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Thermodynamic Fundamentals

1.1 Introduction

Energy plays a critical role in driving almost all practical processes and is essential to sustain life. Energy exists in several forms, for example, light, heat, and electricity. Energy systems are widespread and used in diverse industries such as power generation, petrochemical processing, refrigeration, hydrogen production, chemical processing, and manufacturing. Interest is growing in producing superior energy products at minimal cost, while satisfying concerns regarding environmental impact, safety, and other issues. It is no longer adequate to develop a system that simply performs a desired task. For various reasons, it is often important to optimize processes so that a chosen quantity, known as the objective function, is maximized or minimized. For example, the output, profit, productivity, product quality, and so on, may be maximized, or the cost per item, financial investment, energy input, and so on, may be minimized. The success and growth of industries today is strongly based on their ability to optimize designs and systems.

When an engineer undertakes the analysis of an energy system and/or its application, she or he should deal with several basic factors first. These depend on the type of the problem being studied, and often involve such disciplines as thermodynamics, fluid mechanics, and heat transfer. Consequently, it is helpful to introduce several fundamental definitions and concepts before moving on to detailed energy systems applications, especially for readers who lack a background in thermodynamics, fluid mechanics, or heat transfer.

This chapter provides such a review, and is intended to give novice and practicing energy systems engineers a strong understanding of fundamentals, including physical phenomena, basic laws and principles, and governing relations, as well as a solid grounding in practical aspects. This introductory chapter covers relevant fundamentals involved in the optimization of energy systems. We begin the chapter with a summary of fundamental definitions and physical quantities, with their units, dimensions, and interrelations. We then consider introductory aspects of thermodynamics, with a particular focus on energy, exergy, and heat transfer.

1.2 Thermodynamics

Energy is needed for almost every activity. In simple terms, energy is usually thought of as the ability to carry out useful tasks like producing work and heating. Energy is

contained in the fuel we use, the food we eat, and the places we live. Energy enables such outcomes as transportation, fresh water, and thermal comfort in buildings.

Energy use has drawbacks too. It can be dangerous if not used cautiously and often leads to pollution and environmental damage.

Energy can be converted from one form to another, but cannot be created or destroyed. Work and heat are two categories of energy in transit. Thermodynamics plays a key role in the analysis of processes, systems, and devices in which energy transfers and transformations occur. The implications of thermodynamics are far reaching and applications span the range of human enterprise. Nature allows the conversion of work completely into heat, but not the reverse. Additionally, converting heat into work requires a device, which is often complex (e.g., an engine).

Although energy can be transformed into different forms, the principle of conservation of energy states that the total energy of a system can only change if energy is transferred into or out of the system. This implies that it is impossible to create or destroy energy. The total energy of a system can thus be calculated by adding all forms of energy in the system. Examples of energy transfer and transformation include generating or making use of electric energy, performing chemical reactions and lifting an object. Lifting against gravity performs work on the object and stores gravitational potential energy; if the object falls, gravity does work on the object, which transforms its potential energy into kinetic energy associated with its speed.

The name “thermodynamics” stems from the Greek words *therme* (heat) and *dynamis* (power), which is descriptive of efforts to convert heat into power [1]. The discipline of thermodynamics is based primarily on two fundamental natural laws, known as the first and second laws. The first law of thermodynamics is simply an expression of the conservation of energy principle. It states that energy, as a thermodynamic quantity, is neither created nor destroyed during a process. The second law of thermodynamics states that energy has quality as well as quantity, and that processes naturally occur in the direction of decreasing quality of energy [2].

1.3 The First Law of Thermodynamics

The first law of thermodynamics (FLT) embodies the principle of energy conservation, which states that, although energy can change form, it can be neither created nor destroyed. The FLT defines internal energy as a state function and provides a formal statement of the conservation of energy [2]. However, the first law provides no information about the direction in which processes can spontaneously occur, that is, reversibility aspects of thermodynamic processes. For example, the FLT cannot indicate how cells can perform work while existing in an isothermal environment. The FLT provides no information about the inability of any thermodynamic process to convert heat fully into mechanical work, or any insight into why mixtures cannot spontaneously separate or unmix themselves. A principle to explain these phenomena and to characterize the availability of energy is required. Such a principle is embodied in the second law of thermodynamics (SLT), which we explain later in this chapter.

A simple example of energy conversion is the process in which a body that has some potential energy at some elevation falls, and part of the potential energy is converted into kinetic energy. Experimental data show that the decrease in potential energy is equal to the increase in kinetic energy if air resistance is negligible. This simple example

demonstrates the conservation of energy principle. In order to analyze energy systems, we need to use energy balance equations, which express the balance of the energy entering and leaving a system and the energy change in the system. That is, the net change in the total energy of the system during a process is equal to the difference between the total energy entering and the total energy leaving the system during that process, or

$$\left(\begin{array}{c} \text{Total energy} \\ \text{entering system} \end{array} \right) - \left(\begin{array}{c} \text{Total energy} \\ \text{leaving system} \end{array} \right) = \left(\begin{array}{c} \text{Change in total} \\ \text{energy of system} \end{array} \right)$$

This relation can also be written as

$$E_{\text{in}} - E_{\text{out}} = \Delta E_{\text{system}} \quad (1.1)$$

The energy E may include internal energy U , kinetic energy (KE) and potential energy (PE) terms as follows:

$$E = U + KE + PE \quad (1.2)$$

For a change of state from state 1 to state 2 with a constant gravitational acceleration (g), Equation 1.2 can be used to show the following:

$$E_2 - E_1 = (U_2 - U_1) + \frac{1}{2}m(V_2^2 - V_1^2) + mg(Z_2 - Z_1) \quad (1.3)$$

where m denotes the fixed amount of mass in the system, V the velocity, and Z the elevation. In order to apply the FLT to an energy system, we need to know some further concepts, which are described in the following sections.

1.3.1 Thermodynamic System

A thermodynamic system is a region or device or combination of devices that contains a certain quantity of matter. It is important to carefully define the system under consideration during an analysis and its boundaries. Three important types of systems can be defined:

- **Closed system.** Such a system is defined as one across the boundaries of which no material crosses. It therefore contains a fixed quantity of matter. Sometimes this is also called a control mass.
- **Open system.** This is defined as a system in which material (mass) is allowed to cross the boundaries. The term open system is sometimes referred to as a control volume.
- **Isolated system.** This is a closed system that is independent and unaffected by the surroundings. No mass, heat, or work crosses its boundary.

1.3.2 Process

A process is a physical or chemical change in the properties of matter or the conversion of energy from one form to another. In some processes, one property remains constant. The prefix “iso” is employed to describe such as process, for example isothermal (constant temperature), isobaric (constant pressure), and isochoric (constant volume).

1.3.3 Cycle

A cycle is a series of thermodynamic processes in which the end point conditions or properties of the matter are identical to the initial conditions.

1.3.4 Heat

Heat is the thermal form of energy, and heat transfer takes place when a temperature difference exists within a medium or between different media. The definitive experiment that showed heat to be a form of energy, convertible into other forms, was carried out by Scottish physicist James Joule. Heat transfer always requires a difference in temperature, and higher temperature differences provide higher heat transfer rates. The units for heat are joules or kilojoules in the International System (SI) and the foot pound force or British thermal unit (Btu) in the English system. In terms of sign conventions in thermodynamic calculations, a common one states that heat transfer to a system is considered positive, while heat transfer from a system is negative. If there is no heat transfer involved in a process, it is called adiabatic.

1.3.5 Work

Work is the energy that is transferred by a difference in pressure or force of any kind, and is subdivided into shaft work and flow work. Shaft work is the mechanical energy used to drive a mechanism such as a pump, compressor, or turbine. Flow work is the energy transferred into a system by a fluid flowing into, or out of, it. Both forms are usually expressed in kilojoules. Work can also be expressed on a unit mass basis (e.g., in kJ/kg). By one common convention, work done by a system is usually considered positive and work done on a system (work input) is considered negative. The SI unit for power or rate of work is joules per second, which is a Watt (W).

1.3.6 Thermodynamic Property

A thermodynamic property is a physical characteristic of a substance, often used to describe its state. Any two properties usually define the state or condition of a substance, and all other properties can be derived from these. Some examples of properties are temperature, pressure, enthalpy, and entropy. Thermodynamic properties can be classified as intensive (independent of the size or scale, e.g., pressure, temperature and density) and extensive properties (dependent on size or scale, e.g., mass and total volume). Extensive properties become intensive properties when expressed on a per unit mass basis, such as is the case for specific volume.

Property diagrams of substances can be presented in graphical form and present the main properties listed in property tables, for example refrigerant or steam tables. In analyzing an energy system, the thermodynamic properties should be defined so as to permit the simulation (and hence optimization) of the system. In this book, Engineering Equation Solver (EES) and Refprop software are utilized to calculate thermodynamic properties.

1.3.6.1 Specific Internal Energy

Internal energy represents a molecular state type of energy. Specific internal energy is a measure per unit mass of the energy of a simple system in equilibrium, and can be expressed as the function $c_v dT$. For many thermodynamic processes in closed systems, the only significant energy changes are internal energy changes, and the work done by the system in the absence of friction is the work of pressure-volume expansion, such as in a piston-cylinder mechanism.

The specific internal energy of a mixture of liquid and vapor can be written as

$$u = (1 - x)u_{\text{liq}} + xu_{\text{vap}} = u_{\text{liq}} + xu_{\text{liq,vap}} \quad (1.4)$$

where $u_{\text{liq,vap}} = u_{\text{vap}} - u_{\text{liq}}$.

1.3.6.2 Specific Enthalpy

Specific enthalpy is another measure of the energy per unit mass of a substance. Specific enthalpy, usually expressed in kJ/kg or Btu/lb, is normally expressed as a function of $c_p dT$. Since enthalpy is a state function, it is necessary to measure it relative to some reference state. The usual practice is to determine the reference values, which are called the standard enthalpy of formation (or the heat of formation), particularly in combustion thermodynamics.

The specific enthalpy of a mixture of liquid and vapor components can be written as

$$h = (1 - x)h_{\text{liq}} + xh_{\text{vap}} = h_{\text{liq}} + xh_{\text{liq,vap}} \quad (1.5)$$

where $h_{\text{liq,vap}} = h_{\text{vap}} - h_{\text{liq}}$.

1.3.6.3 Specific Entropy

Entropy is the ratio of the heat added to a substance to the absolute temperature at which it is added, and is a measure of the molecular disorder of a substance at a given state.

The specific entropy of a mixture of liquid and vapor components can be written as

$$s = (1 - x)s_{\text{liq}} + xs_{\text{vap}} = s_{\text{liq}} + xs_{\text{liq,vap}} \quad (1.6)$$

where $s_{\text{liq,vap}} = s_{\text{vap}} - s_{\text{liq}}$.

1.3.7 Thermodynamic Tables

Thermodynamic tables were first published in 1936 as steam tables by Keenan and Keyes; in 1969 and 1978 these were revised and republished. Thermodynamic tables are available for many substances, ranging from water to refrigerants, and are commonly employed in process design calculations. Some thermodynamic tables include steam and vapor tables. In this book, we usually imply these types of tables when we refer to thermodynamic tables. Such tables normally have distinct phases (parts); for example, four different parts for water tables include those for saturated water, superheated water vapor, compressed liquid water, and saturated solid-saturated vapor water. Similarly, two distinct parts for R-134a include saturated and superheated tables. Most tables are tabulated according to values of temperature and pressure, and then list values of various other thermodynamic parameters such as specific volume, internal energy, enthalpy, and entropy. Often when we have values for two independent variables, we may obtain other data from the respective table. In learning how to use these tables, it is important to specify the state using any two independent parameters (unless more are needed). In some design calculations, if we do not have the exact values of the parameters, we use interpolation to find the necessary values.

Beyond thermodynamic tables, much attention has recently been paid to computerized tables for design calculations and other purposes. Although computerized tables can eliminate data reading problems, they may not provide a good understanding of the concepts involved and a good comprehension of the subject. Hence, in thermodynamics

courses, it is important for the students to know how to obtain thermodynamic data from the appropriate thermodynamic tables.

The Handbook of Thermodynamic Tables [3] is one of the most valuable data resources, with data for numerous solid, liquid, and gaseous substances.

1.3.8 Engineering Equation Solver (EES)

EES is a software package that solves a system of linear or nonlinear algebraic or differential equations numerically. It consists of a large library of built in thermodynamic properties as well as mathematical functions. Unlike other available software packages, EES does not solve engineering problems explicitly; rather it solves the equations, and it is the user's responsibility to apply relevant physical laws, relations, and understanding. EES saves the user considerable time and effort by solving the mathematical equations, and has the capability to connect to other professional software such as Matlab.

EES is one of the most suitable software packages for energy systems analyses and thermodynamic properties. The software is straightforward to use, as shown in Figure 1.1, where the thermodynamic modeling of a vapor compression refrigeration system and its components is presented along with the results of a parametric study conducted by varying the temperature at point 1. This software comes with several examples and has been used to model and analyze complex systems such as advanced power plants, combined heat and power systems, desalination plants, hydrogen production plants, and renewable energy-based systems.

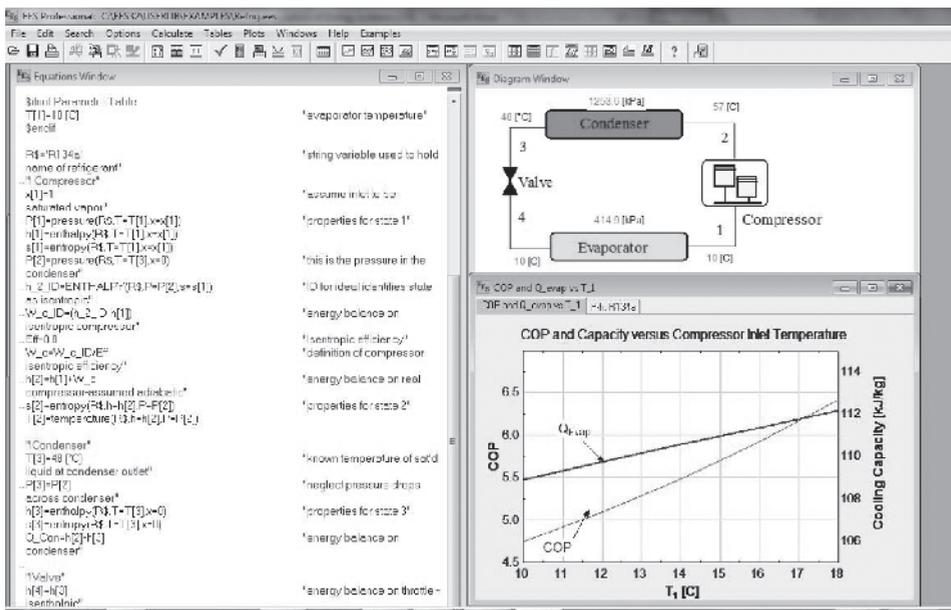


Figure 1.1 Sample screen of Engineering Equation Solver (EES) for thermodynamic analyses of energy systems.

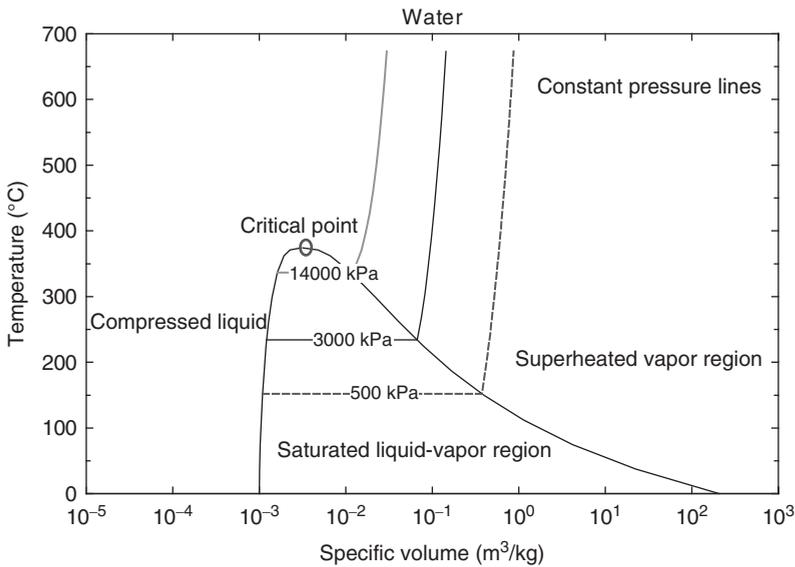


Figure 1.2 Temperature-specific volume diagram for phase changes of water.

The professional version of the software can perform single objective optimization but not multi-objective optimization. However, several methods can be implemented to connect EES with Matlab software to conduct multi-objective optimization, as is discussed in subsequent chapters.

In EES, we can easily create thermodynamic diagrams (e.g., T - V , T - S , P - V , P - h , and h - S). For example, Figure 1.2 shows a temperature-volume diagram for water at several pressures. The state of a system or substance is defined as the condition of the system or substance characterized by certain observable macroscopic values of its properties such as temperature and pressure.

The term “state” is often used interchangeably with the term “phase,” for example solid phase or gaseous phase of a substance. Each of the properties of a substance at a given state has only one definite value, regardless of how the substance reached the state. For example, when sufficient heat is added or removed under certain conditions, most substances undergo a state change. The temperature remains constant until the state change is complete. As shown in Figure 1.2, there are three regions on the T - v diagram for water: compressed liquid, saturated two-phase region (which is also known as the wet region) and superheated vapor region. As the pressure increases, the saturated line continues to shrink, as shown in Figure 1.2, and eventually it becomes a point when the pressure reaches 22.06 MPa for water. This point is called the critical point and is defined as the point which the saturated liquid and saturated vapor are identical. This is indicated in Figure 1.2. EES can also generate temperature-specific entropy (T - s) diagrams for various refrigerants, as shown in Figure 1.3. The software contains a large fluids database. Table 1.1 lists the properties of the various refrigerants shown in Figure 1.3. In this table, T_b^a is the normal boiling point, while P_{cr}^b and T_{cr}^a are the critical pressure and critical temperature, respectively.

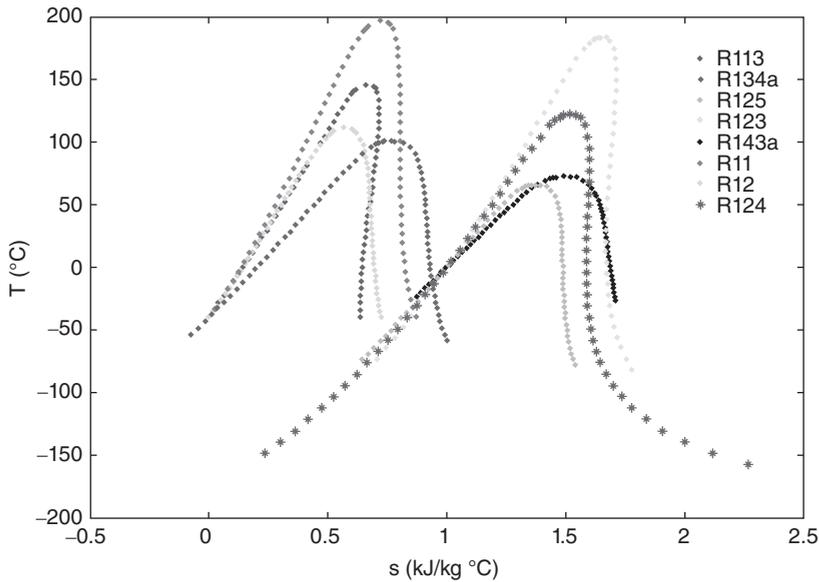


Figure 1.3 T - s diagrams of selected refrigerants, as generated by EES.

Table 1.1 Thermophysical properties of selected working fluids.

Substance	Molecular mass (kg/kmol)	T_b^a (K)	P_{cr}^b (MPa)	T_{cr}^a (K)
R123	152.93	300.97	3.66	456.83
R134a	102.03	247.08	4.059	374.21
R124	136.48	261.22	3.62	395.43
R11	137.37	296.86	4.40	471.11
R12	120.91	243.4	4.13	385.12
R143a	84.04	161.34	3.76	345.86
R113	187.38	320.74	3.39	487.21
R125	120.02	172.52	3.61	339.17
R141b	116.95	305.2	4.46	479.96

Example 1.1: Apply EES to the vapor compression refrigeration cycle using R134a as a working fluid, as shown in Figure 1.4. The working fluid mass flow rate is 0.1 kg/s. Assume that there are no pressure drops across the condenser and that the compressor isentropic efficiency is 0.8.

Part 1) Show the cycle on a P - h diagram with all temperatures at each state point.

Part 2) Calculate the coefficient of performance (COP), compressor specific work and cooling load when the evaporator and condenser temperatures are 10°C and 45°C, respectively.

Part 3) Plot the effect of evaporator temperature on COP and cooling load of the cycle when the evaporator temperature varies from 10°C to 18°C, and discuss the results.

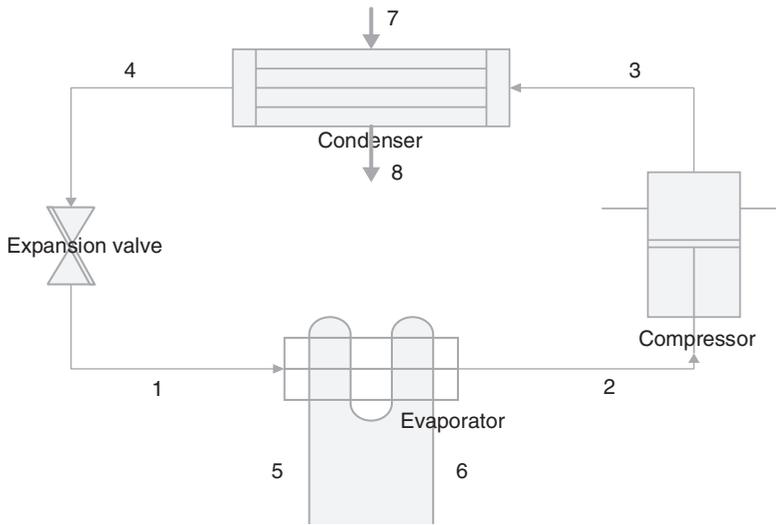


Figure 1.4 Schematic of vapor compression refrigeration cycle.

Solution: A refrigeration system operating on a vapor compression cycle is considered here.

Assumptions: 1: Steady operating conditions exist. 2: Kinetic and potential energy changes are negligible.

Analysis:

- 1) The working fluid leaving the evaporator is a saturated vapor with a quality $x=1$. Therefore this point lies on the saturated vapor line in a P - h diagram, as shown in Figure 1.5. We know that the pressure at point 1, P_1 , is the saturation pressure

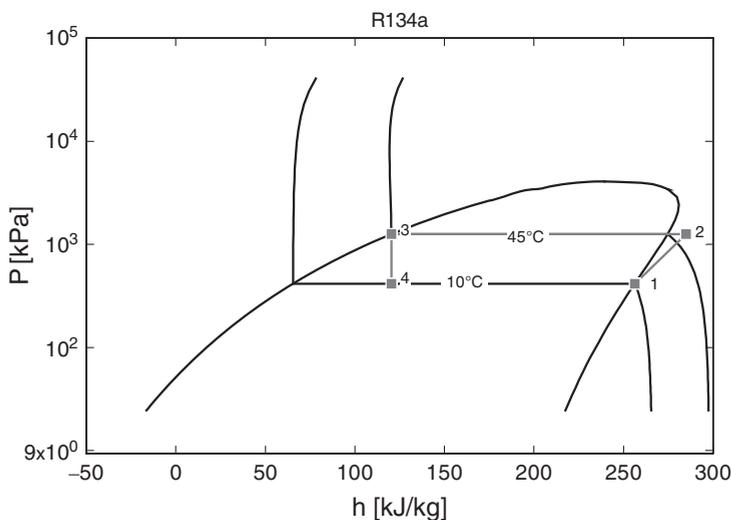


Figure 1.5 P - h diagram of vapor compression refrigeration cycle.

at the evaporator temperature ($T_{\text{EVP}} = 10^\circ\text{C}$). Using EES and the thermodynamic properties for R134a, this pressure is found to be 538 kPa. Since there is no pressure drop across the evaporator, $P_1 = P_4$. Similarly, the pressure at point 3 is equal to the saturation pressure at the condenser temperature. This information yields that $P_3 = 1161$ kPa. Connecting these points forms the P - h diagram.

- 2) In order to calculate the COP and cooling load, the thermodynamic properties at all points need to be determined. Using EES we find:

$$\begin{aligned} x_1 &= 1 \\ P_1 &= \text{pressure (R134a, } T = T_1, x = x_1) = 415 \text{ kPa} \\ h_1 &= \text{specific enthalpy (R134a, } T = T_1, x = x_1) = 256.2 \text{ kJ kg}^{-1} \\ s_1 &= \text{specific entropy (R134a, } T = T_1, x = x_1) = 0.926 \text{ kJ(kg.K)}^{-1} \\ P_2 &= \text{pressure (R134a, } T = T_3, x = 0) = 1161 \text{ kPa} \\ h_{2,\text{ideal}} &= \text{specific enthalpy (R134a, } P = P_2, s_2 = s_1) = 277.5 \text{ kJ kg}^{-1} \\ w_{\text{comp,ideal}} &= (h_{2,\text{ideal}} - h_1) = 21.31 \text{ kJ kg}^{-1} \\ \eta_{\text{comp}} &= \frac{w_{\text{comp,ideal}}}{w_{\text{comp,act}}} \rightarrow w_{\text{comp,act}} = \frac{(h_{2,\text{ideal}} - h_1)}{\eta_{\text{comp}}} = 26.64 \text{ kJ kg}^{-1} \\ h_2 &= h_1 + w_{\text{comp,act}} = 282.8 \text{ kJ kg}^{-1} \\ s_2 &= \text{specific entropy (R134a, } h = h_2, P = P_2) = 0.926 \text{ kJ(kg.K)}^{-1} \\ T_2 &= \text{temperature (R134a, } h = h_2, P = P_2) = 53^\circ\text{C} \end{aligned}$$

Since the condenser temperature is given (45°C) and $P_3 = P_2$ because there is no pressure drop across the condenser, we have:

$$\begin{aligned} h_3 &= \text{specific enthalpy (R134a, } T = T_3, x = 0) = 115.8 \text{ kJ kg}^{-1} \\ s_3 &= \text{specific entropy (R134a, } T = T_3, x = 0) = 0.418 \text{ kJ(kg.K)}^{-1} \end{aligned}$$

The process in the throttle valve is isenthalpic, so $h_4 = h_3$. Since there is no pressure drop across the evaporator, $P_4 = P_1$. Point 4 is in the saturation region and the quality at point 4 is defined as follows:

$$\begin{aligned} x_4 &= \text{quality (R134a, } h = h_4, P = P_4) = 0.26 \\ s_4 &= \text{specific entropy (R134a, } h = h_4, P = P_4) = 0.43 \text{ kJ(kg.K)}^{-1} \\ T_4 &= \text{temperature (R134a, } h = h_4, P = P_4) = 10^\circ\text{C} \end{aligned}$$

Now that the thermodynamic properties at all points are calculated, we can use the energy balance equation for a control volume around the evaporator and compressor in order to determine the cooling load and compressor work rate as follows:

$$\begin{aligned} \dot{Q}_{\text{Evp}} &= \dot{m}(h_1 - h_4) = 14.04 \text{ kW} \\ \dot{W}_{\text{comp}} &= \dot{m}w_{\text{comp,act}} = 2.66 \text{ kW} \end{aligned}$$

The coefficient of performance (COP) of the refrigerator is expressed as

$$\text{COP} = \frac{\text{Cooling load}}{\text{Work input rate}} = \frac{\dot{Q}_{\text{Evp}}}{\dot{W}_{\text{comp}}} = \frac{14.04 \text{ kW}}{2.66 \text{ kW}} = 5.27$$

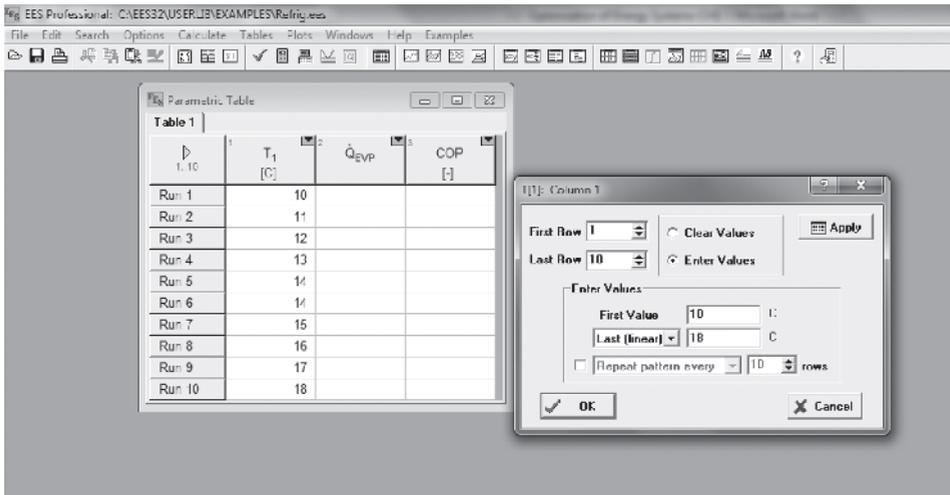


Figure 1.6 Screen shot of the parametric analysis of the system using EES.

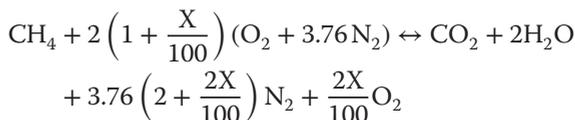
- 3) To assess the effect of evaporator temperature on the COP and the cooling load, we use parametric tables in EES. To do this, we need to remove the evaporator temperature (T_1) in EES and go to the Table option in EES and select New Parametric Table and add T_1 , COP and \dot{Q}_{Evap} . Next, we need to enter the range for evaporator temperature as shown in Figure 1.6. After entering all inputs, we press the green button to run and obtain the results (see Figure 1.7).

Figure 1.7 shows the variation of evaporator temperature on both cooling load and system COP. An increase in this temperature while other design parameters are fixed results in an increase the specific enthalpy at point 1, which eventually leads to an increase in the evaporator cooling load. Similarly, this increase results in an increase in the COP of the system according to the COP definition ($\text{COP} = (\text{Cooling load produced})/(\text{Work input})$). It is clear that the higher the evaporator temperature, the higher the cooling load and the COP of the system.

Example 1.2: Consider the adiabatic combustion of methane at 25°C with a stoichiometric amount of air at 25°C, as shown in Figure 1.8. Plot the variation of adiabatic combustion temperature with percentage of excess air.

Solution: An adiabatic reactor is considered in which combustion takes place with a stoichiometric amount of air at 25°C.

The combustion reaction for methane with stoichiometric air at 25°C and X% excess air is:



Denoting the adiabatic combustion temperature T_f , we can write the energy balance for a control volume around the reactor:

$$\sum N_p H_p = \sum N_R H_R$$

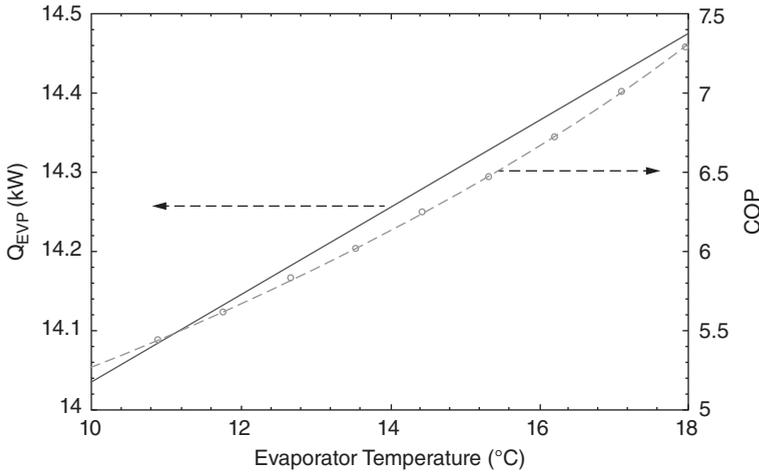


Figure 1.7 Effect of varying evaporator temperature on cooling load and COP of the system.

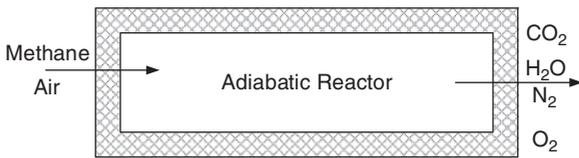


Figure 1.8 Schematic of adiabatic reactor.

where N_p and N_R are the stoichiometric coefficients for products and reactants and H_R and H_p are the enthalpies of the products and reactants, calculated as:

$$\begin{aligned}
 H_R &= \text{enthalpy (CH}_4, T = 298) + 2 \left(1 + \frac{X}{100} \right) \text{enthalpy (O}_2, T = 298 \text{ kJ kg}^{-1}) \\
 &\quad + 3.76 \left(2 + \frac{2X}{100} \right) \text{enthalpy (N}_2, T = 298 \text{ kJ kg}^{-1}) \\
 H_p &= \text{enthalpy (CO}_2, T = T_f) + 2 \text{enthalpy (H}_2\text{O}, T = T_f) \\
 &\quad + 3.76 \left(2 + \frac{2X}{100} \right) \text{enthalpy (N}_2, T = T_f) + \frac{2X}{100} \text{enthalpy (O}_2, T = T_f)
 \end{aligned}$$

Then, we solve the energy balance equation ($\sum N_p H_p = \sum N_R H_R$) for T_f at any given excess air percentage $X\%$ (see Figure 1.9).

1.4 The Second Law of Thermodynamics

As mentioned earlier, the first law is the energy conservation principle. The second law of thermodynamics (SLT) is instrumental in determining inefficiencies of practical thermodynamic systems, and indicates that it is impossible to achieve 100% efficiency (in terms of reversible conversion) in energy conversion processes. Two primary statements of the second law follow:

- Kelvin/Planck statement:** It is impossible to construct a device, operating in a cycle (e.g., a heat engine), that accomplishes only the extraction of heat from some source and its complete conversion to work. This statement describes the impossibility of having a heat engine with a thermal efficiency of 100%.

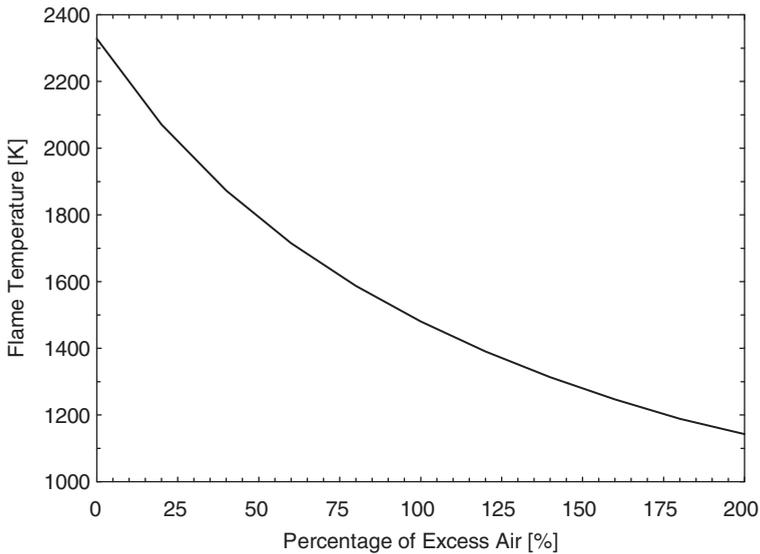


Figure 1.9 Effect of varying excess air on combustion flame temperature.

- **Clausius statement:** It is impossible to construct a device, operating in a cycle (e.g., refrigerator or heat pump), that transfers heat from a low temperature (cooler) region to a high temperature (hotter) region, of itself.

A simple way to illustrate the implications of both the first and second laws is a desktop game (known as “Newton’s Cradle”) that consists of several pendulums (with metal balls at the ends), one in contact with the other. When you raise the first of the balls, you give energy to the system in the form of potential energy. Releasing this ball allows it to gain kinetic energy at the expense of the potential energy. When this ball hits the second ball, a small elastic deformation transforms the kinetic energy, again as a form of potential energy. The energy is transferred from one ball to the other. The last ball again gains kinetic energy, allowing it to rise. The cycle continues, but every time the balls rise to a slightly lower level, until all motion finally stops. The first law concerns why the balls keep moving, while the second law explains why they do not do it forever. In this game the energy is lost in sound and heat, as the motion declines.

The second law also states that the entropy in the universe always increases. As mentioned before, entropy is a measure of degree of disorder, and every process happening in the universe increases the entropy of the universe to a higher level. The entropy of the state of a system is proportional to (depends on) its probability, which provides us with an opportunity to define the second law in a broader manner as “the entropy of a system increases in any heat transfer or conversion of energy within a closed system.” That is why all energy transfers or conversions are irreversible. From the entropy perspective, the basis of the second law is the statement that the sum of the entropy changes of a system plus that of its surroundings must always be positive. Recently, much effort has been invested in minimizing the entropy generation (irreversibilities) in thermodynamic systems and applications.

Dincer and Rosen [2] indicate that exergy, which is based mainly on the SLT, can help with four tasks: design, analysis, performance assessment, and improvement.

Consequently, the second law is the linkage between entropy and the usefulness of energy. Second law analysis has found applications in a wide variety of disciplines, such as chemistry, economics, ecology, environment, and sociology, some of which are far removed from engineering thermodynamic applications.

1.5 Reversibility and Irreversibility

Reversibility and irreversibility are two important concepts in assessing thermodynamic processes and systems. Reversibility is defined by the statement that only for a reversible process can both a system and its surroundings be returned to their initial states, without additional external energy input. Such a process is only theoretical.

Irreversibility during a process describes the destruction of useful energy or its availability. Without new inputs, both a system and its surroundings cannot be returned to their initial states due to the irreversibilities that occur, for example friction, heat transfer or rejection, electrical, and mechanical effects. For instance, an actual system provides an amount of work that is less than the ideal reversible work, with the difference between these two values determining the irreversibility of that system. In real applications, there are always such differences, and therefore real processes and cycles are always irreversible.

1.6 Exergy

Exergy (also called availability) is defined as the maximum amount of work that can be produced by a stream of matter or energy (heat, work, etc.) as it comes to equilibrium with a reference environment. Exergy is a measure of the potential of a flow or system to cause change, as a consequence of not being in complete stable equilibrium relative to a reference environment. For exergy analysis, the state of the reference environment, or the reference state, must be specified completely. This is commonly done by specifying the temperature, pressure, and chemical composition of the reference environment. Exergy is not subject to a conservation law. Rather, exergy is consumed or destroyed due to irreversibilities in any process. Table 1.2 compares energy and exergy from the point of view of thermodynamics.

As pointed out by Dincer and Rosen [2], exergy is a measure of usefulness or quality. It is also a measure of the potential of a flow or system to cause change, and therefore can be seen as a type of measure of the potential of a substance to impact on the environment.

Exergy analysis is useful for improving the efficiency of energy-resource use, for it quantifies the locations, types, and magnitudes of wastes and losses. In general, more meaningful efficiencies are evaluated with exergy analysis than with energy analysis, since exergy efficiencies are always a measure of the approach to the ideal. Therefore, exergy analysis identifies accurately the margin available to design more efficient energy systems by reducing inefficiencies. Many engineers and scientists suggest that thermodynamic performance is best evaluated using exergy analysis because it provides more insights and is more useful in efficiency improvement efforts than energy analysis.

From the point of view of energy and exergy efficiencies, it is important to note that if a fossil fuel-based energy source is used for a low temperature thermal application like

Table 1.2 Comparison between energy and exergy.

Energy	Exergy
<ul style="list-style-type: none"> • Dependent on parameters of matter or energy flow only, and independent of environment parameters. • Has values different from zero (and is equal to mc^2 in accordance with Einstein's equation). • Guided by the first law of thermodynamics for all processes. • Limited by the second law of thermodynamics for all processes (including reversible ones). 	<ul style="list-style-type: none"> • Dependent both on the parameters of matter or energy flow and on environment parameters. • Can equal zero (in dead state, by virtue of being in equilibrium with the environment). • Guided by the first and second laws of thermodynamics for reversible processes (where it is conserved) and irreversible processes (where it is destroyed partly or completely). • Not limited for reversible processes owing to the second law of thermodynamics.

Source: Dincer 2012. Reproduced with permission of Elsevier.

space heating or cooling, there would be a great difference between the corresponding energy and exergy efficiencies, perhaps with values of 50–70% for the energy efficiency and 5% for the exergy efficiency [2]. One may ask why and, to address that question, we point out the following:

- High quality (e.g., capable of high temperature heating) energy sources such as fossil fuels are often used for relatively low-quality (e.g., low temperature heating) processes like water and space heating or cooling.
- Exergy efficiency permits a better matching of energy sources and uses, leading to high quality energy being reserved for high quality tasks and not employed for low-quality end uses.

1.6.1 Exergy Associated with Kinetic and Potential Energy

Kinetic energy is a form of mechanical energy, and therefore can be entirely converted into work. Thus, the exergy of the kinetic energy of a system is equal to the kinetic energy itself regardless of the temperature and pressure of the environment, and is

$$ex_{KE} = \frac{V^2}{2} (\text{kJ kg}^{-1}) \quad (1.7)$$

where V is the velocity of the system in relation to the environment.

Potential energy is also a form of mechanical energy, and can also be entirely converted into work. The exergy of the potential energy of a system is equal to the potential energy itself and does not depend on pressure and temperature [2, 4]. That is,

$$ex_{KE} = gZ \quad (1.8)$$

where g is the gravitational acceleration and Z is the elevation of the system.

In summary, the exergy values associated with kinetic and potential energy are equal for each and they are entirely available to do work. Kinetic and potential exergy have the same values as the corresponding energy terms. Kinetic exergy is particularly relevant where speeds are significant, as in a turbine, whereas potential exergy is especially relevant for electrical or hydraulic systems. In many practical cases involving industrial processes, kinetic and potential exergy terms can be neglected.

1.6.2 Physical Exergy

Physical exergy represents the maximum amount of work that can be obtained from a system as its pressure and temperature are changed to the pressure and temperature of the reference environment. The specific physical exergy ex_{ph} is determined with specific enthalpy and entropy values of the stream at a given temperature and pressure, and the reference environmental state temperature (T_0) and pressure (P_0), as follows [2, 5]:

$$ex_{ph} = [h(T, P) - h(T_0, P_0)] - T_0[s(T, P) - s(T_0, P_0)] \quad (1.9)$$

where $h(T, P)$ and $s(T, P)$ are the specific enthalpy and specific entropy of the stream at a given temperature and pressure, respectively. Values for specific enthalpy and specific entropy can be found either from thermodynamic tables or EES.

1.6.3 Chemical Exergy

Chemical exergy represents the maximum work that can be obtained when a substance is brought from the reference environment state to the dead state by a process including heat transfer and exchange of substances only with the reference environment. The maximum work is attained when the process is reversible. Alternatively, chemical exergy can also be viewed as the exergy of a substance that is at the reference environment state.

Chemical exergy is also equivalent to the minimum amount of work necessary to produce a substance at the reference environment state from the constituents of the reference environment. Chemical exergy has two main parts, reactive exergy resulting from the chemical reactions necessary to produce species which do not exist as stable components in the reference environment, and concentration exergy resulting from the difference between the chemical concentration of a species in a system and its chemical concentration in the reference environment. The concentration part is related to the exergy of purifying or diluting a substance, such as separating oxygen from air.

To determine a substance's chemical exergy, we need to define a reference environment in terms of its temperature T_0 , pressure P_0 , and chemical composition. In some reference environment models, substances present in the atmosphere, the hydrosphere, and upper part of the crust of the earth, at P_0 and T_0 , form the basis of the reference environment. In other models, these substances are allowed to react with each other hypothetically and allowed to reach a stable state with a minimum Gibbs energy, at sea level, at rest without other force fields [2, 5, 6].

Once a reference environment is defined for an exergy analysis, the exergy of any substance at pressure P and temperature T can be evaluated relative to the reference environment. Note that it is not possible to obtain work by allowing substances in the reference environment to interact with each other.

A stream of matter also carries chemical exergy, conceptually determined as discussed above for a quantity of a substance.

1.6.3.1 Standard Chemical Exergy

In thermodynamics, the standard molar chemical exergy of a constituent i is defined as consisting of the molar free enthalpy Δg_f^0 for the formation of the compound in the standard state from its constituent elements and the stoichiometric sum of the standard chemical exergy values of the elements in their stable state at the temperature T_0 and pressure P_0 .

Standard Chemical Exergy for Components of Air In the natural environment, there are many substances that, like nitrogen in the atmosphere, cannot react toward a more stable configuration to produce a new material. They can be considered as part of the reference environment. Transformations, including chemical and nuclear reactions, cannot convert these components into more stable components [6]. So, we cannot extract useful work from these substances and a specific exergy value of 0 kJ mol^{-1} can be assigned to them.

Often, these substances include the normal composition of air (including gases such as N_2 , O_2 , CO_2 , H_2O , Ar, He, Ne), at $T_0 = 298.15 \text{ K}$ and $P_0 = 100 \text{ kPa}$. The partial pressure P_i and molar fraction of each of these substances in air at a given relative humidity are given in Table 1.3.

The standard chemical exergy at P_0 for air can be written as

$$\overline{ex}_{\text{ch}}^0 = RT_0 \ln \left(\frac{P_0}{P_i} \right) \quad (1.10)$$

Standard chemical values for the main constituents of air are listed in Table 1.4. Note that exergy values for elements in their stable condition at $T_0 = 298.15 \text{ K}$ and $P_0 = 101.325 \text{ kPa}$ are called standard chemical exergies, and these are used in the calculation of chemical exergy for various substances.

1.6.3.2 Chemical Exergy of Gas Mixtures

The chemical exergy of a mixture of N gases, in which all are constituents of the environment, can be obtained similarly. In this case, we hypothesize N chambers. If each gas has a molar fraction x_k and enters the chamber at T_0 and with a partial pressure $x_k P_0$, then each gas exits at the same temperature and a partial pressure x_k^e . Summing for all constituents, the chemical exergy per mole of the mixture can be calculated as follows:

$$\overline{ex}_{\text{ch}} = \sum x_k \overline{ex}_{\text{ch}}^k + RT_0 \sum x_k \ln(x_k) \quad (1.11)$$

1.6.3.3 Chemical Exergy of Humid Air

The state of the local atmosphere is determined by its intensive parameters: T_0 , P_0 , and its composition. For humid air, the gas composition for all species other than vapor can

Table 1.3 Partial pressures and molar fractions of various constituents of air.

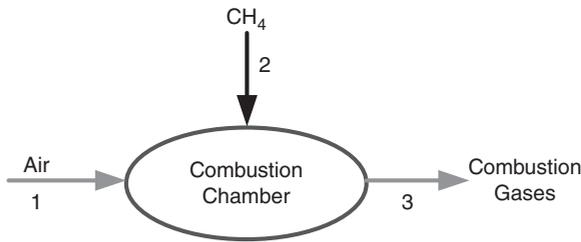
Constituent	P_i (kPa)	Molar fraction (%)
N_2	75.78	75.67
O_2	20.39	20.34
CO_2	0.00335	0.03
H_2O	2.2	3.03
He	0.00048	0.00052
Ne	0.00177	0.0018
Ar	0.906	0.92
Kr	0.000097	0.000076

Source: [7].

Table 1.4 Standard chemical exergy values at P_0 and T_0 of various constituents of air.

Constituent	\overline{ex}_{ch}^0 (kJ/mol)	Constituent	\overline{ex}_{ch}^0 (kJ/mol)
N ₂	0.72	He	30.37
O ₂	3.97	Ne	27.19
CO ₂	19.87	Ar	11.69
H ₂ O	9.49	Kr	34.36

Source: [2, 6].


Figure 1.10 Combustion chamber used in gas turbine cycle.

be considered fixed. So, the composition variation is linked to the moisture content. To calculate the molar fraction of water vapor, we use:

$$x_{\text{H}_2\text{O}}^e = \varphi \frac{P_{\text{gas},0}}{P_0} \quad (1.12)$$

Here φ is relative humidity (RH) and $P_{\text{gas},0}$ is the saturation pressure at T_0 . In the case when the molar fraction of dry air is assumed to be constant, the local atmospheric molar fraction of gases other than water is expressed as $x_i^e = (1 - x_{\text{H}_2\text{O}}^e)x_i^{\text{dry}}$, in which the molar fraction of constituent i corresponds to the atmospheric partial pressure of the species.

1.6.3.4 Chemical Exergy of Liquid Water and Ice

The molar chemical exergy of liquid water is expressed as [7]:

$$\overline{ex}_{ch}^w = v(P_0 - P_{\text{gas},0}) - RT_0 \ln \varphi \quad (1.13)$$

Here v is the molar fraction of compressed water, $P_{\text{gas},0}$ is the saturation pressure at T_0 and φ is relative humidity. This equation is valid for solid water (ice) as well [7].

Example 1.3: The combustion chamber is a major component of both gas turbine and combined cycle plants. A combustion chamber for a gas turbine engine is shown in Figure 1.10. Compressed air enters at point 1, and methane (CH₄) fuel is injected into the combustion chamber at point 2 at a mass flow rate of 1.5 kg s⁻¹. Combustion gases exit at point 3. In this example, air enters the combustion chamber at $T_1 = 550$ K and $P_1 = 10$ bar and the combustion gases exit at $T_3 = 1400$ K. The molar composition of air is taken to be 0.7748 N₂, 0.2059 O₂, 0.0003 CO₂ and 0.019 H₂O.

The following assumptions are invoked:

- The combustion chamber operates at steady state.
- The air and combustion gases can both be treated as ideal gas mixtures.

- Combustion is complete.
 - Changes in potential and kinetic energies are negligible.
- 1) The heat loss from the combustion chamber is 2% of the lower heating value of the fuel. Determine the fuel-to-air ratio, and the molar fractions of the combustion gases.
 - 2) Find the specific physical and chemical exergy values at point 3.

Solution: A combustion chamber is considered here.

Part 1:

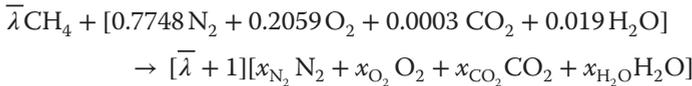
To solve this problem, we first define the molar fuel-air ratio $\bar{\lambda}$ as:

$$\frac{\dot{n}_F}{\dot{n}_a} = \bar{\lambda}$$

So,

$$\frac{\dot{n}_P}{\dot{n}_a} = \frac{\dot{n}_a + \dot{n}_F}{\dot{n}_a} = \bar{\lambda} + 1$$

On a per mole of air basis, the combustion equation occurring in the combustion chamber can be written as:



To find the molar fraction of combustion gases, carbon, hydrogen, oxygen and nitrogen balances are written:

$$\begin{aligned} x_{\text{N}_2} &= \frac{0.7748}{\bar{\lambda} + 1}, & x_{\text{O}_2} &= \frac{0.2059 - 2\bar{\lambda}}{\bar{\lambda} + 1} \\ x_{\text{CO}_2} &= \frac{0.0003 + \bar{\lambda}}{\bar{\lambda} + 1}, & x_{\text{H}_2\text{O}} &= \frac{0.019 + 2\bar{\lambda}}{\bar{\lambda} + 1} \end{aligned}$$

The molar breakdown of the combustion gases is known once $\bar{\lambda}$ is determined. An energy rate balance is used to determine the fuel-air ratio as follows:

$$\dot{Q}_{CV} - \dot{W}_{CV} + \dot{n}_F \bar{h}_F + \dot{n}_a \bar{h}_a - \dot{n}_P \bar{h}_P = 0$$

Since heat loss from the combustion chamber is 2% of the lower heating value of the fuel,

$$\dot{Q}_{CV} = -0.02 \dot{n}_F \overline{LHV} = \dot{n}_a (-0.02 \bar{\lambda} \times \overline{LHV})$$

Combining the above two equations yields

$$-0.02 \bar{\lambda} \overline{LHV} + \bar{h}_a + \bar{\lambda} \bar{h}_F - (1 + \bar{\lambda}) \bar{h}_P = 0$$

Employing ideal gas mixture principles to calculate the enthalpies of the air and the combustion gases, where $T_1 = 550 \text{ K}$ and $T_3 = 1400 \text{ K}$, we obtain:

$$\begin{aligned} \bar{h}_a &= [0.7748 \bar{h}_{\text{N}_2} + 0.2059 \bar{h}_{\text{O}_2} + 0.0003 \bar{h}_{\text{CO}_2} + 0.019 \bar{h}_{\text{H}_2\text{O}}]_{\text{at } T_1} \\ \bar{h}_P &= \frac{1}{\bar{\lambda} + 1} [0.7748 \bar{h}_{\text{N}_2} + (0.2059 - 2\bar{\lambda}) \bar{h}_{\text{O}_2} + (0.0003 + \bar{\lambda}) \bar{h}_{\text{CO}_2} \\ &\quad + (0.019 + \bar{\lambda}) \bar{h}_{\text{H}_2\text{O}}]_{\text{at } T_3} \end{aligned}$$

Then, solving the energy rate balance for $\bar{\lambda}$ yields:

$$\bar{\lambda} = \frac{0.7748\Delta\bar{h}_{N_2} + 0.2059\Delta\bar{h}_{O_2} + 0.0003\Delta\bar{h}_{CO_2} + 0.019\Delta\bar{h}_{H_2O}}{\bar{h}_F - 0.02\overline{LHV} - (-2\bar{h}_{O_2} + \bar{h}_{CO_2} + 2\bar{h}_{H_2O})(T_4)}$$

Using specific enthalpy values from thermodynamic tables [4] and considering

$$\bar{h}_F = -74,872 \text{ kJ/kmol}, \quad \overline{LHV} = 802,361 \text{ kJ/kmol}$$

we find $\bar{\lambda} = 0.0393$. Using this value and the combustion gas molar fractions determined earlier, the following molar breakdown of the combustion products is obtained:

Component	N ₂	CO ₂	H ₂ O	O ₂
Molar breakdown (%)	74.55	3.81	9.39	12.24

Part 2:

To calculate the specific physical exergy at point 3, the specific physical exergy expression described earlier is employed:

$$ex_{ph,3} = (h_3 - h_0) - T_0(s_3 - s_0) = C_p(T_3 - T_0) - T_0 \left[C_p \ln \left(\frac{T_3}{T_0} \right) - R \ln \left(\frac{P_3}{P_0} \right) \right]$$

Since the pressure drop through the combustion chamber is treated as negligible $P_3 = P_1 = 10$ bar. For the combustion gases, we consider a fixed specific heat at constant pressure as $C_p = 1.14$ kJ/kg K. Substituting these values into the specific physical exergy expression yields $ex_{ph,3} = 933.1$ kJ/kg.

To determine the specific chemical exergy at point 3, Equation 3.15 is used:

$$\begin{aligned} ex_{ch,3} &= \sum x_k ex_{ch}^k + RT_0 \sum x_k \ln x_k \\ &= (0.1224 \times 3970 + 0.0381 \times 19870 + 0.0939 \times 9490 + 0.745 \times 720) \\ &\quad + (8.314 \times 298.15) \\ &\quad \times [0.1224 \ln(0.1224) + 0.0381 \ln(0.0381) + 0.0939 \ln(0.0939) \\ &\quad + 0.745 \ln(0.745)] \\ &= 632.1 \frac{\text{kJ}}{\text{kmol}} = 22.95 \frac{\text{kJ}}{\text{kg}} \end{aligned}$$

When a mixture including gaseous combustion products containing water vapor is cooled at a constant pressure, the dew point temperature, which is the saturation temperature corresponding the partial pressure of water vapor, leads to the formation of liquid water. Thus, cooling such a mixture at constant pressure below the dew point temperature can result in condensation. For example, if the combustion gas mixture were cooled to 25°C at a pressure of 1 atm, some condensation would occur. In this case we can model the results at 25°C as a gas phase containing saturated water vapor in equilibrium with a liquid water phase. To find the dew point temperature, we first calculate the partial pressure of water vapor. According to Part 1 of this problem, the molar fraction of H₂O in the combustion gases is 0.0939, so the partial pressure of water vapor is $P_v = x_v P_0 = (0.0939)(1.013 \text{ bar}) = 0.0951$ bar. The corresponding saturation temperature at this pressure is 44.81°C; the reference environment temperature is therefore

below the dew point, which leads to the formation of liquid water. On the basis of 1 kmol of combustion products, the gas phase at 25°C consists of 0.9061 kmol of dry products (0.7455 N₂, 0.3810 CO₂, 0.1224 O₂) plus n_v kmol of water vapor. The partial pressure of water vapor is equal to the saturation pressure at 25°C, which is 0.0317 bar. The amount of water vapor is calculated as $P_v = x_v P_0 = n_v / (0.9061 + n_v) \times P_0$, where n_v is the amount of water vapor. Hence, 0.0317 bar = $(n_v \times 1.013 \text{ bar}) / (0.9061 + n_v)$ which yields $n_v = 0.02927$ kmol. Thus, the molar fractional composition of the combustion products at 25°C and 1 atm is 0.7455 N₂, 0.3810 CO₂, 0.1224 O₂, 0.02927 H₂O (g), and 0.06583 H₂O (l). At point 3 in the present analysis, 0.06583 kmol of liquid water is present on the basis of 1 kmol of mixture, following the method outlined by Bejan *et al.* [5]. Therefore, the specific chemical exergy at point 3 after modification is:

$$ex_{ch,3} = (1 - 0.06583) \times 22.95 + 0.06583 \times \frac{900}{18} = 24.32 \text{ kJ/kg}$$

Here, the first term is the percentage of dry combustion gases multiplied by the specific chemical exergy obtained from part 2, and the second term is the product of the molar fraction of liquid water due to the condensation and specific chemical exergy of liquid water.

Finally, the specific exergy at point 3 can be determined as:

$$ex_3 = ex_{ch,3} + ex_{ph,3} = 24.32 + 933.1 = 957.42 \text{ kJ/kg}$$

1.6.3.5 Chemical Exergy for Absorption Chillers

For the absorption cooling system, because a water and LiBr solution is not ideal, the following expression is used for the molar chemical exergy calculation:

$$\bar{ex}_{ch} = (1/\bar{M}_{sol}) \left[\sum_{i=1}^n y_i \bar{ex}_{ch}^k + \bar{R} T_0 \sum_{i=1}^n y_i \ln(a_i) \right] \quad (1.14)$$

Extending this equation for a LiBr-water solution we obtain:

$$\bar{ex}_{ch} = (1/\bar{M}_{sol}) \left[\bar{R} T_0 (y_{H_2O} \ln(a_{H_2O}) + y_{LiBr} \ln(a_{LiBr})) + y_{H_2O} \bar{ex}_{H_2O}^0 + y_{LiBr} \bar{ex}_{LiBr}^0 \right] \quad (1.15)$$

Here, a_{H_2O} is the water activity defined as the vapor pressure of water in the mixture divided by the vapor pressure of pure water, and a_{LiBr} is LiBr activity defined as the vapor pressure of LiBr in the mixture divided by the vapor pressure of LiBr. This equation consists of two parts, standard chemical exergy of the pure species and exergy due to the dissolution process, defined as follows:

$$\bar{ex}_{ch}^0 = \frac{1}{\bar{M}_{sol}} (y_{H_2O} \bar{ex}_{H_2O}^0 + y_{LiBr} \bar{ex}_{LiBr}^0) \quad (1.16)$$

$$\bar{ex}_{ch}^{dis} = \frac{\bar{R} T_0}{\bar{M}_{sol}} [y_{H_2O} \ln(a_{H_2O}) + y_{LiBr} \ln(a_{LiBr})] \quad (1.17)$$

where y_i is the molar fraction defined as

$$y_{H_2O} = \frac{(1 - x_{1w}) \bar{M}_{LiBr}}{(1 - x_{1w}) \bar{M}_{LiBr} + x_{1w} \bar{M}_{H_2O}} \quad (1.18)$$

$$y_{LiBr} = 1 - y_{H_2O} \quad (1.19)$$

Table 1.5 Standard molar chemical exergy values for selected substances at $T_0 = 298.15$ K and $P_0 = 1$ atm.

Element	\overline{ex}_{ch}^0 (kJ/mol)	Element	\overline{ex}_{ch}^0 (kJ/mol)
Ag (s)	70.2	Kr (g)	34.36
Al (s)	888.4	Li (s)	393.0
Ar (s)	11.69	Mg (s)	633.8
As (s)	494.6	Mn (s_α)	482.3
Au (s)	15.4	Mo (s)	730.3
B (s)	628.8	N ₂ (g)	0.72
Ba (s)	747.4	Na (s)	336.6
Bi (s)	274.5	Ne (g)	27.19
Br ₂ (l)	101.2	Ni (s)	232.7
C (s, graphite)	410.26	O ₂ (g)	3.97
Ca (s)	712.4	P (s, red)	863.6
Cd (s_α)	293.2	Pb (s)	232.8
Cl ₂ (g)	123.6	Rb (s)	388.6
Co (s_α)	265.0	S (s, rhombic)	609.6
Cr (s)	544.3	Sb (s)	435.8
Cs (s)	404.4	Se (s, black)	346.5
Cu (s)	134.2	Si (s)	854.6
D ₂ (g)	263.8	Sn (s, white)	544.8
F ₂ (g)	466.3	Sn (s)	730.2
Fe (s_α)	376.4	Ti (s)	906.9
H ₂ (g)	236.1	U (s)	1190.7
He (g)	30.37	V (s)	721.1
Hg (l)	115.9	W (s)	827.5
I ₂ (s)	174.7	Xe (g)	40.33
K (s)	366.6	Zn (s)	339.2

Source: [2, 8].

Here, x_{1w} is defined as

$$x_{1w} = \frac{x_{LiBr}}{100} \quad (1.20)$$

where x_{LiBr} is the LiBr-water solution concentration in percent, and \overline{M}_{LiBr} and \overline{M}_{H_2O} are 86.85 kg/kmol and 18.02 kg/kmol, respectively.

To calculate the chemical exergy for components not listed in Table 1.5, we may refer to reactions for which the standard chemical exergy of constituents are given. In this case, we can calculate the chemical exergy for the new constituent. Since the standard chemical exergy of LiBr is not listed in Table 1.5, the following reaction is used to calculate the molar chemical exergy of LiBr [8]:

$$\overline{ex}_{ch}^0 = \overline{g}_f^0 + \sum_{i=1}^n \overline{ex}_{ch,i}^0 \quad (1.21)$$



$$\overline{ex}_{\text{ch,LiBr}}^0 = \overline{g}_{f,\text{LiBr}}^0 + \overline{ex}_{\text{ch,Li}}^0 + \frac{1}{2}\overline{ex}_{\text{ch,Br}_2}^0 \quad (1.23)$$

Here, $\overline{g}_{f,\text{LiBr}}^0 = -324 \frac{\text{kJ}}{\text{mol}}$ [9].

Figure 1.11 shows the variation of chemical exergy as a function of LiBr mass basis concentration based on Equations 1.16 and 1.17. As shown in this figure, an increase in LiBr concentration results in an increase in the total chemical exergy of the LiBr–water solution.

Therefore, based on the LiBr concentration, the total chemical exergy at each point in a single effect absorption chiller can be straightforwardly calculated.

1.6.4 Exergy Balance Equation

By combining the conservation principle for energy and non-conservation principle for entropy (i.e., the second law of thermodynamics), the exergy balance equation can be obtained as follows:

$$\sum \text{Exergy Input} = \sum \text{Exergy Output} + \text{Exergy Destruction} \quad (1.24)$$

In terms of symbols, the following exergy rate balance can be written:

$$\dot{Ex}_Q + \sum_i \dot{m}_i ex_i = \sum_e \dot{m}_e ex_e + \dot{Ex}_W + \dot{Ex}_D \quad (1.25)$$

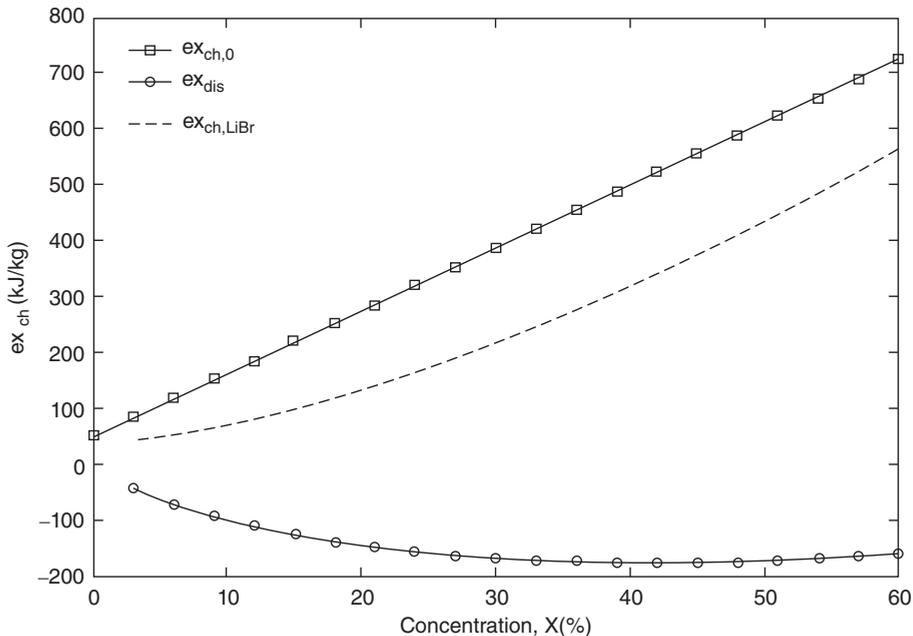


Figure 1.11 Variation of standard chemical exergy ($ex_{\text{ch},0}$), chemical exergy due to dissolution (ex_{dis}) and total specific chemical exergy as a function of LiBr mass basis concentration at $T_0 = 25^\circ\text{C}$.

where subscripts i and e denote the control volume inlet and outlet, respectively, $\dot{E}x_D$ is the exergy destruction rate and other terms are defined as follows:

$$\dot{E}x_Q = \left(1 - \frac{T_0}{T_i}\right) \dot{Q}_i \quad (1.26)$$

$$\dot{E}x_w = \dot{W} \quad (1.27)$$

$$ex = ex_{ph} + ex_{ch} \quad (1.28)$$

Here, $\dot{E}x_Q$ is the exergy rate of heat transfer crossing the boundary of the control volume at absolute temperature T , the subscript 0 refers to the reference environment conditions and $\dot{E}x_w$ is the exergy rate associated with shaft work. Table 1.6 lists exergy destruction rate expressions for some standard components.

1.6.5 Exergy Efficiency

Efficiencies are often evaluated as ratios of energy quantities, and are often used to assess and compare various systems. Power plants, heaters, refrigerators, and thermal storages, for example, are often compared based on energy efficiencies or energy-based measures of merit. However, energy efficiencies are often misleading in that they do not always provide a measure of how nearly the performance of a system approaches ideality. Further, the thermodynamic losses that occur in a system (i.e., those factors that cause performance to deviate from ideality) are often not accurately identified and assessed using energy analysis. The results of energy analysis can indicate the main inefficiencies to be within the wrong sections of a system, and a state of technological efficiency different than actually exists. Exergy efficiency computes the efficiency of a process taking the second law of thermodynamics into account. From the second law of thermodynamics, it can be demonstrated that no real system can ever achieve 100% efficiency. When calculating the energy efficiency of a system, no indication is provided of how the system compares to a thermodynamically perfect one operating under the same conditions. Exergy efficiency is a better measure and shows how a system works compared to a perfect one. The exergy efficiency is usually defined as the product exergy output divided by the exergy input.

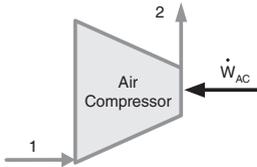
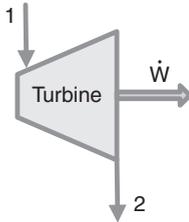
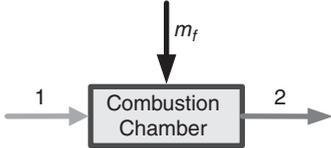
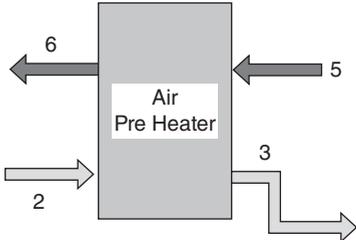
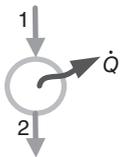
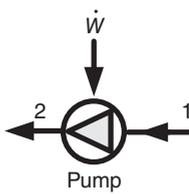
Exergy efficiencies often give more illuminating insights into process performance than energy efficiencies because (1) they weigh energy flows according to their exergy contents, and (2) they separate inefficiencies into those associated with effluent losses and those due to irreversibilities. In general, exergy efficiencies provide a measure of potential for improvement.

1.6.6 Procedure for Energy and Exergy Analyses

A simple procedure for performing energy and exergy analyses involves the following steps:

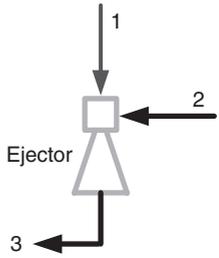
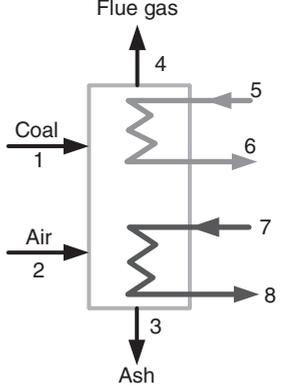
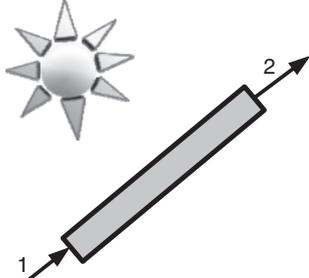
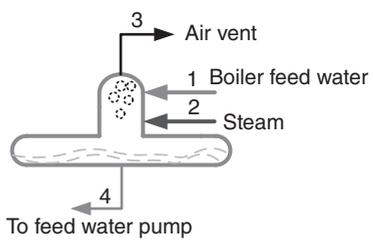
- Subdivide the process under consideration into as many sections as desired, depending on the depth of detail and understanding desired from the analysis.
- Perform conventional mass and energy balances on the process, and determine all basic quantities (e.g., work, heat) and properties (e.g., temperature, pressure).
- Based on the nature of the process, the acceptable degree of analysis complexity and accuracy and the questions for which answers are sought, select a reference environment model.

Table 1.6 Expressions for exergy destruction rates for some selected components.

Component	Illustration	Exergy destruction rate expression
Air compressor		$\dot{E}x_{D,AC} = \dot{E}x_1 - \dot{E}x_2 + \dot{W}_{AC}$
Turbine		$\dot{E}x_{D,T} = \dot{E}x_1 - \dot{E}x_2 - \dot{W}_T$
Combustion chamber		$\dot{E}x_{D,CC} = \dot{E}x_1 + \dot{E}x_f - \dot{E}x_2$ $\dot{E}x_f = \dot{m}_f \times \Phi \times LHV$ $\Phi_{CH_4} = 1.06$ $\Phi_{H_2} = 0.985$
Air preheater		$\dot{E}x_{D,PH} = \dot{E}x_2 + \dot{E}x_5 - \dot{E}x_3 - \dot{E}x_6$
Condenser		$\dot{E}x_{D,Cond} = \dot{E}x_1 - \dot{E}x_2 - \dot{E}x_Q$
Pump		$\dot{E}x_{D,Pump} = \dot{E}x_1 - \dot{E}x_2 + \dot{W}$

(Continued)

Table 1.6 (Continued)

Component	Illustration	Exergy destruction rate expression
Ejector		$\dot{E}x_{D,EJ} = \dot{E}x_1 + \dot{E}x_2 - \dot{E}x_3$
Boiler		$\begin{aligned} \dot{E}x_{D,Boiler} = & \dot{E}x_1 + \dot{E}x_2 + \dot{E}x_5 \\ & + \dot{E}x_7 - \dot{E}x_3 - \dot{E}x_4 - \dot{E}x_6 \\ & - \dot{E}x_8 \end{aligned}$
Flat plate solar collector		$\begin{aligned} \dot{E}x_{D,FPC} = & \dot{E}x_1 + \dot{E}x_{sun} - \dot{E}x_2 \\ \dot{E}x_{sun} = & I_{sun} A_{FPC} \\ & \times \left[1 - \frac{4}{3} \left(\frac{T_0}{T_{sun}} \right) + \frac{1}{3} \left(\frac{T_0}{T_{sun}} \right)^4 \right] \end{aligned}$
Deaerator		$\dot{E}x_{D,DEA} = \dot{E}x_1 + \dot{E}x_2 - \dot{E}x_3 - \dot{E}x_4$

- Evaluate energy and exergy values relative to the selected reference environment model.
- Perform exergy balances including the determination of exergy consumptions.
- Select efficiency definitions, depending on the measures of merit desired, and evaluate values for the efficiencies.
- Interpret the results and draw appropriate conclusions and recommendations. These can relate to such issues as designs and design changes, retrofitted plant modifications, and so on.

1.7 Concluding Remarks

In this chapter, a summary is presented of the general introductory aspects of thermodynamics and related fundamental definitions and physical quantities, to help provide necessary background for understanding energy systems and applications, and their operations. The coverage of fundamentals provided here is particularly useful for the energy, exergy, and other analyses presented subsequently. EES was introduced as useful software for energy systems analyses. Some illustrative examples are presented and discussed. The FLT refers to energy conservation and treats all energy forms equally, thus not identifying losses of energy quality or work potential and possible improvements in the use of resources. For example, energy alone cannot identify the losses in an adiabatic throttling process. However, the SLT involves exergy and entropy concepts and considers irreversibilities and the consequent non-conservation of exergy and entropy.

References

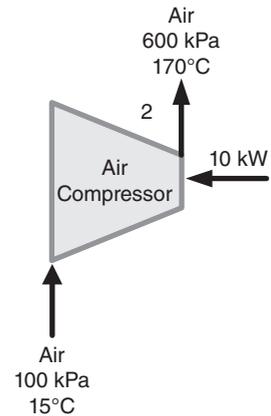
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Study Questions/Problems

- 1 Define the following forms of energy and explain their differences: internal energy, thermal energy, heat, sensible energy, latent energy, chemical energy, nuclear energy, flow energy, flow work and enthalpy.
- 2 What is specific heat? Define two commonly used specific heats. Is specific heat a function of temperature?
- 3 What is the difference between an adiabatic system and an isolated system?
- 4 Define the critical point and explain the difference between it and the triple point.
- 5 Consider example 1.1, and perform an exergy analysis, including calculation of the exergy destruction rate for each component and the exergetic COP of the refrigeration system. Also, plot the variation of reference environment temperature and evaporator temperature with exergetic COP and total exergy destruction, and compare the results.
- 6 Consider example 1.3, for a reference state of $T_0 = 298.15$ K and $P_0 = 101.325$ kPa. Determine the exergy destruction rate and exergy efficiency of the combustion chamber and compare the results with information in the literature.
- 7 Define the terms energy, exergy, entropy, and enthalpy.
- 8 What is a second law efficiency? How does it differ from a first law efficiency?
- 9 What is the relationship between entropy generation and irreversibility?
- 10 When we enter a pool of water at 22°C , it often feels more than cool—it often feels cold. When we walk into a 22°C room, it is comfortable. Why is there such a difference between these cases, even though our body is surrounded by the same temperature?
- 11 How does an exergy analysis help further the goal of more efficient energy-resource use? What are the advantages of using exergy analysis?
- 12 In example 1.3, what is the effect of varying P_1 and T_1 on the specific chemical exergy at point 3 and the total exergy destruction rate of the combustion chamber?
- 13 On a hot day of summer, occupants return to their well-sealed house and find the house is at 32°C . They turn on the air conditioner, which cools the entire house to 21°C in 15 min. If the COP of the air conditioning system is 2.5, determine the power drawn by the air conditioner. Assume the entire mass within the house is equivalent to 700 kg of air for which $C_v = 0.72$ kJ/kg.K and $C_p = 1$ kJ/kg.K.

- 14 Air is compressed steadily by a 10 kW compressor from 100 kPa and 15°C to 600 kPa and 170°C at a rate of 3 kg/min (see Figure 1.12). Neglecting changes in kinetic and potential energies, determine (a) the increase in the exergy of the air, and (b) the rate of exergy destruction during this process. Assume the surroundings to be at 15°C.

Figure 1.12 Schematic of an air compressor.



- 15 Biomass is a biological material formed from living or recently living organisms, and is often viewed as a renewable source of energy. As an energy source, biomass can either be used directly, or converted into other energy products such as biofuels. Calculate the chemical exergy of the biomass “pine sawdust” using the following composition and other data:

Biomass type	Pine sawdust
Moisture content in biomass (by weight)	10%
Elemental analysis (dry basis by weight)	
Carbon (C)	50.54%
Hydrogen (H)	7.08%
Oxygen (O)	41.11%
Sulfur (S)	0.57%

Also, determine the molar composition of the product gases when pine sawdust is combusted according to the following reaction:



- 16 Consider the simple gas turbine power plant shown in Figure 1.13. Air at ambient conditions enters the air compressor at point 1 and exits after compression at point 2. The hot air enters the combustion chamber (CC) into which fuel is injected, and hot combustion gases exit (point 3) and

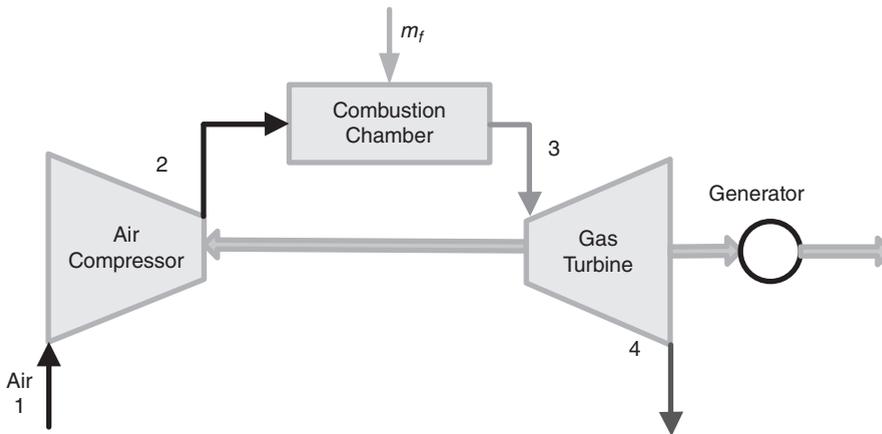


Figure 1.13 Schematic of a gas turbine power plant.

pass through a gas turbine to produce shaft power. The hot gas expands in the gas turbine to point 4. Natural gas (with a volumetric composition of $\text{CH}_4 = 96.57\%$, $\text{C}_2\text{H}_6 = 2.63\%$, $\text{C}_3\text{H}_8 = 0.1\%$, $\text{C}_4\text{H}_{10} = 0.7\%$) is injected into the combustion chamber with a mass flow rate of 2 kg/s. The compressor pressure ratio is 7, the gas turbine inlet temperature is 1400 K and the compressor isentropic efficiency and gas turbine isentropic efficiency are 0.83 and 0.87, respectively. If the net output power of this power plant is 15 MW, and there is no pressure drop in the combustion chamber and heat loss in the compressor and gas turbine:

- Determine the fuel-to-air ratio, and the molar fractions of the combustion gases.
 - Find the specific physical and chemical exergy values at all points.
 - For a reference state of $T_0 = 298.15 \text{ K}$ and $P_0 = 101.325 \text{ kPa}$, determine the exergy destruction rate and exergy efficiency of the all components as well as the overall cycle.
 - If the compressor pressure ratio varies from 6 to 12 while other parameters are fixed, plot the variation of system exergy efficiency with compressor pressure ratio for various gas turbine isentropic efficiencies.
 - If the gas turbine inlet temperature (GTIT) varies from 1100 K to 1500 K, plot the variation of system exergy efficiency and total exergy destruction with GTIT.
- 17 Consider a house with a floor space area of 180 m^2 and average height of 2.7 m. The initial temperature of the house is uniform at 10°C . To maintain thermal comfort inside the house, an electric heater is turned on to raise the temperature to an average value of 22°C .
- a) Determine the amount of energy transferred to the air assuming no air escapes during the heating process.
 - b) Determine the amount of energy transferred to the air assuming some air escapes through cracks as the heated air expands at constant pressure.
 - c) Determine the cost of heat for either case when the cost of electricity in the area is $\$0.075/\text{kWh}$.
- 18 Consider a solar powered steam power plant with feedwater heating, as shown in Figure 1.14. The conditions of the steam generated in the boiler are 8600 kPa and

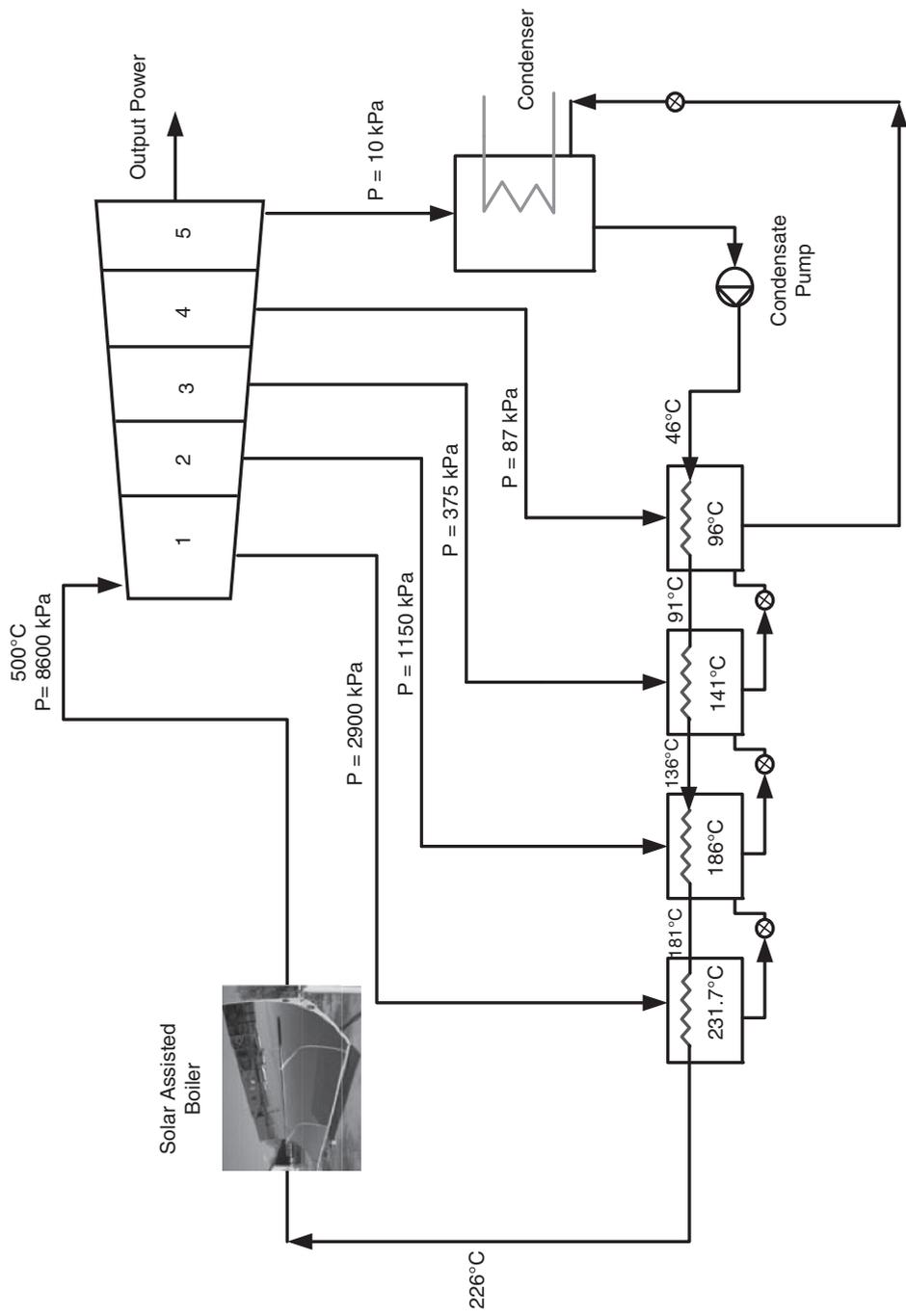


Figure 1.14 Schematic of a solar powered steam power plant with feedwater heating.

500°C. The exhaust pressure of the turbine, 10 kPa, is constant. The saturation temperature of the exhaust steam is therefore 45.83°C. Allowing for slight subcooling of the condensate, we fix the temperature of the liquid water from the condenser at 45°C. The feedwater pump, which operates under exactly the conditions of the pump, causes a temperature rise of about 1°C, making the temperature of the feedwater entering the series of heaters equal to 46°C. The saturation temperature of steam at the boiler pressure of 8,600 kPa is 300.06°C, and the temperature to which the feedwater can be raised in the heaters is certainly less. This temperature is a design variable, which is ultimately fixed by economic considerations. However, a value must be chosen before any thermodynamic calculations can be made. We have therefore arbitrarily specified a temperature of 226°C for the feedwater stream entering the boiler. We have also specified that all four feedwater heaters accomplish the same temperature rise. Thus, the total temperature rise of $226 - 46 = 180^\circ\text{C}$ is divided into four 45°C increments. This establishes all intermediate feedwater temperatures at the values shown in the figure. The steam supplied to a given feedwater heater must be at a pressure high enough that its saturation temperature is above that of the feedwater stream leaving the heater. We have here presumed a minimum temperature difference for heat transfer of no less than 5°C, and have chosen extraction steam pressures such that the T_{sat} values shown in the feedwater heaters are at least 5°C greater than the exit temperatures of the feedwater streams. The condensate from each feedwater heater is flashed through a throttle valve to the heater at the next lower pressure, and the collected condensate in the final heater of the series is flashed into the condenser. Thus, all condensate returns from the condenser to the boiler by way of the feedwater heaters.

- Utilize the following solution procedure:
 - Write a problem statement
 - Show the cycle on a T - s diagram with respect to saturation lines
 - Make appropriate assumptions and approximations
 - Identify relevant physical laws
 - List all relevant properties
 - Write all balance equations (mass, energy, entropy, exergy)
 - Do calculations through the EES software
 - Determine which type of solar collector will be appropriate for this power plant and include solar data in the calculations
 - Conduct a performance evaluation in terms of energy and exergy efficiencies (and exergy destructions)
 - Discuss the results, providing reasoning and verification
 - Discuss performance, environmental, and sustainability issues
 - Make recommendations for better technical performance, environmental performance and sustainability.
- Do a parametric study to show how system performance is affected by varying the operating and environment conditions (e.g., T , P , m).