THE DEGREES OF FREEDOM CONCEPT —EXTENDING THE DOMAIN

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The "degrees of freedom" (DOF) concept is a useful tool that can ensure that a mathematical problem is well-posed; that is, the number of equations is equal to the number of unknowns and therefore there will be a unique solution. Degrees of freedom formalisms have thus been widely applied in chemical engineering for the analysis of macroscopic mass balances, controls, and design problems. The exact history of how and when the DOF concept was first introduced into the chemical engineering (ChE) curriculum is somewhat difficult to trace, however, Luyben[1] provides a review of textbooks published prior to 1996 that offered degrees of freedom instruction. A number of seminal examples are worthy of mention here for completeness and to illustrate what appear to be early pedagogical forms of the concept.

In his 3rd Edition (1974) of the now classic text (first published in 1962), *Basic Principles and Calculations in Chemical Engineering*, Himmelblau[2] provided guidelines for counting macroscopic stream variables and determining the degrees of freedom around simple (single) unit operations and "combined units." Himmelblau's treatment of the subject was brief, only six pages, introduced late in the text and without later use, application, or example.

In *Introduction to Material and Energy Balances*, introduced in 1983, Reklaitis[3] also proposed a formalism for counting macroscopic stream variables, and extended the logic to problems involving chemical reactions. In this early treatment of the subject, Reklaitis is true to his formalism and illustrates its application and embraces it repeatedly throughout the text, revisiting the subject and extending the context as the material becomes increasingly complex.

Current instructional texts, however, provide a better basis from which to begin the present discourse. Felder and Rousseau[4] start with the most generalized degrees of freedom statement and then illustrate it for macroscopic balances:

$$n_{df} = n_{unknowns} - n_{independent\ equations} \qquad (1)$$

where n_{df} is the number of degrees of freedom, $n_{unknowns}$ is the number of "unknown variables," and $n_{independent\ equations}$ is the number of "independent equations" relating the unknown variables. A set of guidelines is also provided that define the term "variables" and the sources of equations. The benefit of this approach is that it retains generality and is applicable to virtually any problem assuming that one knows how to identify relevant unknowns (variables) and independent equations (constraints). Such skills, however, take a great deal of time to develop and students at the introductory level have a very difficult time identifying what variables to count, which equations to use, and how to do the accounting.

The practices of both Himmelblau and Reklaitis offered organizational strategies that afforded the students much more formalized approaches to conduct the accounting practices from which one can easily see how to structure specialized DOF frameworks. One such framework is that introduced by Cerro, Higgins, and Whitaker (CHW).[5] The CHW framework is an elegant DOF formalism and accounting practice for steady-state macroscopic material balances that arguably reduces the level of complexity found in earlier approaches to a set of well-defined DOF equations. Stream compositions,

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flows, and reaction rates are explicitly counted among the variables, which they refer to as "Generic Degrees of Freedom (GDF)." Balances, stream constraints (*i.e.*, the sum of the mole fractions for a given stream must be one), reaction rate relationships, and phase equilibrium relationships are counted among the equations, which they call "Generic Specifications and Constraints" (GSC). The remaining information they call "Particular Specifications and Constraints" (PSC), which must include the sum of all things known such as flowrates, compositions, reaction rates, and other specified constraints such as design specifications, *e.g.*, 90% of component "A" must be recovered in product steam "Z." In summary*:

$$GDF = M \times N + M_{Flows} + N_{Rates} \qquad (2.a)$$

$$GSC = M_{StreamConstraints} + N_{Balances} + RRR \qquad (2.b)$$

$$PSC = F + C + N_R + N_{OC} \qquad (2.c)$$

from which

$$DF = GDF - (GSC + PSC) \qquad (2.d)$$

where M is the number of streams, N is the number of molecular species in the systems, M_{Flows} is the number of stream flowrates (M_{Flows}=M, one for each stream), N_{Rates} is the number of reaction rates (N_{Rates}=N, one for each molecular species), $M_{StreamConstraints}$ is the number of stream constraints of the form ($M_{StreamConstraints}$=M, one for each stream), $N_{Balances}$ is the number of mass balances ($N_{Balances}$=N, one for each molecular species), RRR is the number of independent reaction rate relationships that must be written (referred to as "T" by CHW[5]), F is the number of known stream flowrates, C is the number of known stream compositions, N_R is the number of known reaction rates, N_{OC} is the number of "other (or auxiliary) constraints" *e.g.*, the heat balance if required, and DF is the number of degrees of freedom. The following additional rules are also required but not explicitly enumerated by CHW[5] but are implied:

(Rule 1)   No more than N-1 compositions can be specified for any single stream since the molar or mass fraction constraints are explicitly included in this formalism.

(Rule 2)   At least one extensive parameter must be specified, e.g., *the feed flow rate, or else the balances must be written in terms of ratios to eliminate one degree of freedom from the extensive equation set. Alternatively, this can be stated as, "if no extensive parameters are specified, one can choose an extensive 'basis' or solve the problem using an extensive variable as a functional parameter."*

(Rule 3)   The intensive specifications cannot violate the Gibbs Phase Rule when phase equilibrium is assumed.

Clearly, this is a macroscopic formalism based on the way that the GDF are counted; here, only stream compositions and stream flows are included, no compositions within the control volume are included and no internal flows. The constraints, therefore, must also be macroscopic forms and since stream constraints are imposed, the numbered material balance constraints (N) must cut through the control volume boundary at discrete "streams." This formalism is effective, efficient, and robust for steady-state macroscopic mass balances that may or may not involve phase equilibrium and chemical changes (reactions).

The overarching conclusion, however, that one might draw from these historical and contemporary examples and others is that teaching of the degrees of freedom concept in the chemical engineering curriculum has been limited to the macroscopic domain. This, however, does not prohibit the extension of such to problems involving microscopic balances. Luyben states that:

"Conceptually, the determination of the… degrees of freedom is a simple job of subtracting the number of chemical and physical equations… from the … number of variables…. However,… it is quite easy to not do the accounting precisely…. Equations can be written that are not independent. Variables can be forgotten…. "

Although Luyben was treating steady-state problems, his statement is equally, and even more so, true for the dynamic problem and for problems involving microscopic as well as macroscopic balances. Here, the "macroscopic balance" is defined as an integral or integrated form that describes the balance around the entire process and the "microscopic balance" as the space or space and time distributed-parameter differential form, in keeping with the definitions of Bird, et al.[6] and others. Yet, internal and/or microscopic variables are typically not explicitly counted in DOF formalisms or are hidden by implied assumptions such as the well-mixed condition or equilibrium. And, while there are various treatments of the subject, they are generally targeted for specific applications such as solving macroscopic balances, identifying control DOF, or for assisting in design optimization. In all cases, internal and microscopic details are masked by assumptions or control volume definitions and associated formalism rules.

The following discourse is an alternative approach suggested by the author that "extends the domain" of applicability by including internal and microscopic balance variables and which builds off of his previously published work that illustrates the use of the DOF concept across the chemical engineering (CHE) curriculum.[7] While the prior effort illustrates the application of the CHW formalism, the present work transforms the CHW formalism into an extended concept applicable to closed systems and many dynamic situations.

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*   *The notation used here was embellished to add clarity and is different in some ways from that given by CHW.[5]*

OBSERVATIONS

Once these macroscopic DOF formalisms are internalized (understood), students can typically apply any of them to steady-state problems with ease and effectiveness. Why not then use the concept to likewise facilitate the solution of more complex forms of problems, *e.g.*, batch processes (closed systems, refer to Figures 1a and 2a), dynamic systems, and those requiring microscopic balance forms (refer to Figure 3).

All specialized formalisms, including the Gibbs Phase Rule, are limited by their definitions. The only generalized approach is that given by Felder and Rousseau.[4] And, while generality implies universal applicability, it also requires that the user must be an expert in application. Conversely, specialization, while offering a degree of simplification, implies that the user must understand and respect the boundaries that define the domain of application.

In general, students find it difficult to know when to apply which specialized formalism and how to use them even when they select correctly. In addition, since the DOF concept is not used in other contexts, such as reactor design and when microscopic balances are needed (transport phenomena), students lose connection with the concept (between sophomore and senior year) and will not retrieve it again later when required to perform even steady-state macroscopic balances a semester or two removed, *i.e.*, students seem to have totally forgotten about DOF by the time they reach senior design. In addition, students tend to struggle when required to formulate microscopic balances for purposes of design or analysis of steady and dynamic systems that are continuous or batch in nature; however, DOF is not used in such contexts, *i.e.*, is totally absent from teaching texts on these topics. In all of these cases and others, one can imagine using a DOF formality that could enable students to perform better.

For sure, the DOF concept, however, is no substitute for experience when it comes to the development of mathematical equations (a model) that describe some physical observation. Indeed, there is an element of art that is acquired by studying well-posed examples and tackling problem after problem, see Aris.[8] Nonetheless, the DOF concept can be used as a template to facilitate student learning and enable even the experienced modeler to find errors and test if his or her equations will result in a unique solution.

Students are particularly confused by why their macroscopic DOF formalities do not work for a closed system at equilibrium or for some dynamic cases, *e.g.*, for a batch reactor, and even some steady-state situations, *e.g.*, when a microscopic balance is involved, and so cannot benefit from the power of the DOF concept when learning how to formulate such problems. This tends to lead them to view the Gibbs Phase Rule, for example, and their macroscopic DOF formalism as two distinctly separate things rather than special cases of the same, more generalized, *lemma*, Eq. (1).

A typical example that leaves students with many questions is the open dynamic continuously stirred-tank reactor. The Eq. (2) formalism is, in fact, applicable to the non-steady continuously stirred tank reactor with a feed and product stream (Flow-CSTR); consider Figure 1b. Assume a single phase system with one chemical reaction (operating far from equilibrium), N molecular species, and with one feed and one product stream so that M=2.
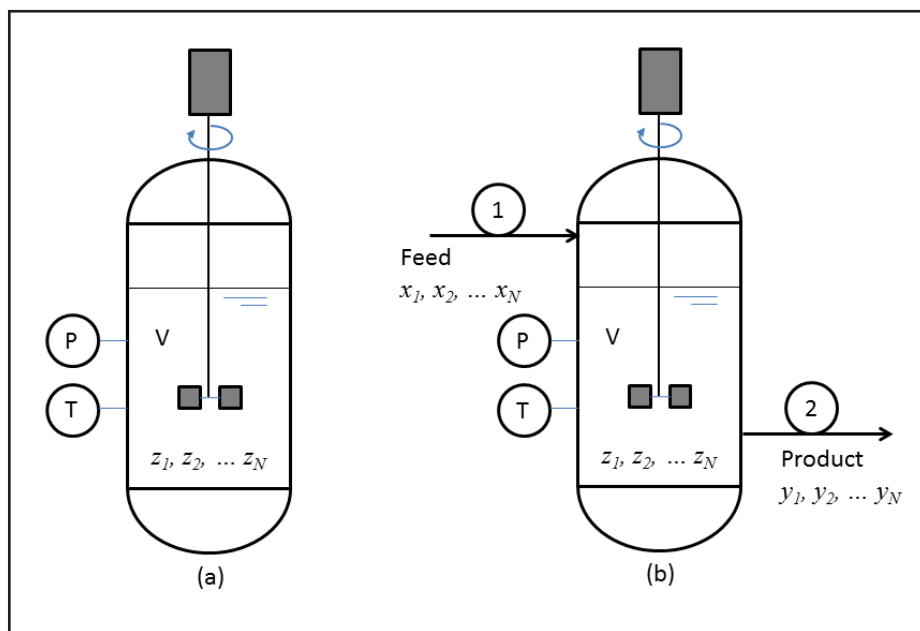

Figure 1. Tank reactor examples: (a) batch stirred-tank reactor; and (b) continuous stirred-tank reactor.

$$\text{GDF} = M \times N + M_{\text{Flows}} + N_{\text{Rates}} + 2 = 2 \times N + 2 + N + 2 = 3N + 4 \quad (3.a)$$

$$\text{GSC} = M_{\text{StreamConstraints}} + N_{\text{Balances}} + \text{RRR}^{\dagger} = 2 + N + N - 1 = 2N + 1 \quad (3.b)$$

$$\text{PSC} = F + C + N_R + N_{OC} + T + P = F + C + N_R + N_{OC} + T + P = 0 \quad (3.c)$$

$$\text{DF} = \text{GDF} - \text{GSC} = 3N + 4 - (2N + 1) = N + 3 \quad (3.d)$$

Here, liberty is taken to include the internal state variables, T and P, as GDF, thus the addition of "+2" in Eq. (3.a). Upon completing the analysis, students see
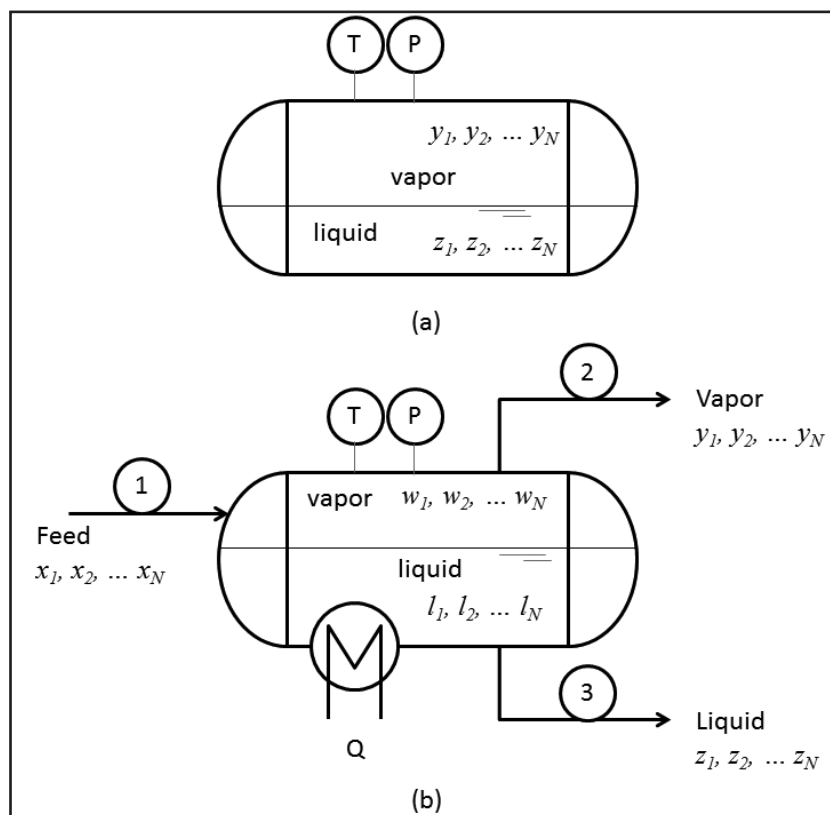
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† *Note that for a system described fully by a single chemical reaction, the number of RRR=N–1, refer to citations 5 and 10.*

that they might specify the T, P, feed flow rate, one reaction rate, *i.e.*, the form of the rate law written for one of the components (molecular species), and the feed composition (N-1 component compositions), for a total of N+3. They also see that there are what appear to be unaccounted-for variables that are either assumed to be specified or are hidden by (in) some assumption. For example, what about the reaction volume and the initial conditions? Students are confused about why these variables are not accounted for in the DF analysis. After all, they can be varied and may or may not be known. Furthermore, what about internal variables such as the composition of the batch? If the reaction rate is specified, that implies that one somehow knows the internal compositions, *i.e.*, the composition of the batch; however, the composition of the batch (the internal compositions) are not explicitly included (counted) among the GDF, and may or may not be known. In this case, the expert immediately assumes that the internal compositions are equal to the product composition by virtue of the continuously stirred assumption, that is, one immediately writes the following balance equation:

$$\frac{d}{dt}\int_V C_T x_i^P \, dV = -\oint_A C_T x_i (\vec{v}_i \cdot \vec{n}) \, dA + \int_V R_i(x_i^P, \, \ldots, \, x_N^P) \, dV, \, i=1\ldots N \, (4.a)$$

rather than the following more appropriate form which identifies the internal variables that are not included in the accounting practice:

$$\frac{d}{dt}\int_V C_T z_i \, dV = -\oint_A C_T x_i (\vec{v}_i \cdot \vec{n}) \, dA + \int_V R_i(z_1, \, \ldots, \, z_N) \, dV, \, i=1\ldots N \, (4.b)$$

(a)

(b)

Figure 2. Vapor-liquid-equilibrium (VLE) examples: (a) batch VLE; and (b) continuous VLE flash separation.

Figure 3. Tubular reactor example.

wherein C_T is the total concentration and R_i is the reaction rate for component "i," the z_i are the internal compositions, and the remaining terms are defined in Figure 1b.

Understandably, the internal compositions are equal to the compositions of the product stream since the reactor is assumed to be well mixed—a "continuously stirred tank." And, while some might suggest that such assumptions are "understood" or "implicit," the inferences for applying such formalisms to more complex cases are of importance, and from a pedagogical perspective, such leaps are not intuitive for most undergraduates, at least at first encounter. For example, such macroscopic formalisms will not work for the tubular reactor analogue of this problem since the internal variables (the z_i) cannot be hidden and must be explicitly identified in the formulation of the macroscopic balance equation, yet such is not obvious, even to the more advanced student or possibly even to the instructor at a glance. Refer to Application No. 3.

Overall, the specialized forms of the degrees of freedom concept presented in most textbooks are powerful and effective tools for steady-state open system problems, but are not applicable to, and indeed were not designed for, cases including when the number of streams is zero (M=0), *i.e.*, for batch processes, or cases that do not inherently collapse to the Gibbs Phase Rule, and/ or for any dynamic cases—macroscopic or microscopic—without invoking various additional assumptions otherwise hidden within the formalism and requiring expert knowledge of the particular situations.

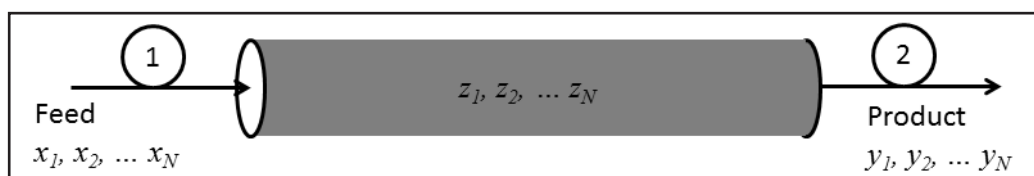One might argue that the more general formalism offered by Felder and Rousseau,[4] Eq. (1), is applicable to any situation. Indeed this is true; however, without

some structure for choosing variables and equations and for correctly specifying the problem, it can be difficult to apply in all but the simplest cases. Thus, a modification to the existing macroscopic formalism is suggested here to extend the domain of applicability and to provide structure for the new learner.

A PROPOSED EXTENDED FORMALISM

In proposing a new formalism, it is important to point out that all such frameworks are nothing more than embellishments of Eq. (1). These embellishments are imposed to make Eq. (1) more transparent for a specific range of applications, *e.g.*, the Gibbs Phase Rule is a specific embellishment that modifies Eq. (1) so that it works only for the closed thermodynamic intensive phase equilibrium problem. However, in doing such, we limit the utility of Eq. (1). Furthermore, it is likewise important to note that such equations are only formalisms, not mathematical theorems, and as such, various formulations, *i.e.*, accounting practices, are able to achieve similar or same outcomes. These things said, the following "extended formalism" inspired by that of Cerro, Higgins, and Whitaker[5] is proposed in an effort to broaden the utility of Eq. (2) and to make its application more transparent and for a wider range of problems:

$$GDF = M \times N + M_{Flows} + N_{Rates} + [2 + \gamma + N_{IC} + N_{BC} + \alpha] \tag{5.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + RRR + [N'(p-1) + \beta] \tag{5.b}$$

$$PSC = F + C + N_R + N_{OC} + [T + P + n_{IC} + n_{BC}] \tag{5.c}$$

The terms added are shown here in square brackets, where in Eq. (5.a) 2 is included to formally and explicitly account for the internal process temperature and pressure, γ is the number of "explicit internal" variables, typically $\gamma = pN$ and accounts for the number of compositions associated with the p phases present within the control volume; α is the number of relevant design variables such as the reaction volume, N_{IC} is the number of initial conditions (zero for steady-state conditions) and N_{BC} is the number of boundary conditions (zero for problems that involve only the macroscopic balance); in Eq. (5.b) N' is the number of components involved in phase equilibrium; and β are internal phase constraints of the form $\sum_{i}^{N} z_i$ and/or *closure*‡ constraints, where applicable, here the term "closure" implies a relationship between the internal compositions (properties) and the external compositions ($\beta = pN$ for example for a well-mixed system wherein the compositions within the tank equal the compositions in the effluent, that is, $z_i = x_i^p$) —the constraints of which are chosen to match the context of the problem.[9] Additional terms, n_{IC} and n_{BC}, included in the PSC account for the number of initial and boundary conditions, respectively, which are specified.

The benefits of this extended formalism are illustrated by example.

Application No. 1 – Closed system at phase equilibrium

The extended formalism can be shown to collapse to the Gibbs Phase Rule for the closed system at phase equilibrium. Consider Figure 2a, M=0, $N_{IC}=0$ (since the system is at equilibrium, by definition it is also at steady state), $N_{BC}=0$ since this is not a boundary value problem, $N_{Rates}=0$ and RRR=0 since there are no chemical changes, and $\gamma = pN$ (since there are p phases and N compositions in each phase; γ, in this case, accounts for all of the internal compositions). Therefore:

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 + \gamma + N_{IC} + N_{BC} + \alpha$$
$$= 0 \times N + 0 + 0 + 2 + pN + 0 + 0 = 2 + pN \tag{6.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + N'(p-1) + RRR + \beta = 0 + 0 + N(p-1) + 0 + p + 0$$
$$= pN - N + p \tag{6.b}$$

$$\text{if the } PSC = F + C + N_R + N_{OC} + T + P + n_{IC} + n_{BC} = 0 \tag{6.c}$$

$$DF = GDF - (GSC - PSC) = (2 + pN) - (pN - N + p) = N - p + 2 \tag{6.d}$$

Since the proposed extended formalism explicitly accounts for internal variables, the Gibbs Phase Rule is directly retrieved for a closed system at phase equilibrium with no chemical reaction. No additional external "rule" is needed to impose the Gibbs Phase Rule. Likewise, the extended formalism works well for any batch (closed) system, dynamic cases, and steady-state cases.

Application No. 2 – The dynamic flow-CSTR

Consider again the case of the dynamic flow-CSTR discussed previously; refer to Figure 1b. Recall that for this case there are

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‡ *The use of the term "closure" here should not be confused with the concept from set theory. See Quintard and Whitaker[9] for explanations as it relates to mathematical modeling.*

N molecular species, a single chemical reaction, a single phase (p=1), one feed and one product stream, and a volume change due to reaction. For this case the extended formalism is reduced to:

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 + \gamma + N_{IC} + N_{BC} + \alpha$$

$$= 2 \times N + 2 + N + 2 + N + (N+1) + 0 + 1$$

$$= 5N + 6 \tag{7.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + N'(p-1) + RRR + \beta = 2 + N + 0(1-1) + (N-1) + N$$

$$= 3N + 1 \tag{7.b}$$

$$\text{if the } PSC = F + C + N_R + N_{OC} + T + P + n_{IC} + n_{BC} = 0 \tag{7.c}$$

$$DF = GDF - (GSC - PSC) = (5N+6) - (3N+1) = 2N+5 \tag{7.d}$$

where γ is equal to N since there are N internal compositions that will be explicitly computed and $\alpha = 1$ since the reaction volume (the volume of material in the reactor at any time) must be computed, an extensive parameter. There are pN+1 initial conditions in this case (N_{IC}=pN+1; pN compositions and the initial reaction volume). For a single phase system this gives N+1 initial conditions. This produces 5N+6 GDF in total. The GSC include two stream constraints, N balances, zero phase equilibrium constraints (single phase system), N-1 RRR, and β=N closure constraints for a total of 3N+1 GSC. If one specifies the N+1 initial conditions (N+1) this leaves N+4 additional process parameters to be specified. If T and P are specified, a balance of N+2 parameters remain to be specified from which one must be an extensive parameter (either the feed or product flowrate), N-1 can be compositions, typically taken as the feed compositions, but not necessarily, leaving two additional parameters that can be chosen from among the remaining independent variables, the product flow rate, other compositions, reaction rates or, alternatively, other process specifications such as the conversion or similar constraints. Thus, the proposed extended formalism not only works for the dynamic flow-CSTR, but it clearly identifies (reveals) the initial conditions and internal relationships that are typically hidden in such applications.

For clarity, the example is completed here by writing the relevant model equations. In summary, 3N+1 equations must be written:

M=2 stream constraints having the form:

$$\sum_i^N x_i^j = 1; j = 1, \ldots M = 2 \tag{8.a}$$

N dynamic balances having the form:

$$\frac{d}{dt} \int_V C_T z_i \, dV = -\oint_A C_T \Psi_i (\vec{v}_i \cdot \vec{n}) dA + \int_V R_i (z_1, \ldots, z_N) dV, i = 1 \ldots N \tag{8.b}$$

where Ψ_i represent the mole fraction of species i at the surface boundary A, *i.e.*, $\psi_i = x_i$ at the inlet and $\psi_i = y_i$ at the outlet.

N-1 Reaction Rate Relationships of the form:

$$R_i = \frac{v_i}{v_k} R_k; i = 1 \ldots N, i \neq k \text{ (k is a single value, 1 or 2 or } \ldots N) \text{ and where the v carry a negative sign for reactants} \tag{8.c}$$

Notably, there are N-1 of these relationships when a single chemical reaction can be used to describe the chemical changes.[10]

One (1) internal phase constraint for p=1 having the form:

$$\sum_i^N z_i = 1 \tag{8.d}$$

and, β = N-1 closure constraints, in this case having the form:

$$z_i = x_i^j; \ i = \text{any N-1 of 1, 2, } \ldots, N \tag{8.e}$$

where j=2 per Figure 1b.

Alternatively, one can use N internal closure constraints and omit the internal phase constraint Eq. (8.d).

Application No. 3 – The Steady Plug Flow Reactor

To demonstrate how the extended formalism can be applied when the closure constraints for a continuously stirred (CS), *i.e.*, well-mixed, process are not applicable, consider a steady plug flow reactor (PFR). Refer to Figure 3. In this case assume N molecular species, one phase, a single inlet and a single outlet stream (M=2), inviscid flow, and a single chemical reaction

for which there is no change in moles. Applying the extended formalism produces the following degrees of freedom analysis:

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 + \gamma + N_{IC} + N_{BC} + \alpha$$

$$= 2 \times N + 2 + N + 2 + N + 0 + 2 \times N + 2$$

$$= 6 + 6N \tag{9.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + N'(p-1) + RRR + \beta = 2 + N + N'(1-1) + (N-1) + N$$

$$= 1 + 3N \tag{9.b}$$

$$\text{if the } PSC = 0 = F + C + N_R + N_{OC} + T + P + n_{IC} + n_{BC} \tag{9.c}$$

$$DF = GDF - (GSC + PSC) = (6 + 6N) - (1 + 3N) = 5 + 3N \tag{9.d}$$

where $\gamma = N$ internal variables, the z_i, $N_{IC} = 0$ since the reactor is at steady-state, $N_B = 2N$ to account for one boundary condition for each of the N compositions at each end of the reactor (domain) and $\alpha = 2$ to account for the length and diameter of the reactor (for example). In addition, $\beta = N$ closure constraints of the form

$$z_i\big|_L = y_i \tag{10.d}$$

There are thus a total of 6+6N GDF and 1+3N GSC giving 5+3N DF.

For this case, one can specify the feed flow rate, temperature, pressure, one reaction rate expression, N-1 feed or other compositions, 2N boundary conditions (compositions at the inlet and composition gradients, for example, at the exit), and the reactor length and diameter for a total of 3N+5 degrees of freedom (PSC to be specified). Therefore, the problem is totally specified and the formalism works. In all, 3N+1 equations must be written:

M=2 Stream constraints have the form:

$$\sum_i^N x_i^j = 1; j = 1, \ldots M = 2 \tag{10.a}$$

N Balances having the form:

$$\frac{d}{dt} \int_V C_T z_i \, dV = -\oint_A C_T \Psi_i (\vec{v}_i \cdot \vec{n}) dA + \int_V R_i (z_1, \ldots, z_N) dV, \, i = 1 \ldots N \tag{10.b}$$

which in this case must be transformed into N microscopic balances having the form:

$$v_i \frac{dz_i}{dl} + r_i (z_i, \ldots, z_N) = 0 \tag{10.c}$$

wherein i=1,… N, and l, is the length along the reactor (alternatively N-1 microscopic balances can be written along with one internal (microscopic) phase constraint of the form $\sum_i^N z_i = 1$).

N Closure Constraints of the form:

$$z_i\big|_L = y_i \tag{10.d}$$

And, finally, N-1 Reaction Rate Relationships must also be written having the form:

$$R_i = \frac{v_i}{v_k} R_k; \, i = 1 \ldots N, \, i \neq k \tag{10.e}$$

where the v carry a negative sign for reactants.

Application No. 4 – Extending the formalism to include heat balance

To extend the formalism to include a heat balance is simple, Eqs. (5) are rewritten to account for the T and P of all streams and one equation for the heat balance by adding the term Q(2M+1) to Eq. (5.a) and adding Q to Eq. (5.b) (changes shown in square brackets):

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 + \gamma + N_{IC} + N_{BC} + \alpha + \big[Q(2M+1)\big] \tag{11.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + RRR + N'(p-1) + \beta + [Q] \tag{11.b}$$

$$PSC = F + C + N_R + N_{OC} + T + P + n_{IC} + n_{BC} \tag{11.c}$$

No other changes are necessary. Now, T and P account for all temperatures and pressures (that of each stream and that within the control volume). Furthermore, one might choose to use closure constraints to specify the T and P of some streams, *e.g.*, $T^j = T$, where T is the temperature within the control volume. Note that Q is a binary parameter (Q=0 when the heat balance is not included and 1 if it is).

To illustrate the application of this formalism, one additional application is provided here. Consider now a continuous, steady-state flash of a single stream containing N chemical species into a vapor and a liquid (M=3) wherein all N species appear to some extent in both the vapor and liquid products, *i.e.*, all N species are in phase equilibrium. Refer to Figure 2b. The degrees of freedom analysis for this case is as follows:

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 + \gamma + N_{IC} + N_{BC} + \alpha + Q(2M+1)$$

$$= 3 \times N + 3 + 0 + 2 + 2N + 0 + 0 + 0 + 1(2 \times 3 + 1) = 5N + 12 \tag{12.a}$$

$$GSC = M_{StreamConstraints} + N_{Balances} + RRR + N'(p-1) + \beta + Q =$$

$$3 + N + 0 + N(2-1) + (2N + 2 \times 2) + 1 = 4N + 8 \tag{12.b}$$

$$PSC = F + C + N_R + N_{OC} + T + P + n_{IC} + n_{BC} = (5N+12) - (4N+8) = N + 4 \tag{12.c}$$

For simplicity, use N=2 for a binary separation. Before specifying the problem, it is important to discuss the value of β in this case. Here, $\beta = (pN + 2(M-1))$. Why is this? Recall that this formalism does not hide internal variable, *i.e.*, the internal T and P and compositions are counted among the GDF. Therefore, closure constraints are needed to provide relationships between internal and external (stream) variables. In flash separation, the formed phases, in this case the liquid and vapor, are typically considered to be well mixed and so it is appropriate to include well mixed closure constraints relating the internal compositions of each phase and their respective stream compositions and state variables. These constraints take the forms, $y_i = \omega_i$, $z_i = l_i$, which number pN, and $P^j = P$ and $T^j = T$, $j \neq f$ (f=feed), which number 2(M-1) for a total of pN+2(M-1) closure constraints.

Finally, the problem can be specified. In this case a total of N+4=6 parameters or constraints must be fixed. One might choose to completely specify the feed composition (N-1=1 parameter) leaving N+3=5 parameters or constraints to be specified. The flash T and P, the feed flowrate, and the feed T and P (T^f and P^f) can be chosen to complete the specifications. See also Biernacki for more details concerning proper specification and superposition.[7]

The equations are also summarized here for completeness and for comparison to a similar example in Biernacki[7] for which the heat balance was not included.

N Balances of the form

$$Fx_i = Vy_i + Lz_i \tag{13.a}$$

M=3 Stream Constraints of the form $\sum_i^N c_i = 1$, where c is a composition fraction

N'(p-1) Phase Equilibrium Relationships (shown here assuming ideal behavior in both phases)

$$\omega_i P_T = \ell_i P_i^\circ(T) \tag{13.b}$$

pN+2(M-1)=2×2+2(3-1)=8 Closure constraints of the forms:

$$y_i = \omega_i, \, i = 1, 2 \tag{13.c}$$

$$z_i = l_i, \, i = 1, 2 \tag{13.d}$$

$$T^j = T, \, j \neq f \tag{13.e}$$

$$P^j = P, \, j \neq f \tag{13.f}$$

Q=1 Heat Balance

$$\frac{d}{dt} C_T V C_p (T - T^\circ) = M^f \sum_i^N x_i H_i^f - \left(M^v \sum_i^N y_i H_i^v + M^L \sum_i^N Z_i H_i^L \right) + q \tag{13.g}$$

where subscripts "f" and "p" are for "feed" and "product," respectively; subscripts "L" and "v" are for "liquid" and "vapor," respectively; q is a heat sink or source term; C_p is the heat capacity of the material within the volume V; T° is the reference-state temperature (a constant); and the M^j and H_i^j are the feed and product molar flowrates and species enthalpies, respectively (j=f, and p). Notably, the feed and product species enthalpies and heat capacity of the reaction mass (C_p) are a function of their

respective thermodynamic intensive conditions [T^j, P^j, and (X_i, Y_i, or Z_i)].

STUDENT RESPONSE

Students in a second-term senior design course were introduced to the extended DOF formalism. These same students participated in intensive training on the use of the baseline formalism of CHW beginning in the first-term sophomore year along with their introductory course in material balances, a brief reintroduction in the first-term junior year in their first thermodynamics course, and then again in an intensive sequence in their first-term design course. After applying the principles to various steady and non-steady problems, students were asked to reflect on their experience and to respond to a series of simple questions and to prepare a brief reflective statement; the details of this study are provided elsewhere,[7] however, they are summarized here as a starting point for the present work.

When asked if they would like to have seen how DOF could be used in other upper-level chemical engineering courses, 100% of the students responded that they would, with 73% stating they would have liked to see DOF used in reactor design and 65% in second-term thermodynamics. This positive response encouraged the present work wherein the extended formalism was developed and introduced for the first time in the second-term senior design course at Tennessee Technological University (TTU).

During the second-term design course, teams of three or four students work collaboratively on a term-long design endeavor. The second-term design course had a total of 64 students divided into 17 teams. During this particular term, students chose to work on one of three projects: solar biodiesel production, pyrolysis of biomass to produce energy resources, or production of acrylonitrile. After conducting a thorough steady-state heat and energy balance including a steady-state kinetic model, students were challenged to develop a dynamic reactor model and to explore the reactor operational stability as part of a process safety management (PSM) sub-project. As part of the in-class activities, the extended degrees of freedom concept was introduced and a companion manual was distributed as a textbook-like supplement, i.e., a

version of this paper including the Application examples, excluding Application 4 and associated formalism for including the heat balance (at that time, students were instructed to include the heat balance by inspection), and description of the extended DOF formalism (Eqs. 5) edited for students. The classroom lecture notes were also distributed to the students.

Teams were then released to complete the assignment over a period of about three weeks. Some teams sought individual help, i.e., coaching from the instructor, while others pushed on without. Meanwhile, the classroom content moved on to other topics.

To ascertain student perceptions and to glean insights into the benefit of using the extended formalism, students were blind surveyed, focus group meetings (feedback sessions) were held, and the dynamic reactor project was scored by the instructor (the author) against a rubric designed to correlate proficiency with the DOF formalism and model formulation. Rather than survey the entire group, two smaller focus groups each containing 11 students were formed. The focus groups were selected using two criteria: (1) students from each of the 17 teams were represented among the two groups and (2) Group 1 was composed of top-scoring students from the first-term design course and Group 2 was composed of lowest scoring students from the first-term design course. The class standing criteria was used since blind surveys and otherwise blind testing make it difficult to discern if students with differing skill levels have similar perceptions and outcomes.

Two focus group meetings were held mid-term (prior to awarding of final grades), one in about the 10th week of a 16-week term and one in about the 13th week. The instructor (the author) ran the focus groups. Prior to distributing a blind survey, i.e., the students were instructed to not identify themselves, the instructor explained that outcomes of the

TABLE 1
Results of student focus group survey

Question	Responses (% of population)		
	Group 1	Group 2	Overall
Number in population	11	11	22
Should the extended formalism be used in the future?*			
Yes	91	100	96
Yes, but more training should be given	55	55	55
Yes, but introduce it in first-term design (Design I)	36	36	36
Yes, but introduce it in the Reaction Engineering course	0	27	14
No	9	0	4
It would be good if the DOF concept was used more uniformly across the curriculum.			
No	18	18	18
Yes	82	82	82
It would be good if the Material Balance, Reaction Engineering, and Design sequence used the same formalisms.			
Yes	82	91	86
No	18	9	14

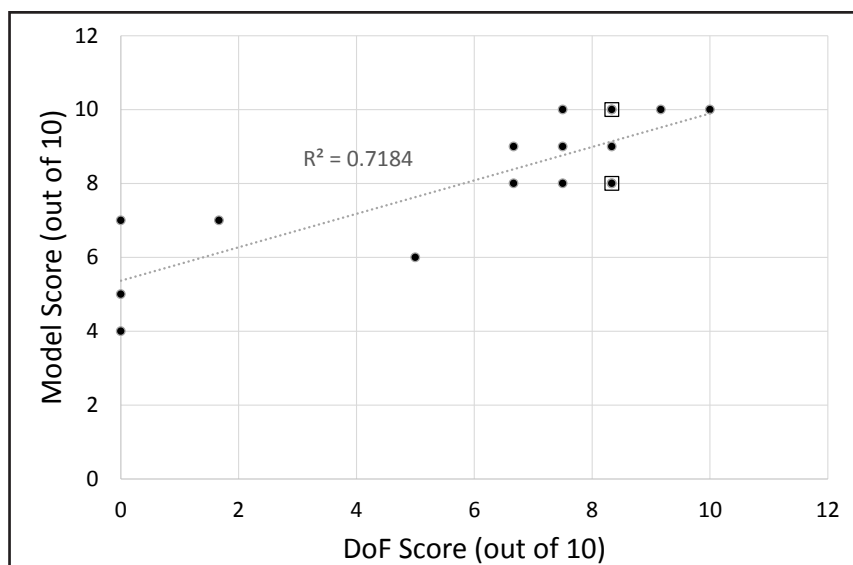* Students were permitted to respond to none or all choices.

Figure 4. Team score for dynamic modeling activity as a function of score on degrees of freedom usage. Points with multiple symbols (solid circle in square) represent teams with same scores.

survey would be used to improve future course offerings and encouraged students to provide candid (honest) responses. In addition, the instructor emphasized that student responses would not influence their grades in any way, reiterating that they were not to identify themselves. This instruction was given to reduce the possibility that student responses would be biased. Students from both groups freely and willingly participated at the request of the instructor.

Table 1 summarizes the survey questions asked and the outcomes. To ascertain if students felt that the extended formalism was helpful they were asked, "Should the extended formalism be used in the future?" This approach is similar to asking, "Would you recommend our service to a friend?" Overall, 96% of the 22 students surveyed (100% response rate) said "yes" it should be taught; however, 55% would have liked additional training, a point that was clearly articulated during focus group feedback sessions. In a separate question, 50% of the students, however, thought it should be introduced earlier in the curriculum—36% suggesting it be introduced in the first-term design course and 14% choosing the reaction engineering course.

In general, 82% of the students thought that the DOF concept should be used across the curriculum, echoing the earlier results of the author that suggested that 100% of students surveyed indicated that they would have liked to see the DOF concept used in one or more other courses.[7] Finally, when asked if the same formalisms should be used in the material balance, reaction engineering, and design sequence, again 86% of the students responded affirmatively.

While there are minor differences in the responses gathered from the two focus groups, in general, the two groups are very consistent. There is no indication that proficiency level with the course material influences the students' perceptions of the extended DOF concept.

The dynamic reactor projects for the 17 teams were scored both for the completeness of the DOF analysis and the reactor model formulation. The model formulation score did not include the DOF score so that the formulation score and DOF score are independent. Notably, some of the teams chose not to apply or at least not to report their DOF analysis; those teams received a score of zero for the DOF analysis. Figure 4 summarizes the scores in the form of a plot of the modeling score vs. the DOF score. In general, there appears to be a reasonable correlation (R^2=0.718) between the DOF and modeling scores. The calculated regression "p" statistic is also well below 0.05§ (on the order of 10^{-5} or less) indicating that the regression coefficients have a high degree of statistical confidence given the 17 data points. These results tend to support the hypothesis that those teams of students that had a better grasp on the DOF concept also had a better grasp on the modeling activity. And, while it is very difficult to draw general conclusions, since one might also find a similar correlation between good kite builders and good mathematical modelers, or good musicians and good modelers or kite builders, one cannot dispute that good DOF skills seem to be correlated to good modeling skills, at least in this context.

Finally, the scored projects were used to glean insights into typical pitfalls that students seem to have. Among student teams that applied the extended DOF formalism, the most common error was associated with counting of the number of initial conditions. The next most common error was identifying how to account for the closure constraints among the GSC. All teams seem to have a good grasp of the concept of DOF and the necessity to establish equality of the GDF and the sum of the PSC and GSC (GDF=PSC+GSC). In general, this seemed to translate into well-posed model formulations.

SUMMARY AND CONCLUDING REMARKS

Application of the degrees of freedom concept in chemical engineering has been used to facilitate solution of macroscopic balance problems, and design and identification of control strategies. Although the most general form of the DOF con-

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§ *The "p" statistic is used to find the confidence level. A value less than 0.05 indicates a confidence level of ≥ 95%.*

cept as presented by Felder and Rousseau[4] is more widely applicable, the specific formalisms offered in what appears to be virtually all other chemical engineering textbooks are limited by design to steady-state applications. An extended formalism is offered here that illustrates the applicability of the degrees of freedom concept to closed systems (batch processes), dynamic processes, and cases that involve microscopic as well as macroscopic balances. In all cases, all such formalisms are nothing more than limited versions of the DOF concept which states that the number of DOF equals the number of variables minus the number of equations. Any additional definitions limit the applicability of this most generalized statement of the DOF concept, *e.g.*, the Gibbs Phase Rule, but at the same time offer structure and efficiency for solving a particular class of problems.

Nonetheless, the proposed extended degrees of freedom formalism provides a single unified approach for both continuous and batch processes (those cases for which M=0), connectivity between macroscopic and microscopic balances, and transparency when handling dynamic systems (inclusive of cases where M=0 or M≠0). In all cases the extended formalism provides insights into the relationship between various elements of the problem; the extensive vs. intensive problems, the internal variables and external variables, and the macroscopic and the microscopic nature, and places each in their proper mathematical juxtaposition.

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