

Using Degrees of Freedom as a Pervasive Strategy for Improving Problems Solving

Dr. Joseph J. Biernacki, Tennessee Technological University

Dr. Biernacki is full Professor of Chemical Engineering at Tennessee Tech University (TTU). Prior to joining TTU in 1997 he spent 15 years work for British Petroleum in various capacities. He is keenly interested in engineering education, particularly in improving problem solving skills through the use of methodologies and formalisms that enable and promote critical thinking.

The Degrees of Freedom Concept –A Pervasive Paradigm

Abstract

Typically, chemical engineering students are introduced to the concept of degrees of freedom (DoF) along with mass balances where the concept is used to help formulate balances and related equations and again in thermodynamics in the context of phase equilibrium. Unfortunately, the concept is not used beyond these contexts, the formalisms are not directly derivable one from the other in an obvious way. As a consequence, students do not ascertain that the DoF *concept* is more generalizable than these specific applications would lead them to believe. Since, the degrees of freedom concept is generally not practiced outside of these isolated contexts, students that learned these formalisms will inevitably revert to "hunt and peck" strategies for solving material balances and for doing thermodynamic phase or reaction equilibrium calculations rather than apply a degrees of freedom analysis as a starting point. This lack of skill and understanding limits the students' ability to accurately formulate problems; an area that can be greatly improved by implementing a pervasive approach to the utilization of a robust and generalized degrees of freedom formalism throughout the curriculum.

Introduction

The undergraduate chemical engineering student is typically introduced to the concept of degrees of freedom for the first time in either a sophomore course on material (and energy) balances or sophomore thermodynamics (usually referred to as "Thermo I"). In either case, this is likely too late and the context typically identified with too narrow an application, either the macroscopic stead-state mass balance (an extensive application) or phase equilibrium (an intensive application). And, in either case, the formalisms used most likely leave the student thinking that "degrees of freedom" are only applicable to that class of problem. In general, students are not introduced to the degrees of freedom concept early enough, nor are they provided with multiple frameworks from which they can use the *power* of degrees of freedom as a pervasive problem solving tool.

Background Review

A review of courses wherein students might encounter the concept of degrees of freedom include, in chronological order, *Algebra* (solution of systems of equations), *General Chemistry* (single phase equilibrium, typically illustrated using water as an example), *Mass and Energy Balances*¹ (in the context of the stead-state mass balances, used to determine the number of variables that must be specified to produce a unique solution), *Thermodynamics*² (single phase equilibrium in Thermo I and multi-component equilibrium in Thermo II for closed systems) and *Stage-wise Separations*³ (specification of equipment design, for example a distillation column). Unfortunately, the degrees of freedom concept is omitted from the Chemical Engineering syllabi for courses focusing on chemical reactor engineering and unit operations analysis; likely in part because many, if not all, of the relevant textbooks omit the subject as well^{4, 5, 6}. Some undergraduate students might also encounter the degrees of freedom concept in *Statistics*^{7, 8}, where the definition does not lend itself to be easily generalized beyond that context and in fact students will not recognize the application of degrees of freedom in statistics and degrees of

freedom as applied to material balances or thermodynamics as being the same concept. One author states about the parameter "r" in the chi-squared distribution^{*}, "for no obvious reason at this time, we call the parameter r the number of degrees of freedom," and then uses the term "degrees of freedom" subsequently without ever offering a definition. Such, further confuses and confounds the problem of teaching students about "degrees of freedom" In the chemical engineering context.

Particularly in upper division courses that involve a higher level of synthesis, students are frequently perplexed about where to begin and what equations to write. Rather than use a degrees of freedom formalism, they typically revert to a schema that involves identifying what type of phenomena is involved, e.g. heat transfer, chemical reaction, mass balance, etc., and proceed with writing of equations by inspection, mostly without concern for exactly what is known and what is unknown; though in most cases, students will attempt to list what is known and in some cases will also attempt to identify what is unknown. First year graduate students suffer from this same characteristic. In a recent survey about the material and energy balance course content, 100 % of the chemical engineering faculty who responded indicated that degrees of freedom is a concept taught⁹. Given the opportunity that faculty have to enable students through the use of the degrees of freedom concept, it is surprising that the degrees of freedom formalism is not used as a pervasive problem solving strategy throughout the chemical engineering curriculum alongside other formalisms such as continuity principles. It should come as no surprise then if our students do not begin a mass balance or reactor design problem, for example, by first conducting a degrees of freedom analysis, nor use degrees of freedom to understand the behavior of process simulation tools such as Aspen/HYSYS, where the degrees of freedom concept is pervasively implemented as part of the equation solving algorithms.

The literature at large appears to be rather thin on the subject of "degrees of freedom analysis." Luyben¹⁰ offers a nice review of texts that contained degrees of freedom content, prior to 1996, and a formalism with rather loosely defined rules for finding the "design" and "control" degrees of freedom for steady state processes. Ravi and Rao¹¹ offer a rather in depth analysis of the degrees of freedom for stage-wise separations, however, do not offer a generalized formalism for a broader range of problems. Rodriguez and Gayosos¹² extended an earlier formalism proposed by Ponton¹³, also for stead-state processes.

Current texts, however, offer a number of starting points that are quite useful. Felder and Rousseau¹ present and illustrate a degrees of freedom approach wherein they state that:

$$n_{df} = n_{unknowns} - n_{independent\ equations} \tag{1}$$

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 very general rules are also provided to help one discern what "variables" are and the "sources" of equations. This approach is likely the most generalized, making Equation (1) applicable to virtually any problem.

^{*} The chi-square distribution is given by $f(y) = \frac{1}{\Gamma(\frac{r}{2})2^{r/2}}y^{(\frac{r}{2}-1)}e^{-y/2}$.

Cerro, Higgins and Whitaker $(CHW)^{14}$ offer a formality derivable from that of Felder and Rousseau which is designed for stead-state balance problems only. In their approach, stream compositions, flows and reaction rates are explicitly counted among the *variables*, which they call "Generic Degrees of Freedom (*GDF*)," and balances, stream constraints and reaction rate relationships are counted among the equations, referred to as "Generalized Constraints (*GC*)." Everything else is lumped into a class called "Particular and Specific Constraints (*PSC*)," which include the sum of all things known such as flowrates, compositions, reaction rates and wherein other specified constraints such as design specifications, e.g. 90% of component *A* must be recovered in product steam *Z*, and phase and chemical equilibrium relationships can be included. In summary, their formalism consists of the following relationships[†]:

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

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

$$PSC = F + C + N_R + N_{OC} \tag{2.c}$$

from which

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

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 CHW¹⁴), *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," and *DF* is the number of degrees of freedom. The following additional rules are also required but are not explicitly enumerated by CHW¹⁴; but are implicit:

- (Rule 1) No more than *N-1* compositions can be specified for any single stream.
- (Rule 2) At least one extensive parameter must be specified, e.g. the feed flow rate, else the balances must be written in terms of ratios to eliminate one degree of freedom from the extensive equation set.
- (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, stream flows and apparent reaction rates are included, no compositions within the control volume are included, no internal flows and no microscopic information (spatial or time-domain localized information such as a local reaction rate or composition). 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." In addition, the temperature and pressure within the control volume are not

[†] The notation used here was embellished to add clarity and is different is some ways from that given by CHW¹⁴.

explicitly counted but must be included in the *GDF* and among the *PSC* if equilibrium is observed or other state-dependent constraints are used. This elegant and simple template provided by CHW¹⁴ makes equation writing for steady macroscopic balances a transparent and natural process without having to memorize or somehow otherwise recall which equations work for what problems. This formalism is effective, efficient and robust for steady-state macroscopic mass balances that may or may not involve phase and chemical equilibrium and chemical changes (reactions) and is thus utilized as the basis in the following framework for embedding the degrees of freedom concept across the chemical engineering curriculum.

Pedagogical Aspects – Suggested Implementation in the Curriculum

While it would be ideal if the concept of degrees of freedom could be introduced in its most generalized form, i.e. as Equation (1), in one or more math courses early in the curriculum, since most engineering programs have little or no control over what is taught at that level, it is suggested that the concept be introduced early as part of CHE course content. The recommended entry point is a freshman "introduction to chemical engineering" course. At the Tennessee Technological University (TTU), a second-term freshman course entitled "Introduction to Computer Applications in Chemical Engineering" has been used as a *forum* for introducing the degrees of freedom concept. This, early entry-point, course is a one credit hour survey of application examples that tie concepts in mathematics, computer applications, chemistry, physics and chemical engineering together with the objective of strengthening the students' math skills, introducing them to computer software that they will need later and making connections with chemical engineering. The degrees of freedom concept is introduced using reaction balancing as an application. This application provides the opportunity to link concepts associated with chemistry (chemical reaction balancing), balances in chemical engineering (the atom or element balance), mathematics (linear equations and linear algebra) and use of software such as MathCad or MatLab for solving systems of equations. At the same time, it is a *perfect* opportunity to introduce the degrees of freedom concept.

Example No. 1 – *Balancing Chemical Reactions (a freshman example)*: Consider a simple chemical reaction between the four compounds ethane (C_2H_6), oxygen (O_2), water (H_2O) and acetic acid (H_3CCOOH). *Any* high school student can balance a reaction between these four molecular species; however, even second-term freshman chemical engineering students do not realize that when they balance such reactions, they are solving a system of linear equations, in their head and by inspection. Furthermore, most are not aware that they are finding one of many solutions to an underspecified linear system and *none* know how to assess the degrees of freedom or how to apply the degrees of freedom concepts to better understand the problem. So, balancing a simple chemical reaction, a problem that is very familiar to second-term chemical engineering students, is a great opportunity to enable students to learn about degrees of freedom and an ideal place to introduce the concept as a tool for enabling problem solving.

While the linear analysis part of this lesson is not the focus of this paper, it provides a context for introducing degrees of freedom concepts and so, some discussion of the problem is helpful here. It is important to emphasize that when balancing a chemical reaction, it is not necessary to know which species are reactants and which are products, a concept that will *disturb* and baffle students at first. Nonetheless, it is important to break the old habits and introduce students to

new, more robust formalisms that enable them to extend their knowledge and not be hindered by old paradigms. The problem:

Given a O_2 , b H_3CCOOH , c C_2H_6 and d H_2O , where a, b, c and d are the number of moles of each species, find a, b, c and d such that a balanced stoichiometric reaction can be written. The solution begins with the writing (forming) of atom balances:

Carbon Balance: $0 \times a + 2 \times b + 2 \times c + 0 \times d = 0$ Oxygen Balance: $2 \times a + 2 \times b + 0 \times c + 1 \times d = 0$ Hydrogen Balance: $0 \times a + 4 \times b + 6 \times c + 2 \times d = 0$

Once again, no signs need to be assumed here, the sings will be determined by solving the equations. It is prudent to questions students at this point concerning the possibility for solving this system. Even though they can balance the reactions easily by inspection, most will not recognize that this system cannot be solved uniquely. All will agree that they use it somehow when balancing this reaction, but virtually *none* will actually recognize that they must use these equations and that they cannot be solved for a unique solution without assuming one parameter, that is, there is "one degree of freedom" for this problem. This is the point at which the generalized degrees of freedom concept can be introduced (from Equation (1)):

Degrees of Freedom (DF) = Number of Unknowns (#UN) – Number of Equations (1)

This example is simple and students will immediately understand and respect the use of this formalism and some may even confirm that they have seen this concept before. The equations can then be solved using any number of techniques that the instructor chooses to use, but the concept of "degrees of freedom" has now been officially introduced and connected to an application.

At this point, one does not want to imply that the degrees of freedom concept is only applicable to this problem or this type of problem and so the instructor should emphasize that the degrees of freedom *axiom* is generally applicable in many fields and can now mention other applications that some of the students may already be familiar with: statistics, thermodynamics (Gibbs Phase Rule) and examples from kinematics, e.g. how many "degrees of freedom" does a human shoulder or knee have?, to name a few obvious ones.

Example 2 – A "degree of freedom" is a "choice" – To further solidify the point that the degrees of freedom concept is a general tool, some less obvious applications might be illustrated. For example, if one is planning to purchase a car and the vehicle of choice comes in 12 colors, two motor types and three interior finishes, how many degrees of freedom are there? Have students discuss such examples in small groups then discuss with the class. Poll student responses and share with all. Students will analyze the problem many ways; some typical answers are 72, 71, 17, 16, 3 and 2. The correct answer is 3. Since there are three "choices," one only has three degrees of freedom before the vehicle is totally specified. Another way to help students to see that 3 is the correct answer is to once again reflect on the reaction balancing problem. There are four variables in the example problem (Example 1), but once one of the variables has been specified, the entire problem is specified completely. Therefore, there is only

one "choice" to be made. This is true despite the fact that the one choice can be made an infinite number of ways. Equating a degree of freedom with a "choice" is a good way to help students to internalize what a degree of freedom actually is, a choice or decision point.

The sophomore material balance course, frequently taught along with energy (heat) balance concepts, is the next opportunity to further develop the degrees of freedom concept. At this point, the formalism suggested by Cerro, Higgins and Whitaker is used in the author's program, however, any similar schema might be introduced. The author *grows* the formalism over the term, rather than presenting it in its entirety, by applying it to many applications that increase in complexity as the course progresses.

Example No. 3 – *Overall Balance around a Dryer* (a sophomore example): Many materials are dried in continuous ovens and kilns to adjust their water content. The material to be dried is fed in at constant feed rate. Dry or partially dry air enters counter-current and moist air exits and is not necessarily in equilibrium with the entering wet material, refer to Figure 1. Such processes are typical examples in popular texts and should always be started using a degrees of freedom analysis regardless of how they are approached by the text author(s). In the example shown in Figure 1, there are four streams (M=4), three components (N=3, air, water and the substance of the material to be dried on a dry basis, e.g. wood, clay brick, etc.). The degrees of freedom analysis for this example follows:

$$GDF = M \times N + M_{Flows} + N_{Rates} = 4 \times 3 + 4 + 0 = 16$$

$$GC = M_{StreamConstraints} + N_{Balances} + RRR = 4 + 3 + 0 = 7$$

$$for PSC = F + C + N_R + N_{OC} = 0$$

$$DF = GDF - (GC + PSC) = (16) - (7 + 0) = 9$$

In this case, nothing has yet been specified so that there are nine degrees of freedom. Here, one might fix the feed flowrate of air and material to be dried and their compositions for a total of 1+1+(3-1)+(3-1)=6 particular and specific constraints. In addition, one can specify the amount of residual moisture in the dried product, the amount of adsorbed air on the dried product (zero) and the amount of dried product in the effluent air (zero). Notably, while it seems trivial that no significant amount of the dried product, such are not necessarily obvious to the new learner and present as significant stumbling blocks in their path.

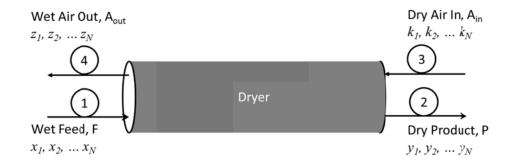


Figure 1. Dryer process flow for Example 3.

With the degrees of freedom analysis done correctly, student are presented with a direct way to know for sure what equations to write and which variables are fixed (specified) and which will be solved for. In this and all cases, set-up in advance with a degrees of freedom formality like this one is straight forward and the equations are easily identified by the *GC*. Here, students must write M=4 stream constraints, and N=3 balances. No additional (other constraints) are required to solve the problem.

Unfortunately, by the time students reach their senior year, e.g. reaction engineering or first term design, they have all but forgotten how to use degrees of freedom or have been *reprogrammed* by colleagues to solve balance by inspection. This, however, can be changed if a concerted effort is made to extend and illustrate the application of the degrees of freedom concept elsewhere, indeed, across the curriculum.

It is a travesty of sorts when flash separation is introduced or in many cases reintroduced in sophomore thermodynamics without the use of a formal degrees of freedom analysis. Yes, arguably, *all* thermodynamics texts introduce the flash separation with a Gibbs Phase primer, however, most do not include a macroscopic degrees of freedom analysis when setting-up and solving the requisite balance equations. The following example is simple and will help to reinforce the use of the degrees of freedom concept in thermodynamics and connect the concept with the Gibbs Phase Rule.

Example No. 4 – *Flash Separation and the Concept of Superposition* (a junior example): For a simple separation process involving N molecular species, two phases (p=2), one feed, and N products at equilibrium (n=N=2) and at steady-state, refer to Figure 2, the formalism produces the following:

 $GDF = M \times N + M_{Flows} + N_{Rates} + 2 = 3 \times N + 3 + 0 + 2 = 5 + 3N$ $GC = M_{StreamConstraints} + N_{Balances} + n(p-1) + RRR = 3 + N + N(2-1) + 0 = 3 + 2N$ $for PSC = F + C + N_R + N_{OC} + T + P = 0$

$$DF = GDF - (GC + PSC) = (5 + 3N) - (3 + 2N) = 2 + N$$

Here, liberty was taken to extend the formalism of CHW¹⁴ to explicitly include the process (internal) temperature and pressure along with the *GDF* and then to require that they be specified among the *PSC* or left unspecified and to be computed. This clearly makes these intensive process variables visible to the student and does not make them some form of *hidden knowledge*. In addition, the phase equilibrium constraints which number n(p-1)=N(2-1) are explicitly included among the *GC*; these could just as well have been included among the N_{OC} other constraints of the *PSC*. Here *n* is the number of the process components that are in equilibrium, in this case n=N, and *p* is the number of phases in equilibrium, in this case p=2. In this example, none of the *PSC* are specified so that the calculated *DF* number 2+N. Therefore, students see that 2+N of the unknowns must be specified. The obvious way to specify this problem is to fix one extensive parameter, e.g. the feed flowrate (F), the temperature (T), pressure (P) and *N-1* of the feed compositions for a total of 2+N of the variables.

For the above example, the following equations would be written:

$$N=2 \text{ Balances}$$

$$Fx_1 = Vy_1 + L z_1$$

$$Fx_2 = Vy_2 + L z_2$$

$$M=3 \text{ Stream Constraints}$$

$$x_1 + x_2 = 1$$

$$y_1 + y_2 = 1$$

$$z_1 + z_2 = 1$$

$$N(p-1)=2(2-1)=2 \text{ Phase Equilibrium Relationships}$$

$$y_1 P_T = x_1 P_1^o(T)$$

$$y_2 P_T = x_2 P_2^o(T)$$

In this case one must comply with the Gibbs Phase Rule, in which case N-p+2=2 of the intensive problem parameters must be specified and no more than two. The intensive problem parameters are y_1 , y_2 , z_1 , z_2 , T and P. By specifying any two of these, the entire intensive problem is specified. To correctly specify the extensive problem, one must specify N additional variables to make N+2 total specified variables. So, one might specify one extensive parameter, e.g. F, and N-1 compositions from among the remaining compositions, the x_i . Unless this superposition of problems, really a problem within a problem, is understood, a student might well specify F, y_I , T and P, thereby specifying N+2 of the variables, yet, violating (over specifying) the Gibbs Phase Rule. Notably, there are other ways to correctly specify this problem in addition to that described here.

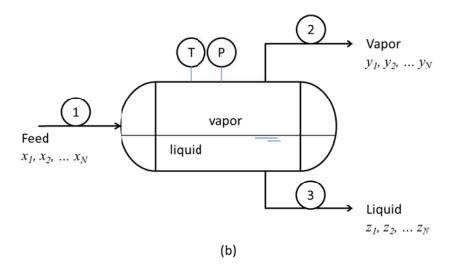


Figure 2. Vapor-liquid-equilibrium (VLE) example, a continuous VLE flash separation for Example 4.

Even at the sophomore level, one should include topics such as the superposition of problems. The concept of superposition of problems effectively means that there are sub-degrees of freedom requirements within the overall degrees of freedom problem. Although degrees of freedom formalisms are typically introduced along with special "rules," e.g. at least one

extensive variable must be specified, the mathematical concepts involving superposition are not generally covered.

Example 5 - Steady State Kinetic Stirred Tank Reactor (a senior example): Chemical reactor calculations should never start without conducting a degrees of freedom analysis; recognize that we, the instructors, are masters, as are the authors of textbooks on reactor design (most of which totally omit the concepts of degrees of freedom) and that our students are not. This said, both chemical reaction engineering and first term capstone design (assuming a two-term capstone design experience) are excellent opportunities to illustrate the power and utility of the degrees of freedom concept beyond sophomore material balance class. In this example, a continuous, stirred tank reactor (CSTR) is considered with one feed, one product (M=2) and a single chemical reaction involving four molecular species (N=4), refer to Figure 3. The conventional protocol that students use is to find the governing equation for a CSTR among the "many, many" equations in some reactor design book and to apply it without ever directly recognizing that this is a mass balance problem. Unfortunately, this protocol and practice disconnects the topic from the rigor already established in the sophomore year and circumvents an opportunity to demonstrate a formality that enables the new learner to realize which fundamental laws are at play. Start instead with a degrees of freedom analysis. Using again the formality of CHW¹⁴ one finds:

$$GDF = M \times N + M_{Flows} + N_{Rates} + 2 = 2 \times 4 + 2 + 4 + 2 = 16$$

$$GC = M_{StreamConstraints} + N_{Balances} + RRR = 2 + 4 + 3 = 9$$

$$for PSC = F + C + N_R + N_{OC} + T + P = 0$$

$$DF = GDF - (GC + PSC) = (16) - (9 + 0) = 7$$

Here we note that there are seven degrees of freedom that we must specify from among the *PSC*. Furthermore, the student is immediately alerted of which equations to write – there must be M=2 stream constraints of the form $\sum x_i^j = 1$, *N* balances of the form $x_i^F F - x_i^P P + R_i = 0$ and three reaction rate relationships $(RRR=3)^{\ddagger}$ numbering nine in all (GC=9). In this case, there is no guessing about which equation to find in a textbook or how to apply it or if it might be the correct one, or, for that matter, what is the correct form of the equation to use. Furthermore, the student has a clear view of all the variables that are being considered since they are counted among the GDF – there are $M \times N=8$ compositions, M=2 flowrates and N=4 reaction rates and two state variables (T and P) that must be specified or determined for a total of 16 GDF. Among these variables, seven must be specified else other constraints (equations) must also be written. Typically in a problem of this sort, the feed composition (N-1=4-1=3), the feed flowrate, the temperature and pressure and one reaction rate in the form of a kinetic rate law are specified for a total of seven *PSC*. The form of the governing equation typically derived in reaction engineering texts is implicit within these mass balance equation along with the reaction rate relationships and so no special equation form is every needed.

[‡] For a single chemical reaction involving four molecular species there will be 4-1=3 reaction rate relationships of the form $R_i = \alpha_{ij}R_j$, where α_{ij} is the ratio of stoichiometric coefficients for species *i* and *j* respective and must carry the sign, positive if both *i* and *j* are reactants or products and negative if one is a reactant and one a product.

Here we have a very clear and concise solution to a CSTR problem without ever having searched a text for the correct equation to use. The balance equations, solved simultaneously with the stream constraints, the reaction rate relationships and the one kinetic rate law, provide a unique solution to this steady-state reactor problem, all illustrated and facilitated in the context a degrees of freedom analysis.

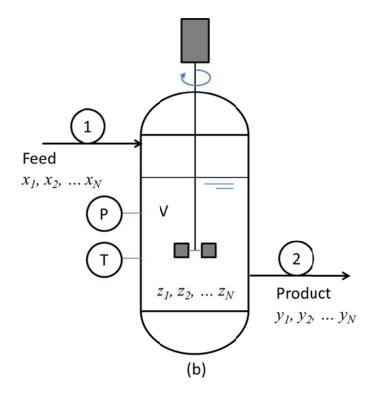


Figure 3. Continuous, stirred tank reactor for Example 5.

Student Feedback and Qualitative Assessment

As part of this on-going effort to investigate the impact of using the degrees of freedom concept as a more pervasive approach to problem solving in chemical engineering, the author has conducted a series of surveys to establish student impressions and preconceptions. Table 1 summarizes the central themes of the survey. Students were surveyed in the 1st term sophomore material balance course, 1st term junior thermodynamics, 1st term senior capstone design and in the required graduate reaction engineering course. Notably, the student populations are not the same students tracked over a period of time but rather are different individuals. All students were asked to respond to a set of seven questions. It is also notable, however, to point out that the majority of the upper classmen, about 80%, moved through the program, i.e. the seniors were once TTU freshmen and juniors. This is not the case, however, for the graduate student body since they are largely from other undergraduate programs. It is important, also, to point out that the survey was conducted primarily to gauge student perceptions and not to measure the effectiveness of the DoF-pedagogy at building better problem solvers. Realizing that an in-depth study is needed to glean any information regarding effectiveness, the survey results below are intended to help guide faculty at taking the next steps in implementing the DoF concept across the curriculum. Finally, the class sizes were large (~50 or more students), except for the graduate class.

The first question was an attempt to ascertain how students perceive engineering/science with respect to equations. Not surprisingly 38% of sophomores think there are "many, many equations." The fraction of students with this disposition appears to consistently decrease to 22% by the time they are graduate students. This question is relevant because it helps to establish one of the reasons why students find it difficult to solve problems in engineering, many feel that there are many equations and that they are uncertain which to use when. In the associate questions, it is interesting to note that as sophomores, 10% feel proficient at using the few laws that govern everything (conservation laws) while that number increases to 16% by the junior year and then falls to zero by the time they enter graduate school. If true, it appears that students become increasingly aware of their inability to solve problems and recognize that they are not proficient at using even the few laws that govern chemical engineering phenomena. Keep in mind that the seniors and graduate students represent the best of the student body since less able students tend to change majors in the sophomore and junior years. Likewise, students become increasingly aware, as they move through the curriculum, that there are indeed few laws and many specialize forms, 52% as sophomores increasing systematically to 78% as graduate students.

It is also good to find that students increasingly would like a structured way of solving problems, increasing from 87% as sophomores to 100% as graduate students. While at all levels student overwhelmingly respond positively to this query, it seems notable that this number increases with experience level.

After exposure to the degrees of freedom concept and specific training using examples and exercises based on and similar to those illustrated above, Question (3) is an attempt to see how students feel about using the concepts. Again, students tend to report greater appreciation of the usefulness of the degrees of freedom concept as they gain experience with it. The exception to this was in the junior thermodynamics course wherein the concept was not used as pervasively as it was in other offerings. This finding needs further investigation after the degrees of freedom concept is more uniformly implemented in 1st term thermodynamics.

Question (4) has the students self-assess their proficiency at using the degrees of freedom concept. Likewise, self-perceived proficiency increases with experience and level of exposure in the course, i.e. the junior thermodynamics course does not follow the trend likely because the level of exposure was lower than in the other courses.

When ask if they had encountered the degrees of freed concept in other courses, students report an increasing level of awareness as they move through the curriculum. The graduate student population does not however follow this trend. Since the majority of the graduate students polled were undergraduates at institutions abroad (not within the United States), it appears that they are clearly not being exposed to the degrees of freed concept. This data point, however, is of interest to this study since it suggests that the degrees of freedom concept is not widely used at other institutions abroad. Question (6) asked student if they would like to have seen the degrees of freedom concept used in other courses. 100% of the students responded that they would like to see the concept used in at least one of a list of courses that included engineering preparatory courses, e.g. chemistry, and other required chemical engineering courses, e.g. transport phenomena. Students also responded increasingly favorably with increasing experience regarding their desire to see degrees of freedom used specifically in upper-division chemical engineering courses.

Finally, Question (7) was asked to gauge the general level of student interest in their own success and preparedness. While their self-desire to be prepared seems to increase with experience, it appears that an overwhelming number of student are interested in their own level of preparedness. This question echoes the finding from Question (2) which indicates that across the board students are overwhelmingly seeking ways to systematically solve problems.

Admittedly, additional assessment needs to be done, a control and treatment group might be used and a more rigorous study design. Nonetheless, the above preliminary data should be a helpful starting point for a more in-depth analysis.

Discussion and Concluding Remarks

The familiar degrees of freedom concept taught in most chemical engineering sophomore material (and energy) balance courses could become a building block for improving our students' ability to set-up and solve problems across the major courses of the curriculum. A prototype for doing this is being tested in select courses in in the Department of Chemical Engineering at Tennessee Technological University. Student impressions of the approach and their self-assessment of achievement has been assessed in a first attempt to gather preliminary impacts data. Overall, as students grow in their knowledge and experience with problems solving, i.e. as they move through the curriculum from sophomore to seniors and then on to graduate students, they tend to also grow in their desire to have a more formalized way to set-up and solve problems and their desire to have used the degrees of freedom concept in other courses wherein it could help them understand how to apply the laws and principles learned. The author suggests introducing the degrees of freedom concept as early as possible and preferably in a freshmen introduction to chemical engineering course and to follow, at a minimum, with rigorous training as part of the sophomore material (and energy) balance course and to revisit the concept as appropriate in thermodynamics (I and II), reaction engineering and then finally solidify the DoF concept as a fundamental building block by reinforcing the concept in capstone design (I and II). Table II, is a summary of suggested across the curriculum integration points for pervasive use of the degrees of freedom concept.

Acknowledgements

The author gratefully acknowledges the contributions of his colleagues Drs. Laura Chavez, Jeffrey Rice and Pedro Arce for permitting him to survey their students. The author also acknowledges his many students that have enabled him to explore and experiment with the concepts presented in this paper.

Question	Material Balances	Thermo I	Design I	Reaction Engineering
Level	1 st term sophomore	1 st term junior	1 st term senior	graduate student
Number of respondents	75	49	50	9
Question No. 1				
I think				
there are many, many equations	38	27	27	22
there are many specialized forms of few basic laws	52	57	61	78
there are few basic laws and I'm proficient at using them	10	16	12	0
Question No. 2				
I'd like a structure way to set-up equations				
yes	87	94	96	100
Question No. 3				
I think DOF is				
somewhat helpful	23	18	30	33
helpful to very helpful	55	22	62	66
useless	11	23	8	0
Question No. 4				
I understand how to use the DOF concept				
somewhat	36	39	30	33
I agree to I totally agree	56	20	70	66
not used in this course at all	0	32	0	0
Question No. 5				
I've seen DOF in				
other courses before	40	73	68	11
never before	60	27	32	89
Question No. 6				
I'd like to see DOF used in				
upper division CHE courses	30-49	50-61	36-66	44-67
% responding positively	100	100	100	100
Question No. 7				
I care about being prepared	95	98	96	100

Table 1. Summary of student survey responses.

Table 2. A suggested progression of examples to use to develop extended high level of competency in the application of the degrees of freedom concept.

Example Form of Degrees of Freedom Formalism Used		Comments		
2 nd term freshman year				
Example 1 – How many choices do you have?	None	A degree of freedom can be equated to a choice or decision you must make. For every decision (choice you have) there is a degree of freedom.		
Equations and variables (unknowns).	DF = #UK – #EQ	The Degrees of Freedom concept should be introduced as a general purpose tool for problem solving when decisions must be made.		
Example 2 – Balancing a simple chemical reaction.	DF = #UK – #EQ	This example brings together the DF concept with equation solving using an application already familiar to every CHE freshman.		
Heat and Material Balances (1 st term sophomore term)				
Example 3 – Simple stead-state macroscopic mass balance without chemical reaction.	$GDF = M \times N + M$ $GC = M + N$ $PSC = F + C + OC$ $DF = GDF - (GC + PSC)$	GDF are defined as the total number of unknowns (#UK). GC are defined as all the equations you can write. PSC are degrees of freedom already specified by the problems.		
Steady-state macroscopic balance with chemical reaction.	$\label{eq:GDF} \begin{split} GDF &= M {\times} N + M + N \\ GC &= M + N + RRR^{\$} \\ PSC &= F + C + OC + N_R \\ DF &= GDF - (GC + PSC) \end{split}$	The concept of the reaction rate relationship is introduced.		
Thermo I (1 st term junior)				
Example 4– Steady-state macroscopic balance involving phase equilibrium, e.g. vapor-liquid equilibrium.	$GDF = M \times N + M + N + 2$ GC = M + N + RRR + N(p-1) $PSC = F + C + OC + N_R + T + P$ DF = GDF - (GC + PSC)			

[§] The number of reaction rate relationships is determined by finding the rank of the matrix used to balance the chemical reactions that are needed to define the chemical changes in the process. This procedure is outlined in detail elsewhere, see reference (14) for example.

Table 2, Continued. A suggested progression of examples to use to develop extended high level of competency in the application of the degrees of freedom concept.

Example	Formalism Used					
Thermo II (2 nd term junior)						
Example 6 – Multiple effect opened, steady systems involving vapor-liquid equilibrium, e.g. distillation tower.	$GDF = M \times N + M + N + 2$ GC = M + N + RRR + N(p-1) $PSC = F + C + OC + N_R + T + P$ DF = GDF - (GC + PSC)	Again, the formalism in not advanced, but rather reinforced, here illustrated for Vapor-Liquid equilibrium, a topic already introduced in CHE 2011, but further detailed here. For the closed system, the Gibbs Phase Rule is recovered, once again illustrating for the students the broad utility and applicability of the formalism.				
Opened, steady systems involving chemical equilibrium and mixed physical and chemical equilibrium.	$\label{eq:GDF} \begin{split} GDF &= M {\times} N + M + N + 2 \\ GC &= M + N + RRR + N(p{\text -}1) \\ PSC &= F + C + OC + N_R + T + P \\ DF &= GDF - (GC + PSC) \end{split}$	The introduction of chemical equilibrium stretched the application, but does not change the degrees of freedom formalism, further illustrating for the students its generality and applicability.				
Chemical	Chemical Reaction Engineering (1 st term senior year)					
Example 5 – Stead-state CSTR balances involving kinetic-based chemical reactions.	$GDF = M \times N + M + N$ $GC = M + N + RRR$ $PSC = F + C + OC + N_R$ $DF = GDF - (GC + PSC)$					
Unsteady balances involving arbitrary chemical reaction.	Requires Extended Formalism	A final extension is made here to include the initial conditions for the unsteady problem.				
Design I/II (1 st term senior year/2 nd term senior year)						
Process steady-state mass balances; various unit operation design and performance modeling including dynamic analysis.	$GDF = M \times N + M + N + 2$ GC = M + N + RRR + N(p-1) $PSC = F + C + OC + N_R + T + P$ DF = GDF - (GC + PSC)	Here students can really "test their mettle" by applying the full formalism to many unit operations for steady and unsteady problems. By now, using the degrees of freedom formalism to enable problem solving should be a "way of being."				

References

¹ R. M. Felder and R. W. Rousseau, "Elementary Principles of Chemical Processes," John Wiley and Sons, pp. 675 (2000).

 ² J. M. Smith, H. C. Van Ness and M. M. Abbott, Introduction to Chemical Engineering Thermodynamics, 7th ed." McGraw-Hill, pp. 817 (2005).

- ³ J. D. Seader and E. J. Henley, "Separation Process Principles," John Wiley and Sons, pp. 886 (1998).
- ⁴ H. S. Fogler, "Elements of Chemical Reaction Engineering, 4th ed.," Prentice Hall, pp. 1081 (2006).
- ⁵ E. B. Nauman, "Chemical Reactor Design, Optimization, and Scale-up, 2nd ed." John Wiley and Sons, pp. 608 (2008).
- ⁶ W. L. McCabe, J. C. Smith, and P. Harriott, "Unit Operations of Chemical Engineering, 7th ed.," McGraw-Hill, pp. 1140 (2005).
- ⁷ G. E. P. Box, W. G. Hunter and J. S. Hunter, "Statistics for Experimenters An introduction to design, data analysis, and model building," John Wiley & Sons, pp. 653, (1978).
- ⁸ R. V. Hogg and J. Ledolter, "Applied Statistics for Engineers and Physical Scientists," 2nd ed., Macmillan, pp. 472, (1992).
- ⁹ D. L. Silverstein, L. G. Bullard, and M. A. Vigeant, "How We Teach: Material and energy Balances," ASEE Annual Meeting, AC 2012-3583 (2012).
- ¹⁰ W. L. Luyben, Design and Control Degrees of Freedom, Ind. Eng. Chem. Res., 35 2204-2214 (1996).
- ¹¹ R. Ravi, D. P. Rao, Phase rule and the Degree of Freedom Analysis of Processes, Ind. Eng. Chem. Res., 44(26) 10016-10020 (2005).
- ¹² M. Rodreguez and J. A. Gayoso, Degrees of Freedom Analysis for Process Control, 16th European Symposium on Computer Aided Process Engineering and 9th International Symposium on Process Systems Engineering, pp. 1489-1494 (2006).
- ¹³ J. W. Ponton, Degrees of Freedom Analysis in Process Control, Chem. Eng. Sci., 49(13) 2089-2095 (1994).
- ¹⁴ R. L. Cerro, B. G. Higgins, and S. Whitaker, "Material Balances for Chemical Engineers," Copyright Cerro, Higgins & Whitaker, online at: <u>https://sites.google.com/site/materialbalancesforche/</u> (2010).