The New Stoichiometry*

EDWARD M. ROSEN
Monsanto Company
St. Louis, Missouri

ERNEST J. HENLEY
University of Houston
Houston, Texas

In May of this year we sent a questionnaire to all AIChE accredited schools to determine the subject matter now included in stoichiometry or the equivalent first course in chemical engineering. The replies to this questionnaire indicate quite clearly that 1) the overwhelming majority of the courses are still in the mold cast by Hougen and Watson in the 1940's, and 2) there is a certain amount of experimentation, dealing mostly with the introduction of computer techniques into the curriculum.

This introduction of computing techniques into material and energy balance courses must ultimately give rise to what we call 'the new stoichiometry.' The new stoichiometry, in turn, will form the foundation for the computer aided design and simulation courses which we expect will find a place in all chemical engineering curriculums within a decade. It seems appropriate to examine first, therefore, the elements of a computer aided design system.

Table I is a partial listing of computer aided chemical design systems. Of the industry programs, the CHEOPS is considered by many to be the grandfather because of the wide publicity it received in the early 1960's. The CHEVRON program, which is oriented towards hydrocarbons, has been made operational at the University of California, Berkeley. The PEDLAN program is one of the first to be written in a problem oriented language and requires a Fortran precompiler.

The CHIPS, KELLOGG, PECOS, and UOS programs are available through service companies, as is PACER, which was originally developed at Purdue and Dartmouth. The CHESS program is in operation at the University of Houston, and its capability is now being greatly extended with help of a Themis grant, ONR Contract N0014-68-A-0151. SLED, under development at Michigan, is analogous to PEDLAN in that it utilizes a problem oriented language. MAEBE is a first generation material and energy balance program, and SPEED-UP is not fully implemented.

If a stochiometry course is to serve as a precursor to a computer aided design course, we must analyze the design system in terms of its com-

*Presented at the Annual Meeting of ASEE, June 17-20, 1968.

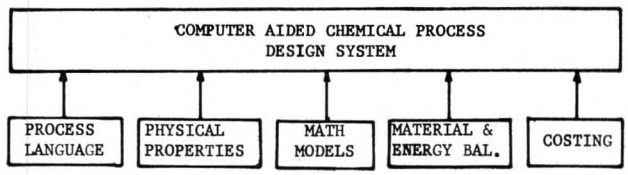


Fig. 1.—Elements in computer aided chemical process design systems.

Table I. Computer Aided Chemical Process Design Systems*

Industry

CHEOPS—Chemical Engineering Optimization System, Shell Oil
CHEVRON—General Heat and Material Balancing Program, CHEVRON Research Company
PEDLAN—Process Engineering Design Language, Mobil Oil Company

Service Companies

CHIPS—Chemical Engineering Information Processing System, IBM Service Bureau
KELLOGG Flexible Flowsheet—M. W. Kellogg
PECOS—Bechtel Company
UOS—Unit Operations Simulator, Bonner and Moore (Fluor Company)

Education Institutions

CHESS—Chemical Engineering System Simulator University of Houston
MAEBE—Material and Energy Balance Execution, University of Tennessee
PACER—Process and Case Evaluator Routine, Dartmouth
SLED—Simplified Language for Engineering Design, University of Michigan
SPEED-UP—Simulation Program for the Economic Evaluation and Design of Unsteady State Processes, Imperial College

*A complete tabulation and discussion of computer aided design systems is given by Evans, Stewart, and Sprague, **CEP**, Vol. 64, No. 4, 1968.

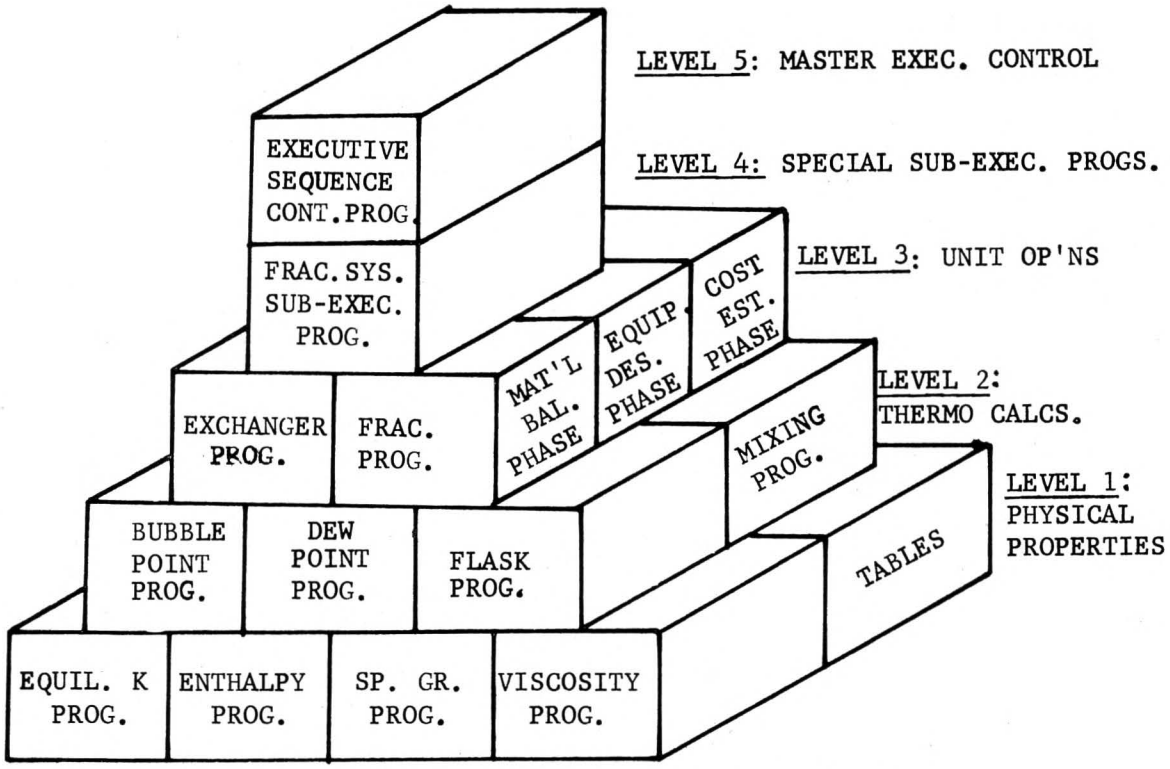


Fig. 2.—Building blocks in a preliminary design and capital cost system for fractionating columns.

ponent parts to see what fundamental principles are involved. Figure I shows the five component parts:

1. The process language which converts the language of the engineer to that of the computer
2. The physical property package which generates the necessary information regarding transport, P-v-T, and thermodynamic properties
3. The mathematical representation of the building blocks (transfer functions, if you will)
4. The material and energy balance 'executive program' which links the building blocks
5. Costing programs, which may include some sort of optimization program.

In Figure 2 we see a more detailed breakdown of the blocks in Figure 1 as they are used in the design of a fractionation column. On the lowest level we have the physical property tables or equations. These are really a part of a system which includes subroutines to produce enthalpy values, equilibrium constants, etc.

Next there is a second level of thermodynamic calculations which use the lower level physical property programs. Dew point, bubble point, and flash programs are the examples cited.

On the third tier we have the transfer functions for the building blocks; the mathematical representation of the classic unit operations. The level four function ties together the block of programs comprising the fractionation system, and overseeing the whole conglomeration of subprograms which comprise the bottom four levels we have an executive control program which takes into consideration all input and output format and everything else that goes into a well formulated system.

If one of the objectives of the 'new stoichiometry' is to train a student to create and use computer aided design systems, it is necessary to define the topics which must be included. In Figure 3 we define the five building blocks for the new stoichiometry.

We have (1) thermodynamics and (2) classical stochiometry; these two blocks together form the manual method block in the 'Hougen-Watson mold.' The other three elements, (3) linear algebra, (4) solution of equations, and (5) algorithm development, together with (1) and (2) are the required building blocks for machine method calculations. The remainder of this paper details the material in building blocks (3), (4), and (5). The examples used are from our forthcoming book "Material and Energy Balance Computation," John Wiley (June 1968).

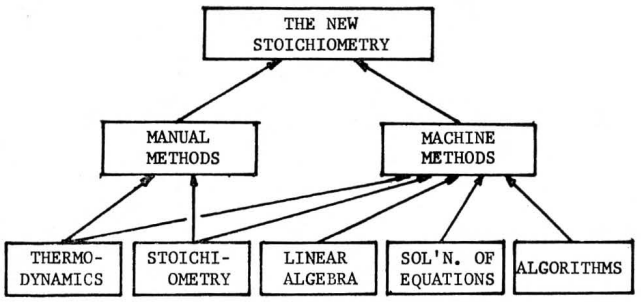


Fig. 3.—Elements of the new stoichiometry.

Linear algebra, in the words of Rutherford Aris, "is the proper language of stoichiometry." Indeed, linear algebra is the only type of algebra digital computers can do; they cannot handle nonlinear problems. Consider, for example, Gibb's Rule of Stoichiometry, Figure 4. It states that the maximum number of linearly independent chemical reactions in a set of reactions is equal to the number of chemical species known (from experiment) to be present, minus the rank of the atom matrix. The atom matrix for a five component mixture consisting of CO, H_2, CH_3OH, CO_2, andH_2O is shown in Figure 5, where the rows are the species and the columns the atoms. The determination of the rank of this matrix is an exercise in linear algebra. A classic technique for determining the rank of a matrix is the Gram-Schmidt method where we attempt to construct a set of m orthogonal vectors, $Y_1, Y_2, \ldots Y_M$ from $X_1, X_2, \ldots X_M$. If the length of a Y vector is zero, then orthogonalization is impossible, and the X vector is parallel to one of the others. The procedure is shown in Figure 6: the rank of the atom matrix in Figure 5 is three. Thus, according to the Gibb's Rule of Stoichiometry, there are are two independent reactions.

Taking the two reactions shown in Figure 7 as the independent reactions, we construct the reaction matrix in Figure 7. The rows are the species; the columns the stoichiometric coefficients for reactions (1) and (2). The matrix formulations of the material balance lead logically and simply to the elegant statement for the conservation of atoms shown in Figure 8. The product of the transpose of the reaction matrix times the atom matrix must be zero. We hope that this example is a convincing demonstration of Aris' axiom.

Next we consider the nature and function of block four, the solution of nonlinear equations. In the isothermal flash vaporization shown in Figure 9, $f_H(\alpha)$ and $f_R(\alpha)$ are two valid and identical solutions of the material balances. In these equations $\alpha = L/V$ and $K_i = y_i/x_i$. Since z_i, the feed composition is known, and K is known,

$$\begin{pmatrix}\text{MAX. NUMBER OF LINEARLY INDEPENDENT REACTIONS}\end{pmatrix} = \begin{pmatrix}\text{NUMBER OF SPECIES}\end{pmatrix} - \begin{pmatrix}\text{RANK OF THE ATOM MATRIX}\end{pmatrix}$$

$$M = N - R$$

Fig. 4.—Gibbs rule of stoichiometry.

	ATOMS		
SPECIE	C	O	H
CO	1	1	0
H_2	0	0	2
CH_3OH	1	1	4
CO_2	1	2	0
H_2O	0	1	2

Fig. 5.—Atom matrix for a five component system, example 1.

GIVEN: $X_1, X_2, \ldots X_M$

$$Y_1 = X_1$$

$$Y_2 = X_2 - \left(\frac{Y_1 \cdot X_2}{Y_1 \cdot Y_1}\right) Y_1$$

$$\vdots$$

$$Y_M = X_M - \left(\frac{Y_{M-1} \cdot X_M}{Y_{M-1} \cdot Y_{M-1}}\right) Y_{M-1} - \cdots - \left(\frac{Y_1 \cdot X_M}{Y_1 \cdot Y_1}\right) Y_1$$

Fig. 6.—The Gram-Schmidt procedure for example 1. Rank, R = 3.

SPECIE	REACTION 1	2
CO	-1	1
H_2	-2	-1
CH_3OH	1	
CO_2		-1
H_2O		1

$$M = 5 - 3 = 2$$

$$CO + 2H_2 = CH_3OH \qquad (1)$$

$$CO_2 + H_2 = H_2O + CO \qquad (2)$$

Fig. 7.—Reaction matrix for two linearly independent reactions.

these are simply non-linear equations in one unknown, α. They can be solved readily by any number of one-dimensional, non-linear root finding techniques.

In Figure 10 we have a plot of both $f_R(\alpha)$ and $f_H(\alpha)$ vs. α. The root, at $f_R(\alpha) = f_H(\alpha)$, has been successfully found and is, as it should be, identical for both equations. There are, however, major differences in the shape of the curves, and we see that the $f_H(\alpha)$ function gives us two roots,

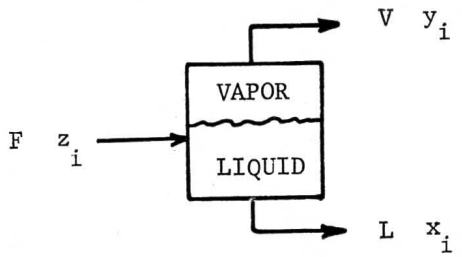
REACTION MATRIX ATOM MATRIX

$$\begin{pmatrix} -1 & -2 & 1 & 0 & 0 \\ 1 & -1 & 0 & -1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 & 0 \\ 0 & 0 & 2 \\ 1 & 1 & 4 \\ 1 & 2 & 0 \\ 0 & 1 & 2 \end{pmatrix} = 0$$

Fig. 8.—The conservation of atoms.

one of which is spurious. Clearly, if we are to avoid such pitfalls we can not blindly set up and solve material and energy balances and feed the resulting equations to a computer.

In this 'one-dimensional' example we had only one non-linear equation to deal with. Let us now examine the multi-dimensional set of equations



$$Fz_i = Vy_i + Lx_i$$

BY REARRANGEMENT:

$$\sum_{i=1}^{N} y_i = \sum_{i=1}^{N} \frac{z_i K_i}{1 + \alpha(K_i - 1)} - 1. = f_H(\alpha)$$

$$\sum_{i=1}^{N} x_i - \sum_{i=1}^{N} y_i = \sum_{i=1}^{N} \frac{z_i(1 - K_i)}{1 + \alpha(K_i - 1)} = f_R(\alpha)$$

Fig. 9.—Isothermal flash equations, example 2.

which will arise from the flowsheet for the catalyting dehydrogenation of propane, Figure 11. We note immediately that there are two recycle streams, S12 and S2, which preclude a straight-through solution to the material and energy balances.

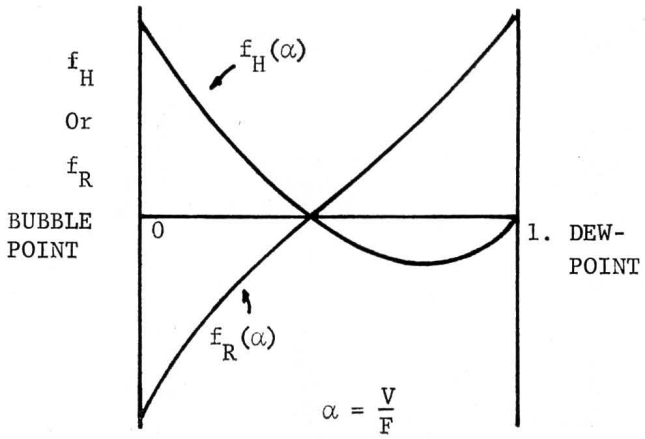


Fig. 10.—Plot of functions $f_H(\alpha)$ and $f_R(\alpha)$ for example 2.

One method of handling problems of this type is by 'tearing' the flowsheet and estimating a composition. If, for instance, we tear stream S13 (between the stripper and absorber) and guess at the composition for S7, we are able to calculate all of the remaining process streams, S1 - S13, in the sequence S8, S12, S10, S11, S2, S3,

S4, S5, S9, S6, S13. If we have guessed the composition S7 correctly, then S13 will equal S7. If not, we have to re-estimate S7 and try again.

This physical situation is given a mathematical formulation in Figure 12. We estimate the stream vector X, calculate the process vector $\phi(X)$ and if $\phi(X)$ equals X we are finished. If not we pass through a convergence block which, hopefully, will give us a new X which is a better approximation to $\phi(X)$. Since the X stands for all unknown parameters of temperature, pressure, compositions, and properties, it is apparent that the solution of problems of this type are primarily exercises in the solution of large sets of non-linear equations in many unknowns.

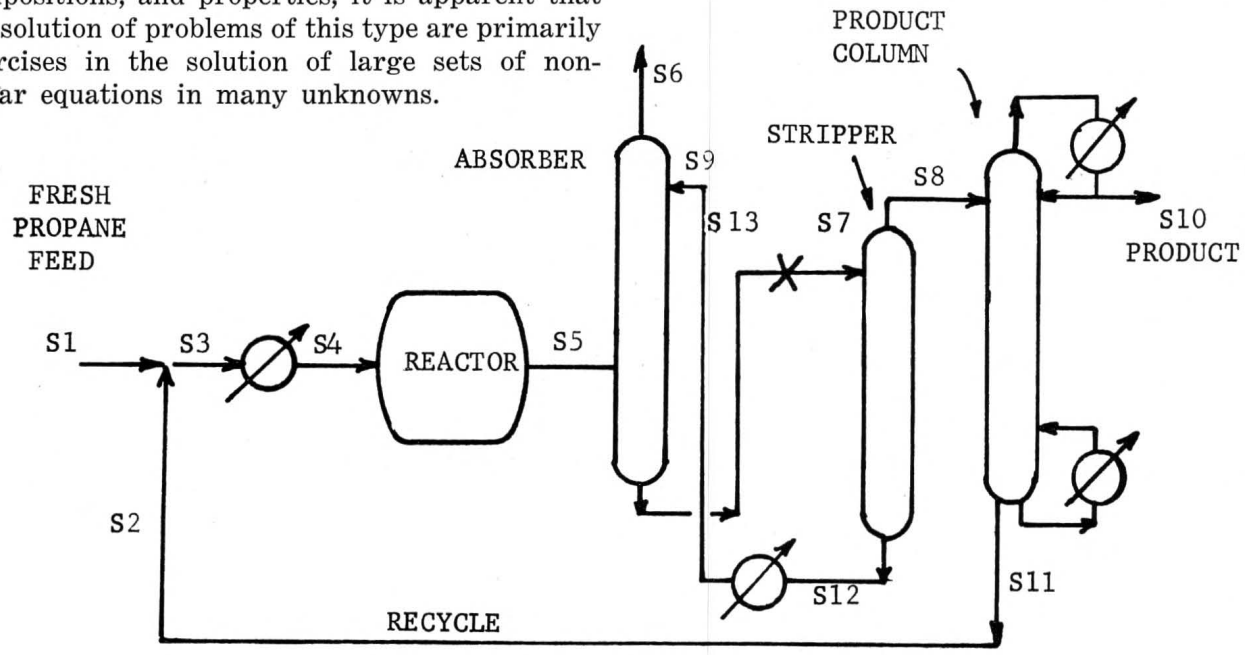
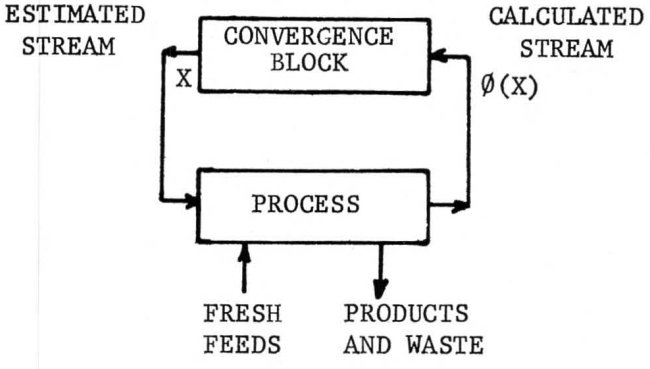


Fig. 11.—Flowsheet for catalytic dehydrogenation of propane to propylene, example 3.

The next block in our 'new stochiometry' is a not-so-new subject, thermodynamics. The rigorous formulation of material and energy balances requires a deeper background in thermodynamics than is now attempted in the majority of material and energy balance courses. For example, if a chemical reaction takes place thermodynamics tells us that at equilibrium the stoichiometric coefficient times the chemical potential equals zero (Figure 13).

In terms of the reaction extent, e, the number of moles of component i present at any time is $n_i = n_{io} + \alpha_i e$, where n_{io} is the initial number of moles. The final equation from which we calculate the composition of the reaction mix given free energy data and the initial number of moles is a non-linear function in one unknown, $\phi(e) = 0$. To obtain this equation we needed thermodynamics.

The methods of the new stoichiometry provide the tools for the development of useful algorithms, which is building block five for the machine methods. By useful algorithms we mean a well defined set of statements that lead to the solution of a problem. In order to obtain the output of any building block as a function of the input to the block, and hence to set up our design system, we must have algorithms. Let us now see how we would use our knowledge of thermodynamics and non-linear equation solving techniques to develop



$$F(X) = \emptyset(X) - X = 0; \quad X \geq 0$$

Fig. 12.—The convergence block as an equation solver.

an algorithm to calculate the composition of a mixture in physical and chemical equilibrium.

CONDITION OF EQUILIBRIUM AT T AND P IS

$$\sum_{i=1}^{N} \alpha_i \mu_i = 0$$

FOR IDEAL CONDITIONS

$$\mu_i = \mu_i^o + RT \ln P_i$$

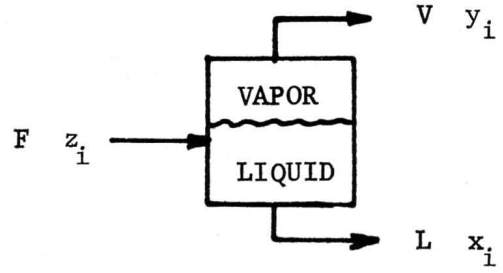
$$RT \sum_{i=1}^{N} \alpha_i \ln P_i = - \sum_{i=1}^{N} \alpha_i \mu_i^o$$

FOR: $n_i = n_{io} + \alpha_i e$

SOLVE: $\phi(e) = 0$

Fig. 13.—Use of thermodynamics, example 4.

In Figure 14 we have a simple system in which we have a flash vaporization plus a series of M chemical reactions (j = 1 to j = M). There are N components (i = 1 to i = N). The component balances as well as the overall balance are shown in Figure 14 and our final equation is shown in Figure 15 in terms of K_i which, as before, is y_i/x_i.



COMPONENT BALANCE

$$Fz_i = Vy_i + Lx_i - \sum_{j=1}^{M} \alpha_{ij} e_j$$

OVERALL BALANCE

$$F = V + L - \sum_{i=1}^{N} \sum_{j=1}^{M} \alpha_{ij} e_j$$

Fig. 14.—Model of process.

If the temperature and pressure and the feed composition z_i are fixed, $f(\alpha)$ is one equation in two unknowns, α and e. To solve the equation we propose the algorithm shown in Figure 15. We (1) estimate the e reaction extents, (2) solve for α, (3) calculate the material balances, (4) check to see if the equilibrium constant has been satisfied. If it is not, we make a new estimate of e and start again. The new estimate is usually made using a Wegstein or similar convergence-forcing routine.

What we have tried to demonstrate in this paper are (1) the techniques now being used by industry in the formulation of computer aided design and simulation systems and (2) how these may be incorporated into existing stochiometry courses to produce the 'new stoichiometry.'

BY REARRANGEMENT

$$\sum_{i=1}^{N} \frac{\left(z_i + \frac{\sum_{j=1}^{M} \alpha_{ij} e_j}{F} \right) (1 - K_i)}{\left(1 - \alpha + \sum_{i=1}^{N} \sum_{j=1}^{M} \alpha_{ij} e_j \right) + K_i \alpha} = f(\alpha)$$

1. ESTIMATE $e_1, e_2 \ldots e_M$
2. SOLVE FOR α
3. CALCULATE x_i AND y_i FROM RESULTS OF STEP 2
4. EVALUATE

$$\left[\frac{\Delta G_T^o}{RT} \right]_j = -\ln K_j = \phi(y_i) \qquad j = 1, 2, \ldots M$$

Fig. 15.—Suggested algorithm.

Professor Henley is Associate Dean and Professor of Chemical Engineering at the Cullen College of Engineering, University of Houston. He received his BS from the University of Delaware and an MS and Dr. Eng. Sci. from Columbia University. He served on the faculty at Columbia from 1953 to 1958, was associated with Stevens Institute of Technology from 1958 to 1964, and from 1964 to 1966 was Chief-of-Party of the AID mission at the University of Brazil. He is the author of over 50 research papers, and five books, and is the editor of the **Advances in Nuclear Science and Engineering.** He has done extensive consulting for government and industry and is a member of the Board of Directors of three publicly-held corporations.