH_3, NO, NO_2 - and how they can change while conserving elements

stoich. extent ξ_1 = 17.1

-66 ▮ 66   set of ISE's chosen for this first example

stoich. extent ξ_2 = 3.96

-66 ▮ 66   ISE 1: 0.5 N_2 + 1.5 H_2O = NH_3 + 0.75 O_2

stoich. extent ξ_3 = 15.84

-66 ▮ 66   ISE 2: 0.5 N_2 + 0.5 O_2 = NO

                  ISE 3: 0.5 N_2 + O_2 = NO_2

Initial composition	Final composition for the stoichiometric extents
33 mol N_2	14.55 mol N_2
33 mol O_2	28.005 mol O_2
33 mol H_2O	7.35 mol H_2O
33 mol NH_3	50.1 mol NH_3
33 mol NO	36.96 mol NO
33 mol NO_2	48.84 mol NO_2

◁ 2 ▷

Stoichiometry

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on line: -   new msg: -

Div 5 Lab 1   Data Set 1

The species - N_2, O_2, H_2O, NH_3, NO, NO_2 - and how they can change while conserving elements

stoich. extent ξ_1 = 16.5

-66 ▮ 66   set of ISE's chosen for this second example

stoich. extent ξ_2 = -1.32

-66 ▮ 66   ISE 1: 2 NH_3 + 1.5 O_2 = N_2 + 3 H_2O

stoich. extent ξ_3 = -29.04

-66 ▮ 66   ISE 2: 2 NO + O_2 = 2 NO_2

                  ISE 3: NH_3 + 1.5 NO = 1.25 N_2 + 1.5 H_2O

Initial composition	Final composition for the stoichiometric extents
33 mol N_2	13.2 mol N_2
33 mol O_2	9.57 mol O_2
33 mol H_2O	38.94 mol H_2O
33 mol NH_3	29.04 mol NH_3
33 mol NO	79.2 mol NO
33 mol NO_2	30.36 mol NO_2

◁ 3 ▷