INTRODUCTION TO

THERMODYNAMICS

CLASSICAL & STATISTICAL

SECOND EDITION

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GORDON VAN WYLEN

Introduction to Thermodynamics
Classical and Statistical

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Preface

In this second edition we have retained the basic objective of the first edition: to present a comprehensive and rigorous treatment of thermodynamics while retaining an engineering perspective and, in so doing, to provide a textbook that offers considerable flexibility for the inclusion of material on statistical thermodynamics.

We have deliberately directed our presentation to students. New concepts and definitions are presented in the context where they are first relevant. The first thermodynamic properties to be defined (Chapter 2) are those that can be readily measured: pressure, specific volume, and temperature. In Chapter 3, tables of thermodynamic properties are introduced, but only in regard to these measurable properties. Internal energy and enthalpy are introduced in connection with the first law, entropy, with the second law, and the Helmholtz and Gibbs functions in the section on availability. Many examples have been included in the book to assist the student in gaining an understanding of thermodynamics, and the problems at the end of each chapter have been carefully sequenced to correlate with the subject matter and provide some progression in difficulty.

We have presented the subject matter so that there are several arrangements by which the material can be covered, both within the classical section, Chapters 1 to 14, and the statistical section, Chapters 15 to 18. This has been done not only for the amount of material from each part to be studied, but also for the sequence in which the topics may be taken up.

Throughout the book we have attempted to maintain an engineering perspective, particularly through the choice of examples and problems. One of the major changes from the first edition is in the problems. Although some of the original problems have been retained, many are new or have been significantly revised. A number of applications of thermodynamics have been introduced in the first chapter, and these serve as a basis for many of the problems. We have retained a chapter on cycles (Chapter 10) because we find that many students enjoy this subject, and it can serve to effectively strengthen the student's understanding of the first and second laws of thermodynamics, and introduce him or her to engineering design and practice. We have also included several comments and problems that relate thermodynamics to environmental concerns.

One of the major changes in this edition has been the inclusion of a formal problem analysis and solution technique within the framework of the example problems in the text. Following its introduction in Chapter 5, this procedure is utulized, where appropriate, throughout the remainder of the book. This technique has been used extensively in undergraduate engineering classes over a period of several years and has proven to be quite successful in helping students to learn to deal with the solution of unfamiliar problems.

In regard to the symbols used in this text, we were guided by two considerations. First, we have used those symbols commonly used in the general literature of both classical and statistical thermodynamics; second, we have tried to maintain a consistency of symbols throughout the book. In a limited number of cases, we have used a given symbol for more than one purpose. We believe, however, that the context will clarify the meaning of the symbol in these cases.

Our philosophy regarding units in this edition has been to organize the book so that the course or sequence can be taught *entirely in SI units* (Le Système International d'Unités). Thus, all the text examples are in SI units, as are the complete problem set and thermodynamic tables. On the other hand, in recognition of the continuing need for engineering graduates to be familiar with English Engineering units, we have included an introduction to this system in Chapter 2. We have also repeated a sufficient number of problems and tables in these units, which should allow for suitable practice for those who desire to do so. Concerning the extensive properties, a lower-case letter (u, h, s) designates the property per unit mass, an uppercase letter (U, H, S) the property for the entire system; a lowercase letter with a bar ($\bar{u}$, $\bar{h}$, $\bar{s}$), the property per unit mole; and an uppercase letter with a bar ($\bar{U}$, $\bar{H}$, $\bar{S}$), the partial molal property. Following this pattern, we have found it convenient to designate the total heat transfer as Q, the heat transfer per unit mass of the system as q, the total work as W, and the work per unit mass of the system as w.

Furthermore, we represent the rate of flow across a system boundary or control surface by a dot over a given quantity. Thus, $\dot{Q}$ represents a rate of heat transfer across the system boundary; $\dot{W}$, the rate at which work crosses the system boundary (i.e., the power); and $\dot{m}$, the mass rate of flow across a control surface ($\dot{n}$ is used when the mass rate of flow is expressed in moles per unit time). The rate of heat transfer across a control surface is designated $\dot{Q}_{c.v.}$. We realize that we have departed from the usual mathematical use of a dotted symbol since, in mathematics, the dotted symbol typically refers to a derivative with respect to time. However, we have used the dotted symbol only to indicate a flow of heat and work across a system boundary, and heat, work, and mass across a control surface, and we believe that it has contributed to a simple and consistent use of symbols for this book.

Perhaps the principal change in this edition has been the reorganization of the material on statistical thermodynamics. First, the introduction to quantum mechanics has been placed at the beginning of this section, especially in order to be able to better demonstrate the concept of quantum states and their grouping according to degenerate energy levels. Second, in developing molecular distributions, we have adopted the philosophy of considering the two quantum statistical models as fundamental, and then obtaining the Boltzmann model only as a special case approximation. Most important, however, the material in this part of the book has all been written and organized so that statistical thermodynamics can be introduced in one of several ways, at different levels of depth of coverage.

The minimum coverage includes the development of an understanding of the important basic concepts of thermodynamic equilibrium and of entropy and can reasonably be achieved in four class periods. This minimum coverage would include Sections 15.1 to 15.4, 16.1, 16.5, and 17.1 to 17.3.

The next level of coverage, in two additional class periods, involves application to the properties of monatomic gases and includes the additional material of Sections 15.5 to 15.6, 17.4 to 17.5, 18.1, and 18.4. A greater depth of understanding can be achieved by taking additional time to include some or all of Sections 15.8, 16.2 to 16.4, 17.4, and 18.3.

Beyond the basic coverage discussed above, the remainder of the material in this part of the text consists of special applications for those who desire to spend additional time on this subject. These topics include Maxwell-Boltzmann velocity distribution and free molecular flow (Sections 18.5–18.6), diatomic gases (15.7 and 18.7), polyatomic gas (18.8), photon gas (18.9), electron gas (18.10), Debye solid (18.11), gas mixtures (18.12), and chemical reactions (18.13). These topics are independent of one another and can be chosen as desired.

We acknowledge with appreciation the suggestions, counsel, and encouragement from many colleagues, both at the University of Michigan and elsewhere. This assistance has been most helpful to us during the writing of both the first and second editions. Several secretaries have aided us immeasurably during this period, and we acknowledge this with many thanks. Students have also aided us. Their perceptive questions have often caused us to rewrite or rethink a given portion of the text. Finally, for each of us, the encouragement and patience of our wives and families have been indispensable, and have made this time of writing pleasant and enjoyable in spite of the pressures of the project.

Our hope is that this book will contribute to the effective teaching of thermodynamics to students who face very significant challenges and opportunities during their professional careers. Your comments, criticism, and suggestions will also be appreciated.

Richard E. Sonntag
Gordon J. Van Wylen

Ann Arbor, Michigan, June, 1981

Symbols

a	acceleration
a, A	specific Helmholtz function and total Helmholtz function
AF	air-fuel ratio
c	velocity of light
C_p	constant-pressure specific heat
C_v	constant-volume specific heat
C_{po}	zero-pressure constant-pressure specific heat
C_{vo}	zero-pressure constant-volume specific heat
d	electron state symbol
D	total dissociation energy
D	atomic term symbol
D_0	observed dissociation energy
e	electron charge
e, E	specific energy and total energy
f	electron state symbol
f	fugacity
$\bar{f}_i$	fugacity of component i in a mixture
F	force
F	atomic term symbol
FA	fuel-air ratio
g	acceleration due to gravity
g, G	specific Gibbs function and total Gibbs function
g_c	a constant that relates force, mass, length, and time
g_j	jth energy level degeneracy
h	Planck's constant
h, H	specific enthalpy and total enthalpy
i	electrical current
I	irreversibility
I	moment of inertia
$\mathbf{j}$	molecular rotational quantum number
$\mathbf{J}$	atomic total angular momentum number
k	specific heat ratio: C_p/C_v
k	Boltzmann constant
$\mathbf{k}_x$, $\mathbf{k}_y$, $\mathbf{k}_z$	x-, y-, z-directional translation quantum numbers
K	equilibrium constant

KE	kinetic energy
$\mathbf{l}$	electron azimuthal quantum number
L	length
lw, LW	lost work per unit mass and total lost work
m	mass
$\dot{m}$	mass rate of flow
$\mathbf{m}_l$	electron magnetic quantum number
$\mathbf{m}_s$	electron spin quantum number
m_r	molecular reduced mass
M	molecular weight
mf	mass fraction
$\mathbf{n}$	electron principal quantum number
n	number of moles
n	polytropic exponent
N	number of particles
N_0	Avogadro's number
p	electron state symbol
P	mathematical probability
P	atomic term symbol
P	pressure
P_i	partial pressure of component i in a mixture
PE	potential energy
q, Q	heat transfer per unit mass and total heat transfer
$\dot{Q}$	rate of heat transfer
Q_H, Q_L	heat transfer with high-temperature body and heat transfer with low-temperature body; sign determined from context
r	radius
r_e	molecular equilibrium separation
R	gas constant
$\bar{R}$	universal gas constant
s	electron state symbol
s, S	specific entropy and total entropy
S	atomic term symbol
t	time
T	temperature
u, U	specific internal energy and total internal energy
u_{v_0}	zero-point energy per mole
v	molecular vibration quantum number
v, V	specific volume and total volume
vf	volume fraction
$\mathbf{V}$	velocity
w	thermodynamic probability—number of microstates
w, W	work per unit mass and total work
$\dot{W}$	rate of work, or power

w_{rev}	reversible work between two states assuming heat transfer with surroundings
x	quality
x	liquid-phase or solid-phase mole fraction
y	vapor-phase mole fraction
Z	partition function
Z	elevation
Z	compressibility factor
Z	electrical charge

SCRIPT LETTERS

$\mathscr{A}$	area
$\mathscr{C}$	number of components
${}_N\mathscr{C}_M$	combinations of N, M at a time
$\mathscr{E}$	electrical potential
$\mathscr{H}$	magnetic field intensity
$\mathscr{M}$	magnetization
$\mathscr{P}$	number of phases
${}_N\mathscr{P}_M$	permutations of N, M at a time
$\mathscr{S}$	surface tension
$\mathscr{T}$	tension
$\mathscr{V}$	variance
$\mathscr{F}$	nuclear charge

GREEK LETTERS

α	volume expansivity
β	coefficient of performance for a refrigerator
β'	coefficient of performance for a heat pump
β_S	adiabatic compressibility
β_T	isothermal compressibility
γ	activity coefficient
η	efficiency
μ	chemical potential
μ_J	Joule-Thomson coefficient
ν	stoichiometric coefficient
ρ	density
ϕ	relative humidity
ϕ	availability for a system
ψ	availability associated with a steady-state, steady-flow process
ω	humidity ratio or specific humidity

SUBSCRIPTS

c	property at the critical point
c.v.	control volume
e	electronic
e	state of a substance leaving a control volume
f	formation
f	property of saturated liquid
f_g	difference in property for saturated vapor and saturated liquid
g	property of saturated vapor
i	energy state
i	state of a substance entering a control volume
i	property of saturated solid
ig	difference in property for saturated vapor and saturated solid
j	energy level
mp	most probable (equilbrium)
n	nuclear
r	reduced property
r	relative value
r	rotation
s	isentropic process
t	translation
v	vibration
0	property of the surroundings

SUPERSCRIPTS

¯	bar over symbol denotes property on a molal basis (over V, H, S, U, A, G, the bar denotes partial molal property)
$^\circ$	property at standard-state condition
$*$	ideal gas
L	liquid-phase
S	solid-phase
V	vapor-phase

Contents

Some Introductory Comments

In the course of our study of thermodynamics, a number of the examples and problems presented refer to processes that occur in such equipment as a steam power plant, a fuel cell, a vapor compression refrigerator, a thermoelectric cooler, a rocket engine, and an air separation plant. In this introductory chapter a brief description of this equipment is given. There are at least two reasons for including such a chapter. First, many students have had limited contact with such equipment, and the solution of problems will be more significant and relevant when they have some familiarity with the actual processes and the equipment involved. Second, this chapter will provide an introduction to thermodynamics, including the use of certain terms (which will be more formally defined in later chapters), some of the problems for which thermodynamics is relevant, and some accomplishments that have resulted, at least in part, from the application of thermodynamics.

It should be emphasized that thermodynamics is relevant to many other processes than those cited in this chapter. It is basic to the study of materials, chemical reactions, and plasmas. The student should bear in mind that this chapter is only a brief and necessarily very incomplete introduction to the subject of thermodynamics.

1.1 THE SIMPLE STEAM POWER PLANT

A schematic diagram of a simple steam power plant is shown in Fig. 1.1. High pressure superheated steam leaves the boiler, which is also referred to as a steam generator, and enters the turbine. The steam expands in the turbine and in doing so, does work, which enables the turbine to drive the electric generator. The low-pressure steam leaves the turbine and enters the condenser, where heat is transferred from the steam (causing it to condense) to the cooling water. Since large quantities of cooling water are required, power plants are frequently located near rivers or lakes. It is this transfer of heat to the water in lakes and rivers that leads to the thermal pollution problem, which is now being extensively studied. During our study of thermodynamics we will gain an understanding of why this heat transfer is necessary and ways in which it can be minimized. When the supply of cooling water is limited, a

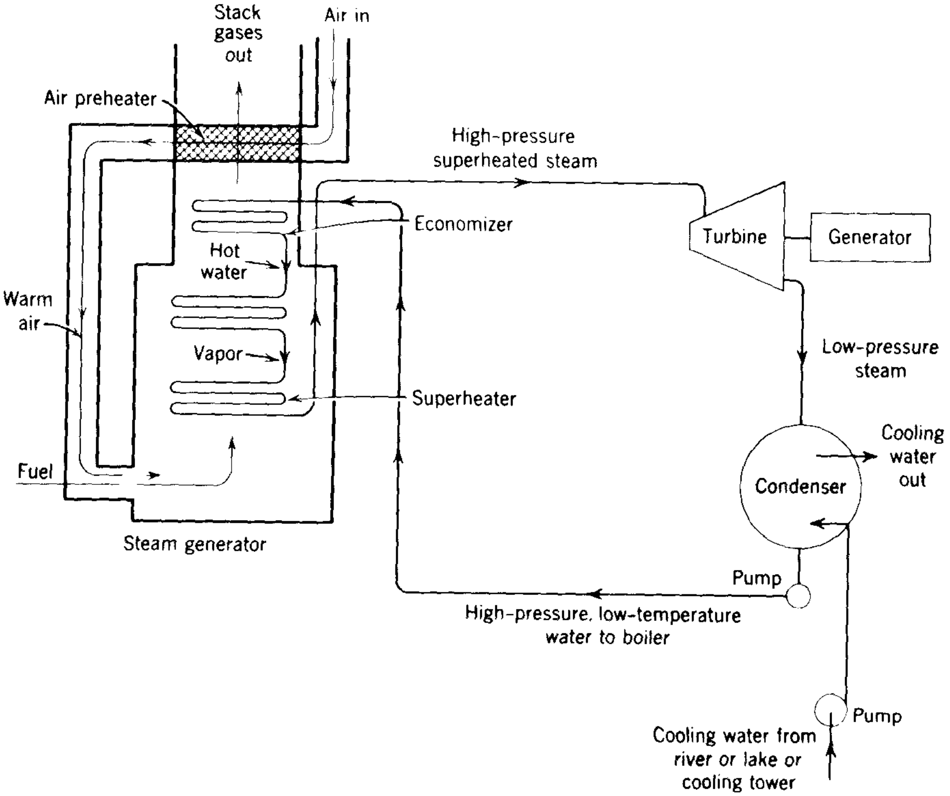

Fig. 1.1 Schematic diagram of a steam power plant.

cooling tower may be used. In the cooling tower some of the cooling water evaporates in such a way as to lower the temperature of the water that remains as a liquid.

The pressure of the condensate leaving the condenser is increased in the pump, thus enabling the condensate to flow into the steam generator. In many steam generators an economizer is used. An economizer is simply a heat exchanger in which heat is transferred from the products of combustion (just before they leave the steam generator) to the condensate, with the result that the temperature of the condensate is increased, but no evaporation takes place. In other sections of the steam generator, heat is transferred from the products of combustion to the water, causing it to evaporate. The temperature at which evaporation occurs is called the saturation temperature. The steam then flows through another heat exchanger known as a superheater, where the temperature of the steam is increased well above the saturation temperature.

In many power plants the air that is used for combustion is preheated in the air preheater by transferring heat from the stack gases as they are leaving the furnace. This air is then mixed with fuel – which might be coal, fuel oil, natural gas, or other combustible material – and combustion takes place in the

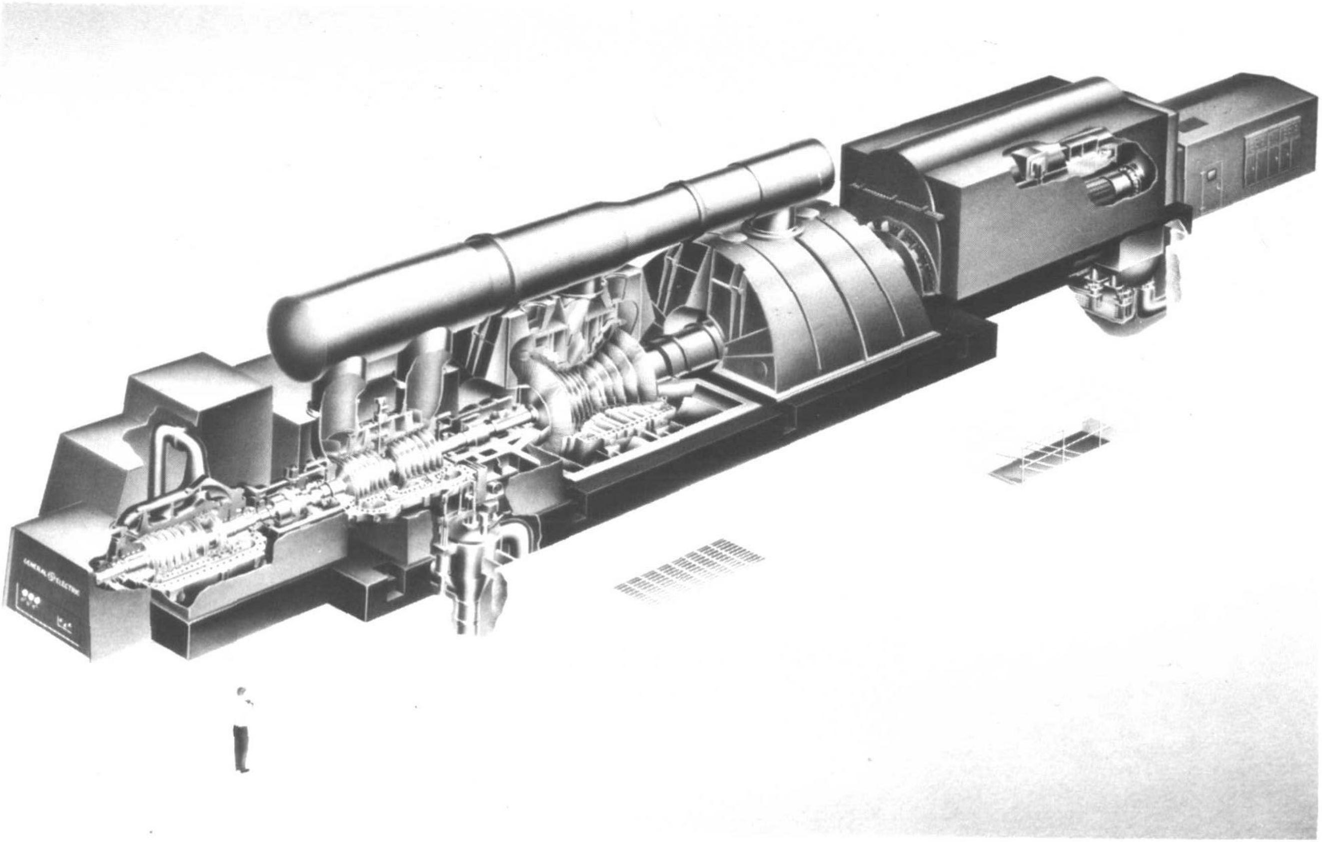

Fig. 1.2 A large steam turbine (Courtesy General Electric Co.).

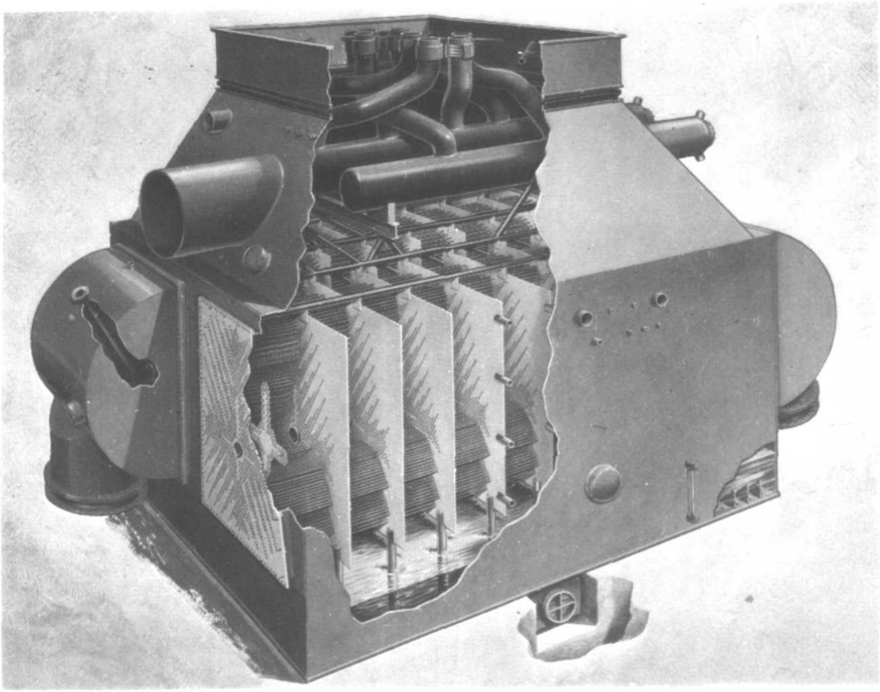

Fig. 1.3 A condenser used in a large power plant (Courtesy Westinghouse Electric Corp.).

furnace. As the products of combustion pass through the furnace, heat is transferred to the water in the superheater, the boiler, the economizer, and to the air in the air preheater. The products of combustion from power plants are discharged to the atmosphere, and this constitutes one of the facets of the air pollution problem we now face.

A large power plant will have many other pieces of equipment, some of which will be considered in later chapters.

Figure 1.2 shows a steam turbine and the generator that it drives. Steam turbines vary in capacity from less that 10 kilowatts to 1 000 000 kilowatts.

Figure 1.3 shows a cutaway view of a condenser. The steam enters at the top and the condensate is collected in the hot well at the bottom while the cooling water flows through the tubes. A large condenser has a tremendous number of tubes, as shown in Fig. 1.3.

Figure 1.4 shows a large steam generator. The flow of air and products of combustion are indicated. The condensate, also called the boiler feedwater, enters at the economizer inlet, and the superheated steam leaves at the superheater outlet.

The number of nuclear power plants in operation has increased substantially in recent years. In these power plants the reactor replaces the steam generator of the conventional power plant, and the radioactive fuel elements replace the coal, oil, or natural gas.

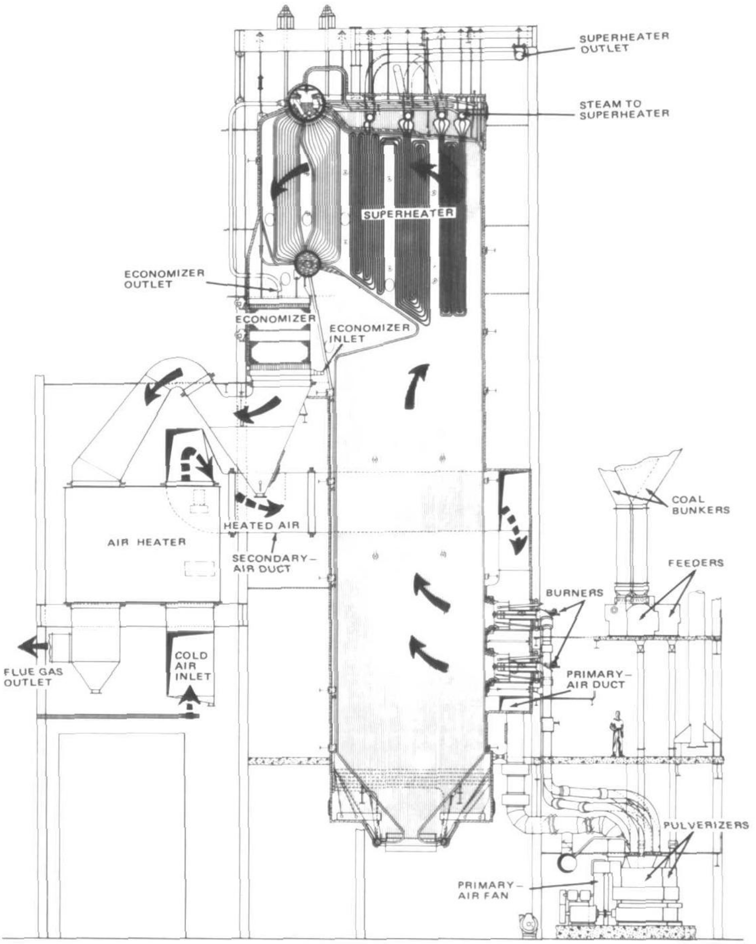

Fig. 1.4 A large steam generator (Courtesy Babcock and Wilcox Co.).

There are several different reactor designs in current use. One of these is the boiling-water reactor, such as the system shown in Fig. 1.5. In other nuclear power plants a secondary fluid circulates from the reactor to the steam generator, where heat is transferred from the secondary fluid to the water, which in turn goes through a conventional steam cycle. Safety considerations and the necessity to keep the turbine, condenser, and related equipment from becoming radioactive are always major considerations in the design and operation of a nuclear power plant.

1.2 FUEL CELLS

When a conventional power plant is viewed as a whole, as shown in Fig. 1.6, we see that fuel and air enter the power plant and products of combustion leave the unit. There is also a transfer of heat to the cooling water, and work is done in the form of the electrical energy leaving the power plant. The

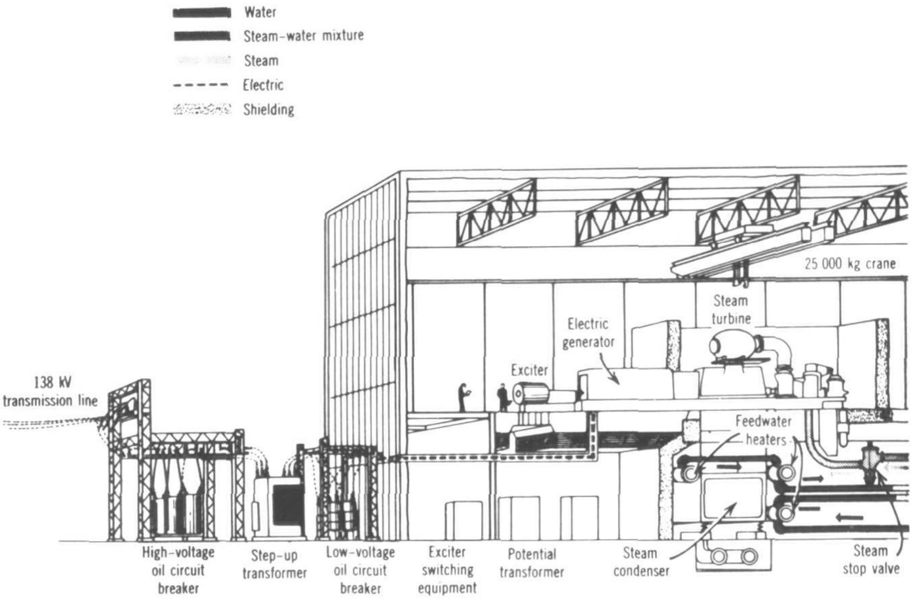

Fig. 1.5 Schematic diagram of the Big Rock Point nuclear plant of Consumers Power Company at Charlevoix, Michigan (Courtesy Consumers Power Company).

overall objective of a power plant is to convert the availability (to do work) of the fuel into work (in the form of electrical energy) in the most efficient manner, consistent with such considerations as cost, space, and safety.

We might well ask if all of the equipment in the power plant, such as the steam generator, the turbine, the condenser, and the pump, is necessary. Is it not possible to produce electrical energy from the fuel in a more direct manner?

The fuel cell is a device in which this objective is accomplished. Figure 1.7 shows a schematic arrangement of a fuel cell of the ion-exchange membrane type. In this fuel cell hydrogen and oxygen react to form water. Let us consider the general features of the operation of this type of fuel cell.

The flow of electrons in the external circuit is from anode to cathode. Hydrogen enters at the anode side and oxygen enters at the cathode side. At the surface of the ion-exchange membrane the hydrogen is ionized according to the reaction

$$2H_2 \rightarrow 4H^+ + 4e^-$$

The electrons flow through the external circuit and the hydrogen ions flow through the membrane to the cathode, where the following reaction takes place.

$$4H^+ + 4e^- + O_2 \rightarrow 2H_2O$$

There is a potential difference between the anode and cathode, and thus there