Put Your Intuition to Rest

WRITE MOLE BALANCES SYSTEMATICALLY

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Conservation laws describe processes in which some quantity of a system is conserved under a particular set of conditions. Material balances are important conservation equations for chemical processes. They consist of two subsets—one that depends on reaction kinetics as well as parameters like the reactor size and type, temperature, pressure, etc., which we call *material balance design equations*, and the other subset that depends **only** on the stoichiometry of the reaction chemistry, which we call *stoichiometric mole balances*, or simply mole balances. Mole balances have been an integral part of the chemical engineering curriculum since its inception. One important use involves estimation of the raw materials consumption and production rates of products in a chemical process. In experiments, mole balances can be used to check the consistency of measured data. They also augment rate equations used in equipment sizing and selectivity modeling.

We develop the analysis for reactions in a continuous process; it is equally applicable to batch processes, however. Consider a system with components A, B, and C. If there are no reactions, the material balances at a steady state are simply

$$\text{Moles of component i per unit time in the outlets} = \text{Moles of component i per unit time in the inlets} \quad i = A, B, C, \qquad (1)$$

Here, the material balances are identical to the mole balances. If reaction A → B +C occurs in the system, at a steady state, the material balances are

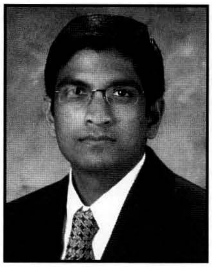
$$\text{Moles of component i per unit time in the outlets} = \text{Moles of component i per unit time in the inlets} + \text{Moles of component i generated per unit time} \quad i = A, B, C, \qquad (2)$$

In this case, however, the material balances involve a generation term that depends on rate expressions and reactor parameters. A subset of Eq. (2) that depends only on the reaction chemistry can be identified from the reaction stoichiometry. The moles of B and C that are produced are equal to the moles of A reacted. Therefore, the mole balances can be written as

$$\left(n_B - n_B^0\right) = \left(n_A^0 - n_A\right) \qquad (3a)$$

$$\left(n_C - n_C^0\right) = \left(n_A^0 - n_A\right) \qquad (3b)$$

where n_i^0 and n_i are the moles of component i per unit time in the inlet and outlet, respectively. This three-component



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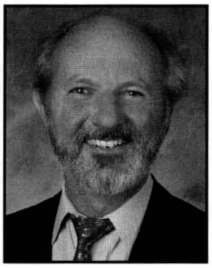

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reaction mixture has two independent mole balances, unlike the case without chemical reactions, which has three independent mole balances. This happens due to the addition of a new variable— the 'extent of reaction' that determines the amount of reaction per unit time in the system. The extent of reaction sets the generation term in the conservation equations and is defined as the ratio of the moles of a component generated in a reaction divided by its stoichiometric coefficient (stoichiometric coefficient is -ve for reactants and +ve for products). The extent of reaction for each component in a given reaction is identical and can either be determined from kinetic models or from experimentally measured data. This paper focuses on the formulation of the mole balances, which are independent of the reaction rates and equipment specifications. If the reaction occurs in a CSTR, Eqs. (2) can be written as

$$n_A = n_A^0 - V\Re \qquad (4a)$$

$$n_B = n_B^0 + V\Re \qquad (4b)$$

$$n_C = n_C^0 + V\Re \qquad (4c)$$

where V is the volumetric holdup of the CSTR, and $\Re$ is the reaction rate in moles reacted per unit volume per unit time (*e.g.*, $\Re = k_1 c_A$). Each equation in (4) is a material balance design equation, and Eqs. (3a,3b) are the stoichiometric mole balances. Equations (3a,3b), along with any one of Eqs. (4a-4c) are equivalent to the three conservation equations shown in Eqs. (4a-4c).

This method not only greatly simplifies the task of deriving mole balances, but also ensures that the mole balances are independent and allows easy determination of the degrees of freedom. The procedure has been applied to other complex reaction chemistries

The task of writing mole balances becomes difficult for complex chemistries with multiple reactions where the extent of each reaction cannot generally be represented in terms of a single component. The extents of reaction depend on variables such as reactor type and size, temperature, reaction kinetics, etc. These variables, however, need not be known in order to formulate mole balances, as shown in the above example. Standard textbooks provide a good collection of examples for developing intuition and skills that are useful in setting mole balances.[1-3] No systematic procedure to formulate mole balances is available to deal with complex chemistries with many reactions. Our aim is to present an algorithmic procedure to eliminate the extents of reaction from the conservation equations to give stoichiometric mole balances. For reaction systems with known components but unknown or incompletely known reaction chemistry, a mathematical procedure to formulate candidate chemistries was published by Aris and Mah[4] and later simplified by Smith and Missen.[5] Aris and Mah's method by itself cannot be used to formulate the mole balances, but can be used in conjunction with the mole balance methodology described here.

Spreadsheets have become tools of choice among undergraduates and many practitioners. Misovich and Biasca[6] describe the use of spreadsheets in teaching mass and energy balances. We will demonstrate the application of the procedure using a commercially available computation program called Mathcad.[7] A Microsoft Excel[8]-based software to formulate the mole balances using the methodology described in the paper is available. The mole balance methodology is presented with useful rules and is illustrated with a few examples.

A SYSTEMATIC METHOD FOR MOLE BALANCES

Systematic treatment of mole balances must provide for an easy and foolproof procedure. The underlying theme of the method is to determine the mole balances expressing the extents in terms of molar flows. Let us consider, as an example, the hydrodealkylation (HDA) of toluene to benzene given by the following simplified scheme of reactions:

$$C_7H_8(T) + H_2(H) \rightarrow C_6H_6(B) + CH_4(M) \qquad (5a)$$

$$2\,C_6H_6(B) \Leftrightarrow C_{12}H_{10}(D) + H_2(H) \qquad (5b)$$

The species present in the reaction system are toluene (C_7H_8), hydrogen (H_2), benzene (C_6H_6), methane (CH_4), and diphenyl ($C_{12}H_{10}$). There are two extents of reaction (one for each reaction), which set the generation or consumption terms. We pick two *reference components* to express the extents of reaction. Once the extents of reaction are written in terms of the reference components, we formulate a mole balance for each of the remaining components. For example, if we choose toluene and diphenyl as the reference components, the extents of reaction are given by

$$\varepsilon_1 = -\left(n_T - n_T^0\right) \qquad \varepsilon_2 = \left(n_D - n_D^0\right) \qquad (6)$$

Writing material balances for the remaining components (benzene, hydrogen, and methane) using Eq. (2), we get

$$n_B = n_B^0 + \varepsilon_1 - 2\varepsilon_2 \qquad (7a)$$

$$n_H = n_H^0 - \varepsilon_1 + \varepsilon_2 \qquad (7b)$$

$$n_M = n_M^0 + \varepsilon_1 \qquad (7c)$$

Substituting for the extents of reaction using Eq. (6), the mole balances are

$$n_B = n_B^0 - \left(n_T - n_T^0\right) - 2\left(n_D - n_D^0\right) \tag{8a}$$

$$n_H = n_H^0 + \left(n_T - n_T^0\right) + \left(n_D - n_D^0\right) \tag{8b}$$

$$n_M = n_M^0 - \left(n_T - n_T^0\right) \tag{8c}$$

Equations (8a-8c) are independent of the reactor type and size, reaction kinetics, etc., and depend only on the reaction chemistry.

An immediate question is, "How can one decide which components to pick as the reference components?" The aim of choosing the reference components is to completely define each extent of reaction. For example, if we choose hydrogen and methane as the reference components, the extents of reaction are

$$\varepsilon_1 = \left(n_M - n_M^0\right) \qquad \varepsilon_2 = \left(n_M - n_M^0\right) + \left(n_H - n_H^0\right) \tag{9}$$

The stoichiometric mole balances can then be written for components toluene, benzene, and diphenyl. There are, however, certain combinations of reference components that will not work. For instance, if we pick toluene and methane as the reference components, the extent for the second reaction cannot be expressed in terms of the mole numbers of toluene and methane since neither of the reference components appears in the second reaction. One can, therefore, choose any combination of reference components so long as the extents of reaction can be explicitly expressed in terms of only those reference components. The number of extents of reaction is equal to the number of independent reactions (R), which is the same as the number of reference components. For a system with c components, one can write c - R mole balances (one for each nonreference component).

GENERAL PROCEDURE FOR MANY REACTIONS

For systems with a few reactions, it is possible to write the extents of reaction in terms of the reference components by inspection. For systems with many reactions, however, the task is not trivial—we use matrix algebra to determine these relationships and a general procedure for any number of reactions and components.

Consider a reaction system consisting of c components undergoing R independent chemical reactions (a block diagram is shown in Figure 1). This process block can contain any complex combination of unit operations or processes, or cells, etc. The inlet to the process is represented by a c-dimensional column vector of inlet molar flow rates for each species, $\mathbf{n}^0$; the outlet of the process is represented by a vector of outlet flow rates for each species, $\mathbf{n}$. The R independent chemical reactions are written as

$$\nu_{1,r}A_1 + \nu_{2,r}A_2 + \cdots + \nu_{c,r}A_c \Leftrightarrow 0 \qquad r = 1, 2, \ldots, R \tag{10}$$

where A_i are the reacting species and $\nu_{i,r}$ is the stoichiometric coefficient of component i in reaction r. The convention used is $\nu_{i,r} > 0$ if component i is a product, and $\nu_{i,r} < 0$ if it is a reactant.

We can write c conservation equations (Eq. 2). The generation term can be expressed in terms of the 'extent of reaction' that relates molar quantities of components. The extent of reaction for reaction r is defined as

$$\varepsilon_r = \frac{\left(n_i - n_i^0\right)r}{\nu_{i,r}} \tag{11}$$

where ε_r is the extent of reaction r, $(n_i - n_i^0)_r$ is the number of moles of component i reacted in reaction r, and $\nu_{i,r}$ is the stoichiometric coefficient of component i in reaction r. The numerical value of the extent of reaction r is the same for each species that participates in reaction r.

Since a component can be present in more than one reaction, we express the overall consumption (production) of reactants (products) in terms of the extents of reaction as

$$n_i - n_i^0 = \sum_{r=1}^{R} \left(n_i - n_i^0\right)_r = \sum_{r=1}^{R} \nu_{i,r}\varepsilon_r \qquad i=1,\ldots,c \tag{12}$$

Therefore

$$n_i - n_i^0 = \boldsymbol{\nu}_i^T \boldsymbol{\epsilon} \qquad i = 1, \ldots, c \tag{13}$$

where n_i^0 is the inlet molar flow-rate of component i, n_i is the outlet molar flow-rate of component i, $\boldsymbol{\nu}_i^T$ is a row vector of dimension R containing the stoichiometric coefficients of component i in each of the R reactions

$$\boldsymbol{\nu}_i^T = \left(\nu_{i,1}, \cdots, \nu_{i,R}\right) \tag{14}$$

and $\boldsymbol{\epsilon}$ is the column vector of the extent of reaction for each of the R reactions

$$\boldsymbol{\epsilon} = \left(\varepsilon_1, \ldots \varepsilon_R\right)^T \tag{15}$$

Equation (13) can be written as

$$\mathbf{n} = \mathbf{n}^0 + \mathcal{V}\boldsymbol{\epsilon} \tag{16}$$

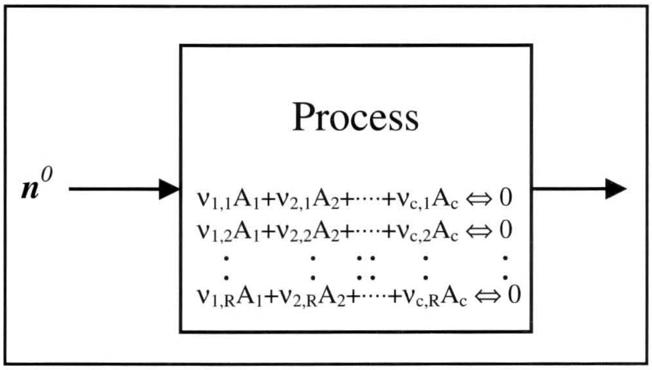


Figure 1. *Schematic of a reaction process.*

where

$$\mathcal{V} = \begin{pmatrix} \nu_{1,1} & \cdots & \nu_{1,R} \\ \vdots & \nu_{i,r} & \vdots \\ \nu_{c,1} & \cdots & \nu_{c,R} \end{pmatrix}$$

is a non-square matrix of dimension (c,R) of the stoichiometric coefficients for the c components in the R reactions, and $\mathbf{n} = (n_1,..., n_c)^T$ is the column vector of dimension c of mole numbers and $\mathbf{n^0} = (n_1{}^0,...,n_c{}^0)^T$ is the column vector of dimension c of the initial mole numbers.

Equations (16) are c conservation equations and have the same structure as those in Eqs. (2). They can be solved once we have specified a value for each of the R extents of reaction. Alternatively, R material balance design equations involving rate expressions, equipment size and type, etc., can be written to determine the extents of reaction. We can, however, eliminate the R extents of reaction from the c conservation equations, giving a set of stoichiometric mole balances that must be obeyed regardless of the constitutive relations or equipment configuration. In this way, we can find a set of balances whose solutions are independent of some of the details arising in rate expressions, etc. This can be accomplished by choosing a subsystem of R equations from among the c equations (16). These define the reference components and the reference equations as

$$\mathbf{n}_{Ref} = \mathbf{n}_{Ref}^0 + \mathcal{V}_{Ref}\boldsymbol{\epsilon} \tag{17}$$

Here,

$$\mathcal{V}_{Ref} = \begin{pmatrix} \nu_{(c-R+1),1} & \cdots & \nu_{(c-R+1),R} \\ \vdots & \nu_{i,r} & \vdots \\ \nu_{c,1} & \cdots & \nu_{c,R} \end{pmatrix} \tag{18}$$

and $\mathbf{n}_{Ref} = (n_{(c-R+1)},...,n_c)^T$ is the column vector of dimension R of mole numbers for the reference components; $\mathbf{n}^0_{Ref} = (n^0_{(c-R+1)},..., n_c{}^0)^T$ is the column vector of dimension R of the inlet molar flow-rates for the reference components. For convenience, the components are numbered so that the reference components are at the end of the column vector of mole numbers. The reference components must be chosen such that the square matrix $\mathcal{V}_{Ref}$ is invertible (this means that the extents of reaction can be explicitly expressed in terms of only the reference components). Any set of reference components that gives an invertible reference matrix is called a "feasible set," and at least one feasible set always exists.

Using Eqs. (17) and (18), the extents of reaction can be expressed as

$$\boldsymbol{\epsilon} = (\mathcal{V}_{Ref})^{-1}(\mathbf{n}_{Ref} - \mathbf{n}_{Ref}^0) \tag{19}$$

Substituting relation (19) in Eq. (13) we get

$$n_i = n_i^0 + \boldsymbol{\nu}_i^{\mathbf{T}}(\mathcal{V}_{Ref})^{-1}(\mathbf{n}_{Ref} - \mathbf{n}_{Ref}^0) \quad i=1,\ldots,c-R \tag{20}$$

Equation (20) is rearranged to write the mole balances in terms of *reaction invariants*, N_i, which take the same values before, during, and after the reaction.[9,10] These are

$$N_i^0 = n_i^0 - \boldsymbol{\nu}_i^{\mathbf{T}}(\mathcal{V}_{Ref})^{-1}\mathbf{n}_{Ref}^0 \quad i=1,\cdots,c-R \tag{21}$$

$$N_i = n_i - \boldsymbol{\nu}_i^{\mathbf{T}}(\mathcal{V}_{Ref})^{-1}\mathbf{n}_{Ref} \quad i=1.....c-R \tag{22}$$

where $\boldsymbol{\nu}_i^{\mathbf{T}}$ is defined in Eq. (14). $N_i{}^0$ are the reaction invariants based on the inlet molar flow rates, and N_i are the reaction invariants based on the outlet molar flow rates. When we equate these reaction invariants, the stoichiometric mole balances for the reacting system are simply

$$N_i^0 = N_i \qquad i = 1,\ldots,c-R \tag{23}$$

We note that the number of stoichiometric mole balances for R independent reactions is c - R and these balances are always linear when written in terms of flow rates. The mole balances in Eq. (23), augmented by R material balance design equations (17), are equivalent to the conservation equations (16). The extents of reaction $\boldsymbol{\epsilon}$, are a function of parameters such as temperature, pressure, molar feed ratios, reactor type, and volume, etc. The mole balances in Eq. (23) are also applicable for reactions in a batch process; the only difference is that $n_i{}^0$ corresponds to the initial number of moles of component i, and n_i corresponds to the number of moles of component i at any given time t.

The reaction invariants are a linear transformation of the number of moles of species to give conservation relationships, which depend only on the reaction chemistry, and these linear transformations correspond exactly to the mole balances.

Rules for Mole Balances

1. *Mole balances are equivalent for any set of the reference components.* The formulation of the mole balances using the reaction invariants methodology requires a choice of a feasible set of reference components that gives an invertible reference matrix. The mole balances for one feasible set of reference components can be obtained by linear combinations of the mole balances for any other feasible set of reference components. Therefore, the mole balances resulting from any feasible set of reference components are equivalent (*i.e.*, they will give the same answers).
2. *Mole balances are unchanged by linear transformations in the reaction chemistry.* For instance, the mole balances for the reaction chemistry (A+B → C+D; 2A → E+D) are equivalent to the mole balances for the chemistry obtained by linear combinations of the reactions (*e.g.*, 2B + E → 2C + D; B + E → A + C).
3. *Mole balances are unchanged by addition of dependent reactions to the reaction chemistry.* For example,

the mole balances for the reaction chemistry (A + B → C + D; 2A → E + D) are equivalent to the mole balances for the reaction chemistry after adding a dependent reaction (2B + E → 2C + D) to the set.

4. *Mole balances for a set of maximum number of independent reactions are equivalent to the element balances.* Any reaction consisting of the given species can be obtained by linear combinations from the set of maximum number of independent reactions for those species. The maximum number of independent chemical reactions can be determined using linear algebra and the chemical formulae of the reaction species.[3] For this case, one can write the element balances (*e.g.*, carbon balance, hydrogen balance, etc.) instead of writing the mole balances.
5. *For any set with less than the maximum number of independent reactions, the element balances are incomplete and form a subset of the mole balances.* In practice, the reaction chemistry is often represented by less than the maximum number of independent reactions.

The mathematical proofs for these rules can be found in Gadewar, *et al.*[10]

Categories of Mole Balances

Case 1: R = 0

For a non-reactive system with c components, the stoichiometric mole balances are given as

$$N_i^0 = N_i \qquad i = 1, \ldots, c \tag{24}$$

From the definitions of the reaction invariants, the mole balances given in Eq. (24) are equivalent to

$$n_i^0 = n_i \qquad i = 1, \ldots, c \tag{25}$$

Equations (25) are the standard mass balances for non-reactive systems with c components.

Case 2: $R = R_{max}$

The mole balances for a system with the maximum number of independent reactions are given as

$$N_i^0 = N_i \qquad i = 1, \ldots, c - R_{max} \tag{26}$$

where R_{max} is the maximum number of independent reactions.[3] These mole balances are equivalent to the element balances.

Case 3: $R < R_{max}$

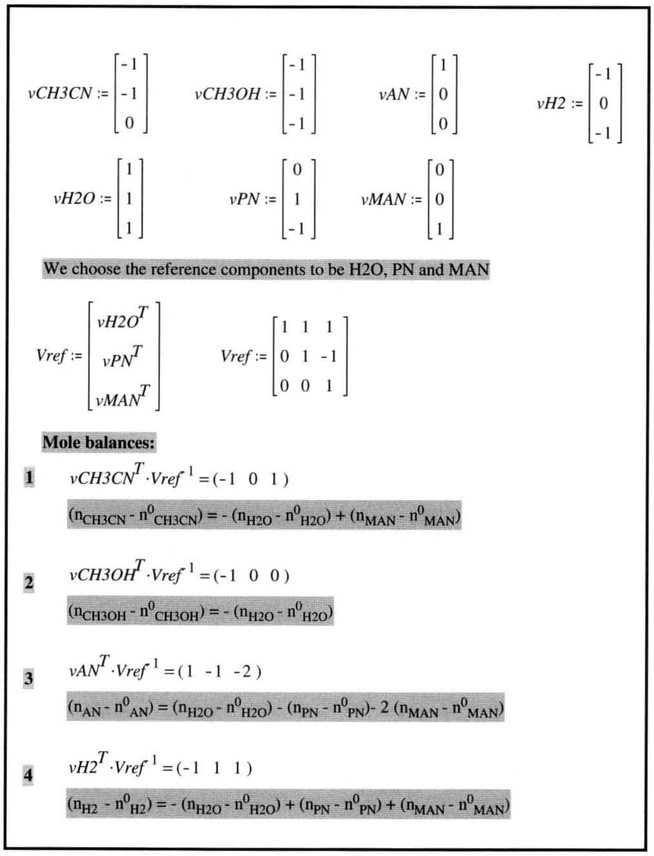
In the case when the number of reactions is less than the maximum number of independent reactions, the mole balances can be written as

$$N_i^0 = N_i \qquad i = 1, \ldots, (c - R_{max}) + r \tag{27}$$

where, $r = R_{max} — R \geq 0$. Therefore, there are more mole balances than independent element balances. For such chemistries, element balances give an *incomplete* set of stoichiometric constraints imposed due to reactions. For example, the hydrodealkylation of toluene to benzene, discussed earlier in the paper, is represented by two reactions instead of $R_{max} = 3$, and a production process to make the pharmaceutical intermediate, 2-methyl pyrazine (described by Gadewar, *et al.*[10]), is represented by six reactions instead of $R_{max} = 7$.

EXAMPLE 1
PRODUCTION OF ACRYLONITRILE

Unsaturated nitriles such as acrylonitrile are important intermediates in the polymer industry. A process for the manufacture of α, β-unsaturated nitriles from methanol over a metal oxide catalyst was published by Kurokawa, *et al.*[11] The species present in the reaction system are: acetonitrile (CH_3CN), methanol (CH_3OH), acrylonitrile (CH_2CHCN or AN), hydrogen (H_2), water (H_2O), propionitrile (CH_3CH_2CN or PN), and methacrylonitrile (C_3H_5CN or MAN). The reactions occurring in the system are



$$vCH3CN := \begin{bmatrix} -1 \\ -1 \\ 0 \end{bmatrix} \quad vCH3OH := \begin{bmatrix} -1 \\ -1 \\ -1 \end{bmatrix} \quad vAN := \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad vH2 := \begin{bmatrix} -1 \\ 0 \\ -1 \end{bmatrix}$$

$$vH2O := \begin{bmatrix} 1 \\ 1 \\ 1 \end{bmatrix} \quad vPN := \begin{bmatrix} 0 \\ 1 \\ -1 \end{bmatrix} \quad vMAN := \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

We choose the reference components to be H2O, PN and MAN

$$Vref := \begin{bmatrix} vH2O^T \\ vPN^T \\ vMAN^T \end{bmatrix} \qquad Vref := \begin{bmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{bmatrix}$$

Mole balances:

1 $vCH3CN^T \cdot Vref^{-1} = (-1 \ \ 0 \ \ 1)$

$(n_{CH3CN} - n^0_{CH3CN}) = -(n_{H2O} - n^0_{H2O}) + (n_{MAN} - n^0_{MAN})$

2 $vCH3OH^T \cdot Vref^{-1} = (-1 \ \ 0 \ \ 0)$

$(n_{CH3OH} - n^0_{CH3OH}) = -(n_{H2O} - n^0_{H2O})$

3 $vAN^T \cdot Vref^{-1} = (1 \ \ -1 \ \ -2)$

$(n_{AN} - n^0_{AN}) = (n_{H2O} - n^0_{H2O}) - (n_{PN} - n^0_{PN}) - 2\,(n_{MAN} - n^0_{MAN})$

4 $vH2^T \cdot Vref^{-1} = (-1 \ \ 1 \ \ 1)$

$(n_{H2} - n^0_{H2}) = -(n_{H2O} - n^0_{H2O}) + (n_{PN} - n^0_{PN}) + (n_{MAN} - n^0_{MAN})$

Figure 2. *Mathcad worksheet for setting mole balances in Example 1. (Shaded areas are text regions.)*

$$CH_3CN + CH_3OH \rightarrow CH_2CHCN + H_2 + H_2O \qquad (28a)$$

$$CH_3CN + CH_3OH \rightarrow CH_3CH_2CN + H_2O \qquad (28b)$$

$$CH_3CH_2CN + CH_3OH \rightarrow C_3H_5CN + H_2 + H_2O \qquad (28c)$$

From Eqs. (21) - (23), the mole balances for the system are $N_i = N_i^0$, or

$$n_i^0 - \boldsymbol{\nu}_i^{\mathbf{T}}\left(\mathcal{V}_{\mathbf{Ref}}\right)^{-1}\mathbf{n}_{\mathrm{Ref}}^0 = n_i - \boldsymbol{\nu}_i^{\mathbf{T}}\left(\mathcal{V}_{\mathrm{Ref}}\right)^{-1}\mathbf{n}_{\mathrm{Ref}} \quad i=1,\ldots,c-R \qquad (29)$$

Degrees of Freedom ($c = 7$, $R = R_{max} = 3$)

There are $2c = 14$ variables and $c - R = 4$ mole balances. Therefore, there are 10 degrees of freedom for solving the mole balances.

Choosing water, propionitrile, and methacrylonitrile as the reference components (any three components can be chosen as the reference components as long as the reference matrix is invertible), the reference matrix is

$$\mathcal{V}_{\mathrm{Ref}} = \begin{pmatrix} 1 & 1 & 1 \\ 0 & 1 & -1 \\ 0 & 0 & 1 \end{pmatrix} \qquad (30)$$

Using Eqs. (28a - 30) , the stoichiometric mole balances after rearrangements are the following system of linear equations:

$$\left(n_{CH_3CN} - n_{CH_3CN}^0\right) + \left(n_{H_2O} - n_{H_2O}^0\right) - \left(n_{MAN} - {}_{MAN}^0\right) = 0 \qquad (31)$$

$$\left(n_{CH_3OH} - n_{CH_3OH}^0\right) + \left(n_{H_2O} - n_{H_2O}^0\right) = 0 \qquad (32)$$

$$\left(n_{AN} - n_{AN}^0\right) - \left(n_{H_2O} - n_{H_2O}^0\right) + \left(n_{PN} - n_{PN}^0\right) + 2\left(n_{MAN} - n_{MAN}^0\right) = 0 \qquad (33)$$

$$\left(n_{H_2} - n_{H_2}^0\right) - \left(n_{H_2O} - n_{H_2O}^0\right) + \left(n_{PN} - n_{PN}^0\right) + \left(n_{MAN} - n_{MAN}^0\right) = 0 \qquad (34)$$

Our methodology systematically identifies the number of independent mole balances, the degrees of freedom, and allows the procedure of writing down the mole balances to be automated. A Mathcad[7] worksheet for determining the above mole balances is shown in Figure 2.

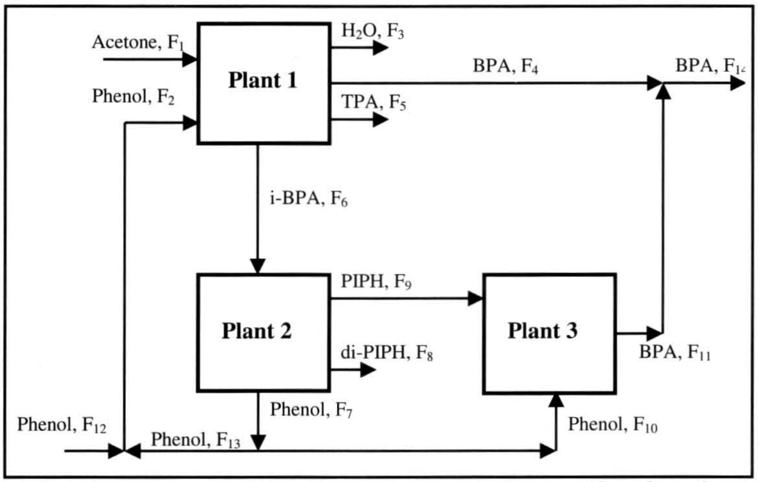


Figure 3. *Process schematic for the manufacture of bisphenol-A.*

We solve the mole balances in Eqs. (31 - 34) using the experimental data from Kurokawa, *et al.*[10] The reaction system feed consists of acetonitrile and methanol. Using a basis of 1 mol/hr of acetonitrile and a molar feed ratio of 10 (methanol to acetonitrile), we have

$$n_{CH_3CN}^0 = 1 \qquad n_{CH_3OH}^0 = 10$$

$$n_{AN}^0 = n_{H_2}^0 = n_{H_2O}^0 = n_{PN}^0 = n_{MAN}^0 = 0$$

From Table 1 of Kurokawa, *et al.*,[10] for a Fe-MgO catalyst, the observed conversion of acetonitrile is 11.2%, and the selectivities to acrylonitrile and propionitrile are 73.2% and 11.6%, respectively. Therefore, $n_{CH3CN} = 0.888$ mol/hr. Since selectivity is defined as the ratio of the moles of product formed to the moles of limiting reactant reacted, we get

$$\frac{n_{AN} - n_{AN}^0}{n_{CH_3CN}^0 - n_{CH_3CN}} = 0.732 \qquad (35)$$

$$\frac{n_{PN} - n_{PN}^0}{n_{CH_3CN}^0 - n_{CH_3CN}} = 0.116 \qquad (36)$$

Therefore, $n_{AN} = 0.08198$ mol/hr and $n_{PN} = 0.013$ mol/hr. Using these values for the 10 degrees of freedom in the mole balances, we solve for the remaining flows (in mol/hr) giving

$$n_{CH_3OH} = 9.87 \qquad n_{H_2} = 0.099$$

$$n_{H_2O} = 0.129 \qquad n_{MAN} = 0.017 \qquad (37)$$

The minimum number of measurements needed from experiments to determine all flows is equal to the degrees of freedom for the mole balances. In case extra measurements are made, they can be used to cross-check the consistency of the experimental data and the proposed chemistry.

The mole balances expressed only in terms of flow rates are linear. Based on the specifications, sometimes the mole balances become nonlinear (*e.g.*, when ratios of flow rates are specified). Westerberg, *et al.*,[12] describe analytical and numerical approaches to solving linear and nonlinear equations. Both the linear equations and nonlinear equations can be solved using standard mathematical computation programs such as Mathcad, Matlab,[13] etc.

EXAMPLE 2
MANUFACTURE OF BISPHENOL-A

The purpose of this example is to write the mole balances for a system consisting of multiple plants, to identify the degrees of freedom, and to solve the balances by satisfying the necessary degrees of freedom. This example is more involved than the first one since it consists of interconnected reaction systems. The process for the manufacture of bisphenol-A consists of multiple plants—each plant either produces the desired product or an intermediate that leads to the desired product. A schematic for the system is given in Figure 3. The flows in and out for each plant are identified in the figure. Each plant can be a complex combination of unit operations, with one or more reaction systems; we will determine the overall input-output balances for the plants.

The species in the reactions are

- phenol
- acetone
- bisphenol-A (BPA)
- isomer of bisphenol-A (i-BPA)
- water
- trisphenol-A (TPA)
- phenyl isopropyl hydroxide (PIPH)
- dimer of PIPH (di-PIPH)

The reactions are

Plant 1 (75°C, P = 15 psia)

$$2\text{ Phenol} + \text{Acetone} \rightarrow \text{BPA} + H_2O \tag{38a}$$

$$2\text{ Phenol} + \text{Acetone} \rightarrow \text{i} - \text{BPA} + H_2O \tag{38b}$$

$$3\text{ Phenol} + 2\text{ Acetone} \rightarrow \text{TPA} + 2\ H_2O \tag{38c}$$

Plant 2 (250°C, P = 4 psia)

$$\text{i} - \text{BPA} \Leftrightarrow \text{Phenol} + \text{PIPH} \tag{39a}$$

$$2\,\text{PIPH} \Leftrightarrow \text{di} - \text{PIPH} \tag{39b}$$

Plant 3 (70°C, P = 15 psia)

$$\text{Phenol} + \text{PIPH} \rightarrow \text{BPA} \tag{40}$$

The aim is to write the overall stoichiometric mole balances for Figure 3. The complete set of mole balances consists of $(c - R)_p$ balances for each plant, p, and species balances for each mixer and splitter.

▶ *Balances Around Plant 1*

There are six components (c = 6) in this plant and three independent reactions (R = 3). The process block represents a complete plant, and if we assume perfect separation of reactants and products within the plant, only the reactants enter the plant and only products leave. Unreacted reactants are recycled within the process block. Therefore, the flow rates of the products, by-products, and intermediates in the inlet, and the reactants in the outlet, of Plant 1 are set to zero. The reactants for this plant are acetone and phenol, while the by-products are water and TPA; i-BPA is an intermediate that is sent to Plant 2, and the desired product is BPA. Three (c - R = 3) independent mole balances can be written for Plant 1. We choose BPA, TPA, and i-BPA as the reference components, and from Eqs. (21-23) the stoichiometric mole balances are

$$F_1 - F_4 - 2F_5 - F_6 = 0 \tag{41a}$$

$$F_2 - 2F_4 - 3F_5 - 2F_6 = 0 \tag{41b}$$

$$F_3 - F_4 - 2F_5 - F_6 = 0 \tag{41c}$$

Note that Eqs (41a,b,c) are obtained by substituting $n^0_{\text{Acetone}} = F_1$, $n_{\text{Acetone}} = 0$, etc. (see Figure 3 for the meaning of each stream).

▶ *Balances around Plant 2*

There are four components (c = 4) and two independent reactions (R = 2) in this plant. Therefore, two (c - R = 2) independent mole balances can be written. In this plant, i-BPA is a reactant, di-PIPH is an unwanted by-product, and PIPH and phenol are intermediates. The flow rates of PIPH, di-PIPH, and phenol in the inlet and the flow rate of i-BPA in the outlet of Plant 2 are zero, since no products, by-products, or intermediates enter the plant and no reactants leave. We choose phenol and di-PIPH as the reference components, and from Eqs. (21-23) the stoichiometric mole balances are

$$F_6 - F_7 = 0 \tag{42a}$$

$$F_7 - 2F_8 - F_9 = 0 \tag{42b}$$

Equations (42a,b) are obtained by substituting $n^0_{\text{i-BPA}} = F_6$, $n_{\text{i-BPA}} = 0$, etc.

▶ *Balances around Plant 3*

There are three components (c = 3) and one independent reaction (R = 1) in this plant. Therefore, two (c - R = 2) independent mole balances can be written. PIPH and phenol are reactants for the plant and BPA is the desired product. The flow rate of BPA in the inlet, and the flow rates of PIPH and phenol in the outlet of Plant 3 are zero. We choose BPA as the reference component, and from Eqs. (21-23), the stoichiometric mole balances are

$$F_9 - F_{11} = 0 \tag{43a}$$

$$F_{10} - F_{11} = 0 \tag{43b}$$

Equations (43a,b) are obtained by substituting $n^0_{\text{PIPH}} = F_9$, $n_{\text{PIPH}} = 0$, etc.

▶ *Mixer-Splitter Balances*

To complete the mole balances, we must write balances for flows that are mixed or split. In Figure 3, F_{12} and F_{13} are mixed to get F_2, F_4 and F_{11} are mixed to get F_{14}, and F_7 is split into F_{10} and F_{13}. Therefore, we write the following balances for mixers and splitters:

$$F_{12} + F_{13} = F_2 \tag{44a}$$

$$F_4 + F_{11} = F_{14} \tag{44b}$$

$$F_7 = F_{10} + F_{13} \tag{44c}$$

▶ ***Solutions***

Equations (41a) to (44c) are the mole balances for the plant complex and must be solved simultaneously. Since they are all linear equations, this is not a difficult task. There are 14 variables and 10 mole balances leaving 4 degrees of freedom. We choose to specify the overall production rate of BPA, F_{14} = 100 mol/hr. Also, from experiments, the selectivity to i-BPA in Plant 1 is $F_6/F_4 = 0.8$, the selectivity to TPA in Plant 1 is $F_5/F_4 = 0.05$, and the selectivity to PIPH in Plant 2 is $F_9/F_6 = 0.95$. The solution of the mole balances yields

$$\begin{gathered} F_1 = 107.95 \quad F_2 = 213.06 \quad F_3 = 107.95 \quad F_4 = 56.81 \\ F_5 = 2.84 \quad F_6 = 45.45 \quad F_7 = 45.45 \quad F_8 = 1.13 \\ F_9 = 43.18 \quad F_{10} = 43.18 \quad F_{11} = 43.18 \\ F_{12} = 210.79 \quad F_{13} = 2.27 \end{gathered} \tag{45}$$

Note that all flow rates have units of mol/hr. To produce 100 mol/hr of BPA, we need 107.95 mol/hr of acetone fresh feed and 210.79 mol/hr of phenol fresh feed. The plant complex produces 107.95 mol/hr of water, 2.84 mol/hr of TPA, and 1.13 mol/hr of di-PIPH as unwanted by-products.

CONCLUSIONS

We have described a systematic method for writing mole balances for complex reaction systems. The procedure is completely general and straightforward to implement. We use a mathematical program to demonstrate the implementation of the procedure. The procedure is applied to the process for manufacturing bisphenol-A, which involves interconnected reaction systems. This method not only greatly simplifies the task of deriving mole balances, but also ensures that the mole balances are independent and allows easy determination of the degrees of freedom. The procedure has been applied to other complex reaction chemistries—for example, manufacture of an anticonvulsant drug CI-1008 consisting of 11 reactions and 27 components.[14]

FURTHER READING

Mole Balances in Biological Systems

Metabolism in living organisms is a chemical phenomenon and is usually represented by sets of chemical equations called metabolic networks. Varma and Palsson[15] published a method of metabolic flux analysis that combines the stoichiometric mole balances together with an optimization algorithm to predict the flow rates of the species in a metabolic network under specified process conditions. The reaction invariants methodology can be used to simplify the formulation of the metabolic flux analysis equations for biological systems. A good review on the basics and applications of metabolic flux analysis can be found in Edwards, *et al.*,[16] and Vallino and Stephanopoulos.[17]

Mole Balances in Conceptual Process Design

Conceptual design generates potentially profitable alternatives based on the laboratory analysis of chemical routes to produce a desired product from available raw materials. During the process of generation and evaluation of alternatives, estimation of the raw materials requirement is essential. The reaction invariants methodology can be used to formulate the overall mole balances for process flowsheets with single or multiple reaction systems. Details on a method used to automate the formulation of mole balances for interconnected reaction systems with application to petrochemical and pharmaceutical production can be found in Gadewar, *et al.*[14]

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