In summary, the book will make a good text for a graduate-level chemical engineering mathematics course oriented towards numerical methods. The instructor will find it necessary to amplify some parts of the book, and will generally wish to use a broader range of examples and homework problems than it provides. □

AVAILABILITY (EXERGY) ANALYSIS

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This is a 100-page self-instruction manual, which is divided into four parts. In Part I, the concept of availability, also referred to as exergy, is defined, explained, and related to enthalpy and entropy. Applications are given for a number of simple physical processes. In Part II, changes in availability for chemical-reaction processes are analyzed, with the results presented in graphical form. Second-law efficiencies based on availability, are defined in Part III. Available energy costing (thermoeconomics) is considered in Part IV. An appendix tabulates standard chemical availabilities referred to 25°C, 1atm and a set of final reference products for 137 different compounds. Professor Sussman advises the reader to read the manual in a sequential manner. However, keyword or short summaries placed in the margins permit the reader to readily skip material that is already familiar.

In order to follow the presentation of material in the manual, the reader should have at least a fundamental understanding of the first and second laws of thermodynamics and be able to compute changes in enthalpy and entropy for pure compounds and ideal mixtures. Such backround is generally the subject of an undergraduate course in engineering thermodynamics. In addition, some elementary knowledge of solution thermodynamics would be helpful. A pretest, included before Part I, permits the reader to determine if he(she) is properly prepared to proceed. At the end of each of the four parts, exit tests, with detailed solutions, are provided to help determine if the reader has mastered the material.

In Part I, the following points are developed in a lucid, interesting, and sometimes historical fashion:

1. **Both quantity and quality of energy should be considered.**
2. **The quality of energy refers to the fraction of that energy that can be extracted as useful work.**
3. **The first law makes no distinction based on the quality of energy.**
4. **Maximum work extraction occurs in an ideal (reversible) process.**
5. **The availability, which is a state property closely related to the Gibbs free energy, is a quantitative measure of the quality of energy and depends on the choice of the environmental reference (dead) state.**
6. **The change in availability is independent of the process path and the choice of dead state.**

Throughout Part I, the chemicals considered are mainly water, air, nitrogen, and oxygen; that is, chemicals that are found in the environment. For these, examples are given of calculations of both availability and change in availability. When other chemicals are involved, only the change in availability is considered. Part I is concluded by 12 excellent examples of the calculation of availability or the change in availability for proceses involving no chemical reaction. Of particular importance are some additional concepts that are presented in: 1) Example (c)iii, which illustrates the effect on availability of bringing the material of a given composition to a different dead-state compostion; 2) Example (k), which defines the work equivalent of heat; and 3) Example (*l*), which notes that shaft work and electrical energy are exactly equivalent to availability. It is unfortunate that these very important concepts are buried in examples and are not discussed thoroughly in the main text.

In Part II, chemical reactions are considered, and it now becomes necessary to carefully elucidate the composition of the environmental reference (dead) state. This has been the subject of much discussion and controversy among researchers, with no general agreement. As an example, Gaggioli and Petit [Chem Tech 7, 496-506 (1977)] use the following dead state:

$$T = 25°C, \qquad P = 1\ atm$$

Gas:

Constituent	Mole Fraction
N_2	0.7567
O_2	0.2035
H_2O	0.0303
A	0.0091
CO_2	0.0003
H_2	0.0001
	1.0000

Liquid: Pure H_2O
Solids: $CaCO_3$, $CaSO_4 \cdot 2H_2O$, NaCl, etc.

Sussman uses a different dead state; namely,

the standard products of combustion, e.g., $H_2O(l)$ $CO_2(g)$, $SO_2(g)$, etc., in their pure state at 25°C and 1 atm. Thus, he does not deal with a single dead state, but with a collection of dead states. These two approaches can lead to different values for the standard availability of a pure chemical in a particular state of aggregation at 25°C and 1 atm as shown in the following table:

	Standard Availability, Btu/lb mole	
Chemical Species	Gaggioli & Petit	Sussman
$H_2(g)$	101,190	102,100
$H_2O(g)$	3,700	3,700
$H_2O(l)$	0	0
$CO_2(g)$	8,650	0
$CH_4(g)$	357,130	352,100
$SO_2(g)$	122,670	0

The differences are considerable for $CO_2(g)$ and particularly $SO_2(g)$. If only the *change* in availability is of importance, then the dead state basis cancels out and is not a factor. If the actual availability is of importance, then the choice of dead state is very important. Gaggioli and Petit assume that the ultimate dead state of the sulfur atom is as $CaSO_4{\cdot}2H_2O_{(s)}$ and not as pure $SO_2(g)$. Also, they assume that $CO_2(g)$ ultimately becomes $CO_2(g)$ at a mole fraction of 0.0003 and not pure $CO_2(g)$, which serves as Sussman's basis. To obtain Sussman's values for standard availability, one need only compute, from free energies of formation, the negative of the standard change in free energy for combustion of the particular compound. Calculated values for 137 different compounds appear in the Appendix.

The major portion of Part II is devoted to a series of three excellent detailed examples involving chemical reaction, the last of which deals with a complete methane reforming process. Availability diagrams are used to conveniently illustrate availability flows, and particularly availability losses, in each process example. It is made clear that while energy is conserved, availability is not. The exit test involves further calculations on the methane reforming process and directs the reader to assess the points of greatest availability loss and to find ways of reducing availability losses. Just prior to the exit test, Sussman lists some reasons why availability losses occur.

Part III is a short chapter, which begins by defining an overall second-law efficiency for a process as the ratio of availability outputs to availability inputs. By means of examples, this efficiency is contrasted to that given by the first law. Sussman shows clearly that this definition of second-law efficiency can give negative results when the chosen reference state does not correspond to that of the lowest free energy. An alternative definition (extractive second-law efficiency) is also presented, but it is not general either because it only applies when streams entering a process do not mix with other streams. The exit test questions are relatively short exercises.

An introduction to thermoeconomics is presented in the final chapter, Part IV. The problem is how to determine a cost for a stream of energy. Based on availability considerations, a joule of electricity should be worth more than a joule of high-pressure steam, which should be worth more than a joule of low-pressure steam. Methods for assigning costs are developed by applying various costing rules to a process that cogenerates these three energy streams. The simplest rule presented assumes that all three energy streams have the same cost per unit of availability. The resulting costs per kwh of energy content are \$0.0211, \$0.0080, and \$0.0053 for electricity, 250 psia steam, and 50 psia steam, respectively. Other cited costing rules involve such matters as whether the energy streams are for internal or external use and if they must compete with the open market. The exit test at the end of Part IV involves the application of one of these alternative costing rules to the same cogeneration process.

Although written by a chemical engineer, the chemical engineering literature on second-law analysis is essentially ignored in the manual. In particular, the paper by Denbigh [Chem. Eng. Sci., *6*, 1-9 (1956)], in which he derives the availability function and availability loss by combining the first and second laws, is not mentioned. Denbigh's derivation is much more general than the derivation of Equation (8) in the manual.

Separation processes, such as distillation, which are very important industrially and generally inefficient from a second-law analysis, are almost totally ignored. Nevertheless, the beginner, who knows little or nothing about second-law analysis will find his time well spent by studying the concise text and the many execellent, detailed examples and exit tests. He can then strengthen his understanding, learn of other viewpoints, and see other applications by reading the previously mentioned papers by Denbigh and by Gaggioli and Petit, in addition to de Nevers [Chem. Tech., *12*, 306-317 (1982)] and Smith and Van Ness ["Introduction to Chemical Engineering Thermodynamics," McGraw-Hill (1975), Chapter 13]. □