The book is very inclusive in the treatment of the chemical and physical principles that determine the behavior of substances in chemical processes. There is much material on phase equilibrium and material and energy balances in staged systems. The book is liberally supplied with examples, problems and data tables.

The more likely reason for selecting this book would be the desire to emphasize the new stoichiometry. The three unique chapters, then, are of special interest. Of these, Chapter 5 deals with "The Solution of Equations." In this chapter, methods for solving sets of linear and non-linear equations are presented. The methods are applied to given equations, not to process problems in this chapter. Especially worthy of note is that an appendix includes complete FORTRAN IV program listings for four of the methods discussed. They are: GMST, Gram-Schmidt method of constructing orthogonal vectors for sets of linear equations; GELG, Gaussian elimination method for solving a set of linear equations; ROOT, finds the root of a one-dimensional, non-linear equation; and, BSOLVE, Marquardt's method to solve a set of non-linear equations. Each program includes the solution to an example problem from the text. This chapter could be useful in many contexts for it presents in a reasonably clear and concise form several useful algebraic-equation-solving techniques.

Chapter 8 emphasizes developing solution algorithms for certain process calculations, namely flash vaporization and equilibrium-extent-of-reaction in both homogeneous and heterogeneous systems. This chapter requires a rather thorough understanding of the principles of phase-and chemical-equilibria. A number of excellent examples of problem formulation and algorithm development are included.

Chapter 9 emphasizes process material and energy balances by computer process simulation. The building-block approach is clearly presented. The contents of the building-blocks tend to be somewhat obscure. Indeed an example illustrating the individual block calculations includes a reactor where conversion is kinetically determined. The equations cannot be very meaningful to a student, for nothing in the book has prepared him for a non-equilibrium chemical reactor.

Chapter 9 presents and compares direct substitution, the quasi-Newton method and an extension of Nagiev's method of split-fractions for handling recycle loops. It represents a reasonably good introduction to the rapidly developing field of computer process simulation and design. The level of chapters 8 and 9 would seem to be above that of a first course, but they contain valuable material for chemical engineering curriculum.

In summary, this book could be used as a traditional stoichiometry book. It offers a very thorough treatment of the physical and chemical bases of material and energy balances, though in this reviewer's opinion the treatment of some topics lacks clarity. It offers material unique in this type of book in the way of the mathematics and the use of a digital computer for solving sets of equations, the development of algorithms for certain complex process operations, and an introduction to computer simulation of chemical processes. This new material is welcome in textbook form, though much of it appears to be above the level of the typical first course.

This book is sufficiently important that all teachers of chemical engineering undergraduate courses should examine it. They might choose to use portions of it in several courses.

Ronald E. West
University of Colorado

ChE problems for teachers

Simplified Approach to POLYTROPIC PROCESSES

FRANK M. TILLER AND FRED LOWRY
University of Houston
Houston, Texas 77004

Q. Derive expressions for polytropic processes.

A. Little attention is given to developing new techniques for teaching elementary concepts in thermodynamics in comparison to emphasis on advanced research. When new methods can be found which simplify and afford clearer presentation of basic principles, the student can proceed more rapidly and confidently to advanced aspects of the subject. The authors believe that one of the surest methods for providing more time and better understanding of advanced topics arises from improving approaches to the simpler topics of thermodynamics.

We have explored a new way of deriving the well-known expression pV^n = constant, which is straight forward in approach and appealing to the student. The proposed method can be restricted to processes, or it may be broadened to include irreversible effects. The instructor can take up the simpler reversible case or go into more depth by treating lost work. While more explanation is required when friction effects are included, a broader understanding is produced; and an introduction to irreversibility is commenced.

In the simpler reversible case, the method consists of assuming that the polytropic specific heat for an ideal gas is constant and then deriving the expression pV^n = constant. This procedure is the reverse of that which is usually encountered in textbooks, where it is first assumed that the expression pV^n = constant is valid; and then the polytropic specific heat is shown to be constant. In many texts, derivation of pV^k = constant for a reversible adiabatic process is the first step toward the more general expression. In the proposed method, the more general pV^n = constant is derived, and it is then demonstrated that $n = k$ is a special case.

In the second case involving lost work, it is possible to introduce the concept of a quasi-equilibrium process with friction, and then derive a more general expression of the form pV^{n_i} = constant. The exponent n_i reduces successively to n for a reversible operation and then to k for the added constraint of adiabaticity.

In the reversible case, the first law of thermodynamics

$$d'Q = dU + d'W \tag{1}$$

becomes

$$NCdT = NC_v dT + pdV \tag{2}$$

with the assumptions of an ideal gas constant specific heat, and reversibility. Introducing irreversibility, it is possible to say

$$d'W = d'W_r + d'L_w = (1 \pm r)pV \tag{3}$$

Various postulates concerning friction are possible. For our purposes, we assume that the lost work is proportional to the reversible work, because that assumption leads to the answer we want in the form pV^{n_i} = constant. The sign prefixing the factor r is dependent upon whether the process involves expansion or compression of the gas as demonstrated in Figure 1.

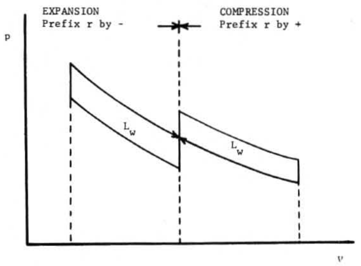

FIGURE 1

For the irreversible case, the first law becomes

$$NC_i dT = NC_v dT + (1 \pm r)pdV \tag{4}$$

where C_i is an irreversible specific heat. Utilizing $pV = NRT$, the differential dT can be eliminated from Equations (2 and (4) to give

$$\frac{dp}{p} = -\left(\frac{C_p - C}{C_v - C}\right)\frac{dV}{V} \tag{5}$$

$$\text{or} \quad \frac{dp}{p} = -\left[\left(\frac{C_p - C_i}{C_v - C_i}\right) \pm r\left(\frac{C_p - C_v}{C_v - C_i}\right)\right]\frac{dV}{V} \tag{6}$$

whose solutions are, respectively,

$$pV^n = \text{Constant} \qquad pV^{n_i} = \text{Constant} \tag{7a,b}$$

$$\text{where} \quad n = \frac{C_p - C}{C_v - C} \quad \text{and} \quad n_i = \left(\frac{C_p - C_i}{C_v - C_i}\right) \pm r\left(\frac{C_p - C_v}{C_v - C_i}\right)$$

Various thermodynamic relations for irreversible processes can similarly be developed for expansion and for compression.

IT IS POSSIBLE to derive a series of equations for Q, W, ΔU, ΔS, and pVT relationships gased on Equation (7a,b). For example, the irreversible specific heat is given by

$$C_i = C_v - \left(\frac{1 - r}{n_i - 1}\right) R \tag{8a}$$

for expansion and

$$C_i = C_v - \left(\frac{1 + r}{n_i - 1}\right) R \tag{8b}$$

for compression. The isobaric specific heat with $n_i = 0$ becomes

$$C_{pi} = C_v - (1 \pm r)R = C_p \mp rR \tag{9}$$

For $r = 1$, corresponding to complete irreversibility in an isobaric expansion,

$$C_{pi} = C_p - R = C_v \tag{10}$$

For an adiabatic process, the pV relation is

$$pV^{k \pm r(k-1)} = \text{Constant} \tag{11}$$

When $r = 1$, the process corresponds to an unrestrained expansion, and the exponent in (11) becomes unity as expected.

The entropy change offers a good opportunity to show that $dS \neq dQ_i/T$. The first law can be written as

$$d'Q_i = dU + (1 \pm r)pdV \tag{12a}$$

$$= dU + pdV \pm rpdV \tag{12b}$$

where Q_i is used to emphasize that the heat transfer occurs in an irreversible operation. The quantity $dU + pdV$ can be replaced by TdS, thereby leading to

$$dS = \frac{d'Q_i}{dT} - \frac{d'L_w}{dT} = NC_i \frac{dT}{T} - (\pm r)\frac{pdV}{T} \tag{13}$$

Substituting $NR/V = p/T$ leads to

$$\Delta S = NC_i \ln(T_2/T_1) - (\pm r)NR\ln(V_2/V_1) \tag{14}$$

For an adiabatic process, (14) reduces to

$$\Delta S = rNR\ln V_2/V_1 \tag{15}$$

for an expansion.

It is possible to have an isentropic expansion which is not reversibly adiabatic. By placing $\Delta S = 0$ in (14), manipulation leads to

$$\left(\frac{T_2}{T_1}\right)^{C_i} = \left(\frac{V_1}{V_2}\right)^{rR} \tag{16}$$

as the condition for an isentropic process.

Nomenclature

C	Reversible polytropic specific heat
C_i	Irreversible polytropic specific heat
C_p	Reversible specific heat at constant pressure
C_{pi}	Irreversible specific heat at constant pressure
C_v	Specific heat at constant volume
k	Adiabatic exponent
L_w	Lost work
n	Reversible polytropic exponent
n_i	Irreversible polytropic exponent
p	Pressure
Q	Heat transferred
Q_i	Heat transferred in irreversible process
r	Irreversibility factor
R	Universal gas constant
S	Entropy
T	Temperature
U	Internal energy
V	Volume
W	Work
W_r	Reversible work