CHAPTER 1

FUNDAMENTALS OF THERMODYNAMICS

1.1.   INTRODUCTION

Any action in the known universe requires energy to happen, whether it is associated to life or not. It is also known that energy is conserved, i.e., it is not created or destroyed, but is converted in form. As a result, it is reasonable to state that evolution resulted from the countless energy conversion processes throughout the history of the universe. On earth, humanity learned how to make use of energy available in nature to its advantage, mainly using fossil fuels in the past two hundred years, and advance to a level of development that allowed for enormous population growth. The supplies of fossil fuels are likely to remain adequate for the next few generations, but unacceptable environmental long-term consequences are expected, and scientists and policy makers must search for alternative sources of energy [1, 2]. The broad discussion of global concerns and their relation to energy led Smalley[+] [3] to propose a prioritized list of the top ten problems humanity has to face in the 21st century: 1. Energy; 2. Water; 3. Food; 4. Environment; 5. Poverty; 6. Terrorism and war; 7. Disease; 8. Education; 9. Democracy, and 10. Population. Smalley [3] argued that with energy as the key at the top, all the others are possible to be solved, but without cheap energy, there is no acceptable answer. Therefore, energy is the single most important factor that impacts the prosperity of any society.

In that context, in the beginning of the 21st century Dresselhaus and Thomas [1] pointed out that there was a need for increased push towards alternative energy technologies to replace fossil and nuclear sources in the near future, in order to determine what is scientifically possible, environmentally acceptable and technologically promising. Also, the authors recalled that policy, science and technology need to work together harmoniously, which are responsible for acceptability, possibility and practicability, respectively. The same challenges continue to be up to date as discussed by Chen et al. [4] who recently argued that technically and economically viable renewable energy generation and storage are major hurdles to be overcome. For that, on the basis of their own research experiences, the authors listed research areas that need to be pursued in the energy field: energy materials; electrochemical energy conversion and energy storage; solar cells; solar fuels; LED and display devices, and last but not least theory and computational modeling.

Chapter 1 therefore reviews the thermodynamics fundamentals that are necessary for a full understanding of the physical principles of all thermal machines treated in this book. Moreover, thermodynamics brings to light the principles on: i) how energy is conserved in the universe (1st law of thermodynamics), and ii) how to quantify the imperfections of all existing physical systems (2nd law of thermodynamics). Since our society is also based on currency exchange, in order to make physical analyses even more useful, the chapter also reviews thermoeconomy (or exergoeconomy) [5], as a branch of thermodynamics, that has been increasingly gaining importance in engineering design since the 1970's energy crisis [6]. Furthermore, the knowledge of such basic concepts allows the engineering designer to mathematically model physical systems (e.g., thermal machines) and computationally simulate their behavior, which makes possible affordable system control, design and optimization. Finally, recognizing the need to think of alternative forms of energy to fossil fuels, a discussion on energetic sustainability is presented, and the role of renewable energy for sustainable thermal machines design.

[+] Richard Errett Smalley (June 6, 1943 – October 28, 2005): along with Robert Curl, and Harold Kroto, was the recipient of the 1996 Nobel Prize in Chemistry for the discovery of a new form of carbon, buckminsterfullerene, also known as buckyballs. He was the Gene and Norman Hackerman Professor of Chemistry and a Professor of Physics and Astronomy at Rice University, in Houston, Texas.

1.2.   FUNDAMENTAL CONCEPTS AND TERMINOLOGY

During the development of classical thermodynamics, an objective language was necessary to be established to analyze physical systems on a common ground. Hence, a few selected concepts are listed and defined in this section to review the technical terminology used throughout the book, as follows:

1. **Energy:** it is the physical quantity that refers to the potential to make an action happen. In physics, it is a fundamental concept that is accepted without definition and appears in nature in several forms. The conversion of the different forms of energy into one another was experimentally demonstrated by Joule [7]. Some examples of forms of energy are the **kinetic energy** (nonstationary system), the **potential energy** (system position under a gravitational, electric or magnetic field), the **elastic energy** (solid system shape change), the **chemical energy** (made available by exergonic reactions), the **radiant energy** (transported by electromagnetic waves or photons), and the **thermal energy** (associated to system temperature);

2. **System:** it is the region of space (or entity) that is of interest to analyze – it is vital to be adequately defined in order to evaluate precisely system response and determine the location and the magnitude of the thermodynamic irreversibility (or losses);

3. **Frontier or boundary:** it is the line that delimits the system and, mathematically has no thickness ($=0$), so there is no matter, nor does it occupy a place in space – the value of a property at the boundary is shared by the system and its neighborhood (Continuum Mechanics);

4. The system can be **isolated** (without mass flow and energy across the boundary), **closed** (no flow of mass across the boundary) or **open** (with mass and energy flows across the boundary), which is also named as **control volume** delimited by a **control surface**;

5. **Ports:** the parts of the boundary that allow mass to flow in and out of the system (inlet or outlet ports);

6. **Thermodynamic properties:** physical quantities that characterize the state that a system is in at a given time (e.g., pressure, temperature, volume, enthalpy, internal energy);

7. **Non properties:** physical quantities of interest in the analysis of a system that are not properties (e.g., work, heat, generation of entropy), as they depend on system history;

8. **State:** identification of the condition in which a system is at any instant in time, that is characterized by a set of thermodynamic properties (e.g., two independent properties define the state of a simple system);

9. Properties can be **extensive** (dependent on the size of the system) and **intensive** (independent of system size);

10. **Specific property:** it is the extensive property divided by the mass of the system. Ex: specific volume $v = V/m$;

11. **Phase:** is the collection of all parts of the system that have the same intensive state and the same values of extensive properties (e.g., liquid-vapor mixture has two phases: liquid water and steam);

12. **Process:** it is the change of the system from an initial state to a final one – in order to analyze the process, it is necessary to know the interactions experienced by the system with the surroundings (e.g., heat, mass, work transfer);

13. **Path:** it is the succession of states that the system visited during the process, and

14. **Cycle:** it is the special process with the same initial and final thermodynamic states.

1.3.   THE FIRST LAW OF THERMODYNAMICS

The discovery of fire by men dates to approximately 200,000 years [8], i.e., the point in time when humanity started to use thermal energy. However, thermal sciences historically

evolved at a slower pace than solid mechanics which had already achieved several fundamental advances by the end of the 17th century, including Newton's laws.

1.3.1. Closed systems

Despite having different historical chronologies, in principle, work transfer and heat transfer are equivalent, as possible forms of energy interactions. Such principle was clearly stated in the first law of thermodynamics. The first formal statement of the first law was provided by Clausius for cyclic processes, and also for a general thermodynamic process, defining a system thermodynamic property, the internal energy [9, 10], as follows: "In a thermodynamic process involving a closed system, the increment in the internal energy is equal to the difference between the heat accumulated by the system and the work done by it". The statement led to the currently well-known first law of thermodynamics equation for a closed system:

$$\Delta U = Q - W \qquad (1.1)$$

in which Clausius established the system internal energy variation in the process as ΔU, and defined Q and W, as the net heat and work transfer, respectively, to or from the system due to the interaction with its neighborhood. In Equation (1.1) there is an implicit sign convention adopted by Clausius, which is: $Q > 0$ for heat entering the system and $Q < 0$ otherwise, and $W < 0$ for work entering the system and $W > 0$ otherwise. Originally, the convention was motivated by heat engines which deliver useful work as a result of heat input.

The discussion on what is physically possible or not is clarified by the second law of thermodynamics, which allows for quantifying the imperfections (or irreversibilities) of all processes in the known universe. The second principle states that all fluxes produced by any physical quantity (e.g., temperature, pressure, concentration) happen in one direction, from high to low. The nonidealities, or the generation of entropy, are always present in any physical process that happens in the universe. Such facts led Rudolf Clausius to acknowledge that the entropy of the universe is always increasing in the direction of a state of maximum entropy in a statement that addressed simultaneously the two laws of thermodynamics as follows: "a. The energy of the universe is constant, and b. The entropy of the universe strives to attain a maximum value" [11]. The latter statement will be further discussed in this chapter in the presentation of the second law of thermodynamics in section 1.4.

At this point, it is important to highlight that the laws of thermodynamics are a result of the experimental observations done by the scientists who proposed them, therefore recognized as postulates or principles. As a result, no formal mathematical proof is required for them to be accepted. Any postulate or principle is accepted to be valid until a counter example is presented against its validity. So far, no counter proof against the validity of the accepted laws of thermodynamics has been successfully presented.

In this treatment, the first law is discussed first, followed by the second law, according to tradition. However, the first and second laws of thermodynamics formulations as currently known were developed concomitantly by several scientists (William John MacQuorn Rankine, Rudolph Clausius, and William Thomson – Lord Kelvin) mostly in the first half of the nineteenth century [12]. In fact, the principle of conservation of energy in mechanics is a little older than the first and second thermodynamics principles.

After the concept of system internal energy variation originally introduced by Clausius, which is intrinsically associated to system temperature, several other forms of system energy storage were identified. Therefore, the formulation proposed by Eq. (1.1) was amended by several other scientists. The final common understanding was in terms of system total energy,

which was made up of four macroscopic contributions: i) the change in kinetic energy, linked to whole system motion; ii) the change in system gravitational potential energy, iii) the change in system internal energy, and iv) the change in other possible forms of energy.

As a result, since the beginning of the twentieth century, the mathematical formulation for the closed system first law of thermodynamics for a process from state 1 to 2 is given by [13 – 15]:

$$\Delta E_{1-2} = \left(\Delta E_k + \Delta E_p + \Delta U + \Delta E_{other} \right)_{1-2} = Q_{1-2} - W_{1-2} \tag{1.2}$$

in which ΔE_k, ΔE_p, and ΔE_{other} are the system kinetic, potential, and other forms of energy variations, respectively. Each form of system energy variation should be included or not in Eq. (1.2) after a case-by-case analysis. For example, for power and refrigeration systems, only the three first forms are usually necessary, i.e., kinetic, potential, and internal energy. Depending on the system, other forms of energy variation need to be accounted for, which could be uncoupled or coupled. Examples of uncoupled energy variations are those in which constitutive relations are independent of one another, such as electrical capacitance and inductance, kinetic rotational, spring translational and rotational [13]. Regarding coupled behavior, the most common systems to be cited are energy conversion systems, such as the electromechanical energy of an electric motor that could be altered via shaft work transfer or electrical work transfer independently, and by shaft work and electrical work transfer combined.

The left-hand side of Eq. (1.2), $\Delta E_{1-2} = E_2 - E_1$, is the system energy change in the process, which depends only on the initial and end states. The right hand side of Eq. (1.2) shows that the energy interactions experienced by the system during the process, Q_{1-2} and W_{1-2}, do not have the same characteristics, since they depend on the end states and on the history (path) of process 1-2. Mathematically, the unique result $\Delta E_{1-2} = E_2 - E_1$ could be obtained with different values of Q_{1-2} and W_{1-2}, i.e., the system can proceed from state 1 to state 2 along an infinity of paths.

A simple numerical example demonstrates that clearly. If $E_1 = 1 \text{ kJ}$ and $E_2 = 3 \text{ kJ}$, then $\Delta E_{1-2} = 2 \text{ kJ}$. States 1 and 2 are unique, and the only possible result for the system energy change is $\Delta E_{1-2} = 2 \text{ kJ}$. However, the pair $\left(Q_{1-2}, W_{1-2} \right)$ is not unique so that $\Delta E_{1-2} = 2 \text{ kJ}$, i.e., any combination of Q_{1-2} and W_{1-2} that results in $\Delta E_{1-2} = 2 \text{ kJ}$, according to Eq. (1.2) would be acceptable. Therefore, Q_{1-2} and W_{1-2} depend on states 1 and 2, but also on the history (path) of the process. For example, $\left(Q_{1-2}, W_{1-2} \right) = \left(6 \text{ kJ}, 4 \text{ kJ} \right)$ or $\left(Q_{1-2}, W_{1-2} \right) = \left(-6 \text{ kJ}, -8 \text{ kJ} \right)$ would be two different paths from 1 to 2 that would comply with the first law of thermodynamics expressed by Eq. (1.2). As a result, the system total energy, E, is a thermodynamic property, because its variation depends only on the initial and end states of the process. Conversely, Q and W depend also on the history (or path) of the process, therefore they are classified as physical quantities of interest that are not properties.

1.3.2. Open systems

An **open system** is also defined as a **control volume** [15] and is a system in which mass and energy flow through the boundary to and from the surroundings. Therefore, the analysis starts by recalling the mass conservation principle: "nothing is lost, nothing is created, everything is transformed", as it was originally stated by Antoine Lavoisier [16]. So, in a closed system, in which there is no mass flow across the boundary, the total system mass is **constant**.

As a result, mathematically, the mass conservation principle formulation for a nonreactive open system is derived with the help of Fig. 1.1.

Mass conservation

Consider a closed system whose mass is deformable and represented in Fig. 1.1 by the highlighted area. In Figure 1.1, for the analysis, the open system boundary is defined by the rigid and impermeable walls drawn with solid lines, and the dotted lines at the inlet and outlet ducts. The deformable mass of the closed system (highlighted area) is allowed to flow through the open system. Therefore, for a process that goes from t to $t + \Delta t$, mass conservation applied to the closed system states that:

$$M_{cs} \text{ (constant)} = M_{os,t} + \Delta M_{in} = M_{os,t+\Delta t} + \Delta M_{out} \tag{1.3}$$

where M_{cs} is the total and constant (fixed) mass of the closed system, M_{os} the mass of the open system (or control volume).
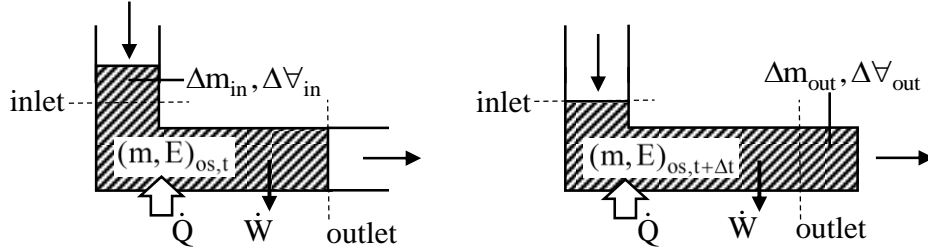

Figure 1.1. The process from t to $t + \Delta t$ of a closed system represented by the highlighted area through an open system (or control volume).

Rearranging Eq. (1.3) and dividing by Δt, the following relation is obtained:

$$\frac{M_{os,t+\Delta t} - M_{os,t}}{\Delta t} = \dot{m}_{in} - \dot{m}_{out} \tag{1.4}$$

in which, $\dot{m}_{in} = \dfrac{\Delta M_{in}}{\Delta t}$ and $\dot{m}_{out} = \dfrac{\Delta M_{out}}{\Delta t}$.

Next, taking the limit of Eq. (1.4) as $\Delta t \to 0$, and assuming as many inlets and outlets as desired to represent the actual physical system, the result is given by:

$$\frac{dM_{os}}{dt} = \sum_{in} \dot{m} - \sum_{out} \dot{m} \tag{1.5}$$

which is the general mass conservation principle for an open system.

Energy conservation

The derivation of the first law of thermodynamics for open systems starts by considering the process from a state at time t to another state at time $t + \Delta t$ undergone by the closed system shown schematically in Fig. 1.1. For that, the first law of thermodynamics states that:

$$E_{cs,t+\Delta t} - E_{cs,t} = Q - W + (P\ \Delta\forall)_{in} - (P\ \Delta\forall)_{out} \tag{1.6}$$

where $Q = \dot{Q}\ \Delta t$; $W = \dot{W}\ \Delta t$, and the remaining terms on the right-hand side account for the work linked to the fluid pressure as mass gets in and out of the control volume. Indeed, $(P\ \Delta\forall)_{in} = (P\ A\ \Delta s)_{in} = (F\ \Delta s)_{in} = W_{fluid,in}$ is the work done by the matter flowing (flow work) through the inlet port, and at pressure P_{in} that results in the force F_{in} that pushes the closed system for a distance Δs_{in} into the open system, thus negative, which explains the positive sign in Eq. (1.6), and, analogously, $(P\ \Delta\forall)_{out}$ is the work done by the closed system (flow work) at pressure P_{out} through the outlet port on the environment, thus positive, which explains the negative sign in Eq. (1.6), according to Clausius' thermodynamics signs convention [9, 10].

In like manner to Eq. (1.3), it is possible to find relations between the energy inventories of the closed and open systems as follows:

$$E_{cs,t} = E_{os,t} + \Delta E_{in} = E_{os,t} + (e\ \Delta M)_{in} \tag{1.7a}$$

$$E_{cs,t+\Delta t} = E_{os,t+\Delta t} + \Delta E_{out} = E_{os,t+\Delta t} + (e\ \Delta M)_{out} \tag{1.7b}$$

where e is the fluid specific energy. Analogously, it is possible to write $\Delta\forall_{in} = (v\ \Delta M)_{in}$ and $\Delta\forall_{out} = (v\ \Delta M)_{out}$, using v the fluid specific volume.

Combining Eqs. (1.6) and (1.7) in order to eliminate $E_{cs,t}$ and $E_{cs,t+\Delta t}$, and dividing the expression by Δt, the result is written as follows:

$$\frac{E_{os,t+\Delta t} - E_{os,t}}{\Delta t} = \dot{Q} - \dot{W} + \left\{ (e + Pv)\ \frac{\Delta M}{\Delta t} \right\}_{in} - \left\{ (e + Pv)\ \frac{\Delta M}{\Delta t} \right\}_{out} \tag{1.8}$$

Taking the limit of Eq. (1.8) as $\Delta t \to 0$, and assuming multiple inlets and outlets, the general first law of thermodynamics for open systems is given by

$$\frac{dE_{os}}{dt} = \dot{Q} - \dot{W} + \sum_{in} \dot{m}(e + Pv) - \sum_{out} \dot{m}(e + Pv) \tag{1.9}$$

Equation (1.9) accounts for the energy transfers to the open system due to mass flow in and out, which are represented by the two last terms of the right-hand side. Additionally, it is instructive to recognize that when kinetic, gravitational and internal energy are the dominant macroscopic forms of energy in the system, $e + Pv = u + Pv + \frac{1}{2}V^2 + gz$.

Using the fluid specific enthalpy $h = u + Pv$, Eq. (1.9) is rewritten as follows:

$$\frac{dE_{os}}{dt} = \dot{Q} - \dot{W} + \sum_{in} \dot{m}\left(h + \frac{1}{2}V^2 + gz \right) - \sum_{out} \dot{m}\left(h + \frac{1}{2}V^2 + gz \right) \tag{1.10}$$

which is the energy conservation principle for an open system.

Finally, taking $h^0 = \left(h + \dfrac{v^2}{2} + gz \right)$, which is the property specific methalpy [13], the first law of thermodynamics is alternatively written for a general open system (or control volume) shown schematically in Fig. 1.2 as follows:

$$\frac{dE_{CV}}{dt} = \dot{Q}_{CV} - \dot{W}_{CV} + \sum_{in} \dot{m}\, h^0 - \sum_{out} \dot{m}\, h^0 \tag{1.11}$$

where the subscript CV refers to the control volume (or open system) under analysis, and with a boundary defined by a control surface represented by the dashed line in Fig. 1.2.
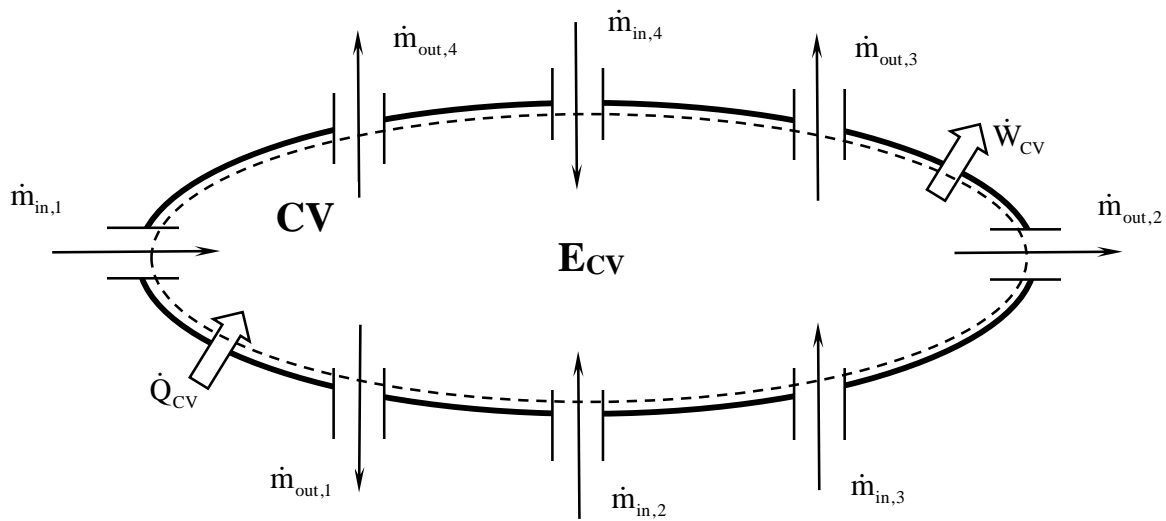

Figure 1.2. Schematic diagram of a general control volume delimited by a control surface represented by the dashed line.

Next, to complete the analysis, it is necessary to quantify the control volume net work and heat transfer rates across the boundary of the control volume. Note that Equations (1.2), (1.10) and (1.11) do not explicitly relate such quantities to the system geometry, which is required for adequate system design. For that, other branches of science are needed, such as electromagnetism, electricity, classical mechanics, solid and fluid mechanics, and heat transfer.

1.3.3. Work transfer

In classical mechanics, the work produced or consumed by a system as a function of forces, $\vec{F}$, and displacements, $\vec{r}$, is given by [15]:

$$W = \int_1^2 \vec{F} \cdot d\vec{r} \tag{1.12}$$

In thermodynamics, the concept of work needs to be amplified to comprise other types of interactions. Work transfer is defined in a more general way that includes electrical and

magnetic work interactions was proposed by Hatsopoulos and Keenan [17]: "Work is an interaction between two systems such that what happens in each system at the interaction boundary could be repeated while the sole effect external to each system was the change in level of a weight." For example, consider liquid water inside a container with an immersed paddle wheel as the system to be analyzed. The paddle wheel axle is connected by a cord to a weight placed at a high level. The paddle wheel is then rotated by the axle that crosses the system boundary as the weight descends and does work on a fluid inside the system increasing its internal energy, therefore transforming mechanical in thermal energy, as it was originally demonstrated by Joule [7]. Although there is no displacement of the originally defined system boundary, the work transfer could be quantified by Eq. (1.12) accounting for the forces and circular displacement of the paddle wheel in the fluid. Also, the same work would be transferred due to electrical energy from a power line that fed an electric motor connected to the paddle wheel axle. Based on this broad definition, as a result of doing work, it is seen that energy was transferred to and stored in the system. Hence, work is a means for transferring energy.

Finally, it is important to recognize that in the absence of (or negligible) system heat loss to the surroundings, the energy input to the axle could be transferred in its entirety to the system by the paddle wheel [7]. Joule showed with his experiment that the weight potential energy variation due to going from a higher to a lower level was equal to the internal energy gained by the water through friction with the paddle. Therefore, by definition, work transfer is an interaction free of thermodynamic losses. This aspect is crucial to understand the distinction between work and heat transfer. Equation (1.12) and other variations allow for explicitly relating system energy variation to system geometry, so that system design is made possible.

1.3.4. Heat transfer

At this point, it should be noted that although the first law of thermodynamics does not make a distinction between heat and work transfer, there is a fundamental distinction between them. Both are energy interactions and are measured with the same energy physical units. However, heat transfer happens together with entropy transfer (thermodynamic loss), and work transfer does not. Such fundamental distinction appears clearly through the derivation of the mathematical formulation of the second law of thermodynamics, which will be presented in section 1.4.

Heat transfer was simply defined by Poincaré as the energy interaction that results from the temperature difference between the system and its surroundings [13]. Such definition is in agreement with the three different heat transfer modes (conduction, convection and radiation) that were quantified mathematically based on temperature differences with empirically based expressions.

Conduction

Conduction is the mode of heat transfer that occurs in a **stationary medium** (solid, liquid or gas), and there must be **mass** so that energy flows due to temperature difference. The concept is understood as the transfer of energy from the more energized to less energized molecules.

The conduction heat flux, W m^{-2}, is macroscopically determined by the generalized Fourier's law as follows:

$$q''_i = \left(\frac{\dot{Q}}{A} \right)_i = -k_{ij} \frac{\partial T}{\partial x_j} \tag{1.13}$$

where $T(t,\vec{x})$ is the local temperature, which is a function of time t and space in terms of the position vector $\vec{x} = (x_1, x_2, x_3)^T$; the spatial dimensions are indicated by the subscripts $i, j = 1, 2, 3$; k_{ij} are the **thermal conductivities** that are given functions of $\vec{x}$, experimentally measured and tabulated for known substances – if k_{ij} are uniform, i.e., independent of space, then the system is said to be **homogeneous**, and when the material is **isotropic**, i.e., k_{ij} is independent of direction, $k_{ij}(\vec{x}) = k(\vec{x})\,\delta_{ij}$ where δ_{ij} is the Kronecker delta, so that for an homogeneous and isotropic system $k_{ij}(\vec{x}) = k\,\delta_{ij}$, and the minus sign accounts for Clausius sign convention for heat transfer to be positive entering the system, i.e., when $\dfrac{\partial T}{\partial x_j}$ is negative.

As a result, the heat transfer rate due to a temperature gradient through an homogeneous and isotropic system in the x direction, $\dot{Q}_x$, is given by:

$$\dot{Q}_x = -kA\frac{\partial T}{\partial x} \tag{1.14}$$

where A is the plane area perpendicular to the x direction in the system under analysis, e.g., a plane wall.

Example 1.1) A straight copper rod with 0.1-m diameter and 0.8-m length has its lateral surface thermally insulated, with bare tips. One of the tips is attached to a heat source, where the measured temperature is 800 K. On the other tip, the measured temperature is 400 K at the point where it is connected to the generator component of an absorption refrigerator. What is the heat transfer rate supplied to the generator in kW?
The thermal conductivity of copper is $k_c = 400 \text{ W m}^{-1}\text{K}^{-1}$.

Given
0.8 m long, and 0.1 m diameter copper rod
Thermal conductivity of copper (k_c) = 400 W m^{-1} K^{-1}
Temperature of the hot tip (T_H) = 800 K
Temperature of the cold tip (T_L) = 400 K

Find
The heat transfer rate supplied to the absorption refrigerator generator $\dot{Q}_c$

Assumptions
One dimensional heat flow
The system has reached steady state

Solution
The solution is based on Eq. (1.14) and accounts for unidirectional conduction, i.e., the temperature variation is linear, therefore:

$$\dot{Q}_c = -k_c A \frac{\partial T}{\partial x} = -k_c A \frac{T_L - T_H}{L} \quad \begin{cases} T_L = 400 \text{ K} \\ T_H = 800 \text{ K} \\ L = 0.8 \text{ m} \\ D = 0.1 \text{ m} \end{cases}, \text{ i.e., } \frac{\partial T}{\partial x} < 0$$

and the copper rod cross sectional area is

$$A = \frac{\pi D^2}{4} = \frac{3.14159\ldots \times (0.1 \text{ m})^2}{4} = 0.00785 \text{ m}^2$$

Therefore, the heat transfer rate that is supplied to the absorption refrigerator generator is given by

$$\dot{Q}_c = -400 \frac{W}{m \text{ K}} \times 0.00785 \text{ m}^2 \times \frac{800 - 400}{0.8} \frac{K}{m} = 1,570 \text{ W} = 1.57 \text{ kW}$$

Comment:
Note that the calculation of the conduction heat transfer rate with Fourier's law allowed for assessing the rod geometry and how it impacts the resulting heat transfer rate. ∎

Convection

Convection is defined as the mode of heat transfer that occurs between a **moving medium** (fluid: liquid, gas or fluidized bed – fluid carrying solid particles), and another **stationary or moving medium** at a different velocity, i.e., in presence of a velocity gradient between the entities that exchange heat. Therefore, there must be **mass** with physical contact, so that energy flows from the more to the less energized medium, from the higher to the lower temperature. Alternatively, convection could be simply defined as the study of heat transport processes effected by the flow of fluids and allows to understand and predict how a fluid flow will act as a "carrier" or "conveyor belt" for energy and matter [18].

The Newton's law of cooling, that was empirically derived, shows that the convection heat flux, W m^{-2}, between two entities at temperatures T_1 and T_2 is proportional to their temperature difference, as follows:

$$q''_{conv} = \left(\frac{\dot{Q}}{A} \right)_{conv} = h \ (T_1 - T_2) \tag{1.15}$$

in which A_{conv} is the heat transfer area between the two entities in relative motion, as described previously, $\dot{Q}_{conv}$ the convection heat transfer rate, W, and h is the proportionality factor first proposed by Newton, namely, the **convection heat transfer coefficient**. It should be noted, that $\dot{Q}_{conv}$ is positive when $T_1 > T_2$. Therefore, when modeling physical systems, the sign convention adopted by Clausius should be respected, which is: $\dot{Q}_{conv} > 0$ for heat entering the system and $\dot{Q}_{conv} < 0$ otherwise.

The heat transfer coefficient is a proportionality factor between q''_{conv} and the temperature difference $T_1 - T_2$, and is not a thermodynamic property. In fact, it depends on

several characteristics of the interaction between the two entities exchanging heat. It is a coefficient of empirical nature, as originally proposed by Newton, but it could be estimated by the solution to momentum and energy conservation equations (velocities and temperatures) in a domain comprised by the two entities, either analytically or numerically. The heat transfer coefficient depends on the flow regime (laminar, transition or turbulent), the fluids thermophysical properties, and morphology (geometry). Additionally, convection could be **external** (fluid external to a solid) or **internal** (fluid internal to a solid); **forced** (with work input, i.e., fluid moves due to fans, compressors, or pumps) or **natural** (no work input, i.e., fluid moves due to buoyancy effects), and **single phase** or **multiphase** (e.g., condensation, boiling, melting). Hence, the accurate determination of the convection heat transfer coefficient is often considered a challenging problem. Through the years, scientists have thoroughly studied the heat transfer coefficient behavior in many situations of physical interest, mainly for engineering design, so that much is currently known with respect to the order of magnitude of h in such situations. Figure 1.3 shows one of the available compilations of typical values of the heat transfer coefficient, h, in terms of orders of magnitude [19], that have been shown to be useful in systems engineering preliminary design for reduced-order mathematical models [20].
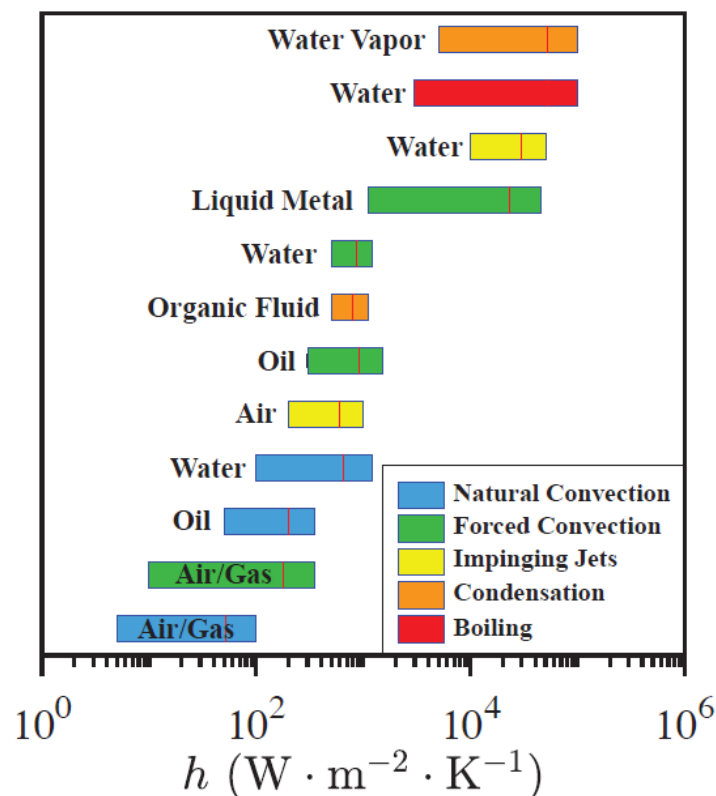

Figure 1.3. Range of convection heat transfer coefficients for different fluids and cooling techniques [19].

Radiation

Radiation is the third mode of heat exchange between two systems at different temperatures. The physical mechanism is not yet completely understood. Two viewpoints are accepted to explain the phenomenon of radiation heat transfer: i) transported by electromagnetic waves (continuous description), and ii) carried by discrete particles (photons), assumed with

zero rest mass, namely the quantum theory [21]. In both descriptions, heat travels at the speed of light.

Some fundamental characteristics need be emphasized: a) The radiation heat transfer rate between systems 1 and 2 depends on $(T_1^4 - T_2^4)$, in terms of absolute temperatures, not on $(T_1 - T_2)$ like in conduction or convection. As a result, radiation has intensified importance at high absolute T levels; b) No medium (matter) need be present between the 2 systems, and c) It is the mechanism by which bodies can exchange heat from a distance, without direct contact, even in vacuum.

Thermal radiation is defined as radiant energy emitted by a medium (matter) in virtue of its temperature. The emission of thermal radiation is governed by the temperature of the emitting body, which in turn reflects the matter molecular agitation level. Kirchhoff's experiment showed that blackbody emissive power, for a given wavelength (or frequency), depends only on temperature [22]. As a result, temperature is a property of thermal radiation.

In either description (continuous or discrete particles), thermal radiation is characterized by its frequency, ν (s^{-1}), or range of frequencies or wavelengths, that are related as follows:

$$\lambda = \frac{c}{\nu} \quad \text{with} \quad c = \frac{c_0}{n} \tag{1.16}$$

in which c is the wave or photons velocity; $c_0 = 2.998 \times 10^8 \, \text{m s}^{-1}$, that is the light speed in vacuum, and n the medium index of refraction. For gases, $n \simeq 1$.

The thermal radiation wavelength band is $0.1 \, \mu\text{m} < \lambda < 100 \, \mu\text{m}$, which encompasses the visible range (what is seen by the human eye), i.e., $0.4 \, \mu\text{m} < \lambda < 0.7 \, \mu\text{m}$. The band also contains the full infrared range and part of the ultraviolet range. Further, no stream is of a single wavelength, λ, but if the band is narrow, i.e., between λ and $\lambda + d\lambda$, it is said to be **monochromatic** radiation.

The total radiation heat flux, W m^{-2}, arriving on the system surface is denoted by $\dot{I}$. For a general surface, $\dot{I}$ could be absorbed, reflected or transmitted. Indeed, conservation of energy and the intrinsic characteristics of the surface determine how $\dot{I}$ is split as follows:

$$\alpha\dot{I} + \rho\dot{I} + \tau\dot{I} = \dot{I} \quad \text{or} \quad \alpha + \rho + \tau = 1 \tag{1.17}$$

where α, ρ and τ are the surface properties absorptivity, reflectivity, and transmissivity, respectively.

The thermal radiation emitted by a system (solid surface, gas or liquid) is quantified with respect to an idealized perfect emitter (or absorber) body, namely, a **black body** ($\rho = 0, \tau = 0$), in terms of a material property named emissivity, ε. In a black body, $\varepsilon = 1$. Therefore, for a typical body $0 < \varepsilon < 1$. The emissivity in general varies with respect to wavelength, but when the surface emissivity is approximately independent of λ, the so called **gray surface model**, originally proposed by Planck [21] is utilized, and ε is assumed constant as the total hemispherical emissivity, i.e., for all wavelengths that the surface emits radiation [22]. The model also assumes that the surface is a diffuse emitter, absorber, and reflector (i.e., isotropic – properties are the same in all directions), and additionally is opaque ($\tau = 0$). The gray surface model approximates well the behavior of many materials found in thermal engineering, such as metals, paints and paper.

Kirchhoff's law establishes an important relation between emissivity and absorptivity as functions of wavelength, λ. A complete derivation of Kirchhoff's law was reported by

Planck [21]. Fundamentally, for a system in thermodynamic equilibrium the law establishes for each surface that

$$\varepsilon_\lambda = \alpha_\lambda \qquad (1.18)$$

Equation (1.18) was derived for surfaces in thermodynamic equilibrium with the medium, but since emissivity and absorptivity are surface properties that depend only on surface characteristics and temperature, it also applies for nonequilibrium conditions [22]. Further, for a gray surface, it follows that:

$$\varepsilon = \alpha \qquad (1.19)$$

In order to quantify the energy amount that arrives or leaves a surface, envisioning one single ray is not representative of the phenomenon. Therefore, the concept of **radiation intensity**, i $(\text{W m}^{-2}\text{sr}^{-1})$, is adopted, which is the radiant energy arriving or leaving a surface per unit of area normal to the collection of rays, per unit of solid angle, $d\omega = dA_h / r^2$, which is the steradian (sr), and per unit time, as shown in Fig. 1.4, in which dA_h is the surface element on the hemisphere, and r the hemisphere radius.

As a result, it is possible to calculate the radiant energy flux, e (W m^{-2}), from the surface to the hemispherical space above the surface. First, the radiant energy per unit time and unit area in the direction θ within the solid angle $d\omega$ is calculated by:

$$i = \frac{de}{d\omega \cos \theta} \qquad (1.20)$$

Therefore, the radiant energy flux is given by

$$e = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} i \cos \theta \, d\omega = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi/2} i \cos \theta \, \sin \theta \, d\theta \, d\phi \qquad (1.21)$$

Although the analysis has been conducted for the total energy flux (over all wavelengths), Eqs. (1.20) and (1.21) also apply to monochromatic radiation. In this case, the results would be obtained for a specific wavelength in terms of i_λ and e_λ, respectively. Then, the total hemispherical intensity and energy flux, i and e, would be calculated by the integrals of i_λ and e_λ, from $\lambda = 0$ to ∞, respectively.

The second law of thermodynamics allows for the demonstration that a maximum amount of radiant energy that can be emitted at a certain temperature and wavelength exists. A system that emits such radiant energy is named a black body emitter. Planck's law [21] presented a mathematical expression that was derived based on quantum statistics thermodynamics for correlating the blackbody emissive power as a function of temperature and wavelength (or frequency), $e_{b,\lambda}(T)$. Integrating $e_{b,\lambda}(T)$ from $\lambda = 0$ to ∞, it is possible to obtain the Stefan-Boltzmann law, that was originally experimentally derived [22, 23] as follows:

$$e_b = n^2 \sigma \, T^4 \qquad (1.22)$$

where $n \simeq 1$ for gases; $\sigma = 5.670373 \times 10^{-8}$ W m^{-2}K^{-4} is the Stefan-Boltzmann constant, and T the system surface absolute temperature, K.

By taking $i = i_b(T)$, the total blackbody intensity (over all wavelengths), i.e., a diffuse emitter (intensity does not depend on direction), using Eq. (1.21) and Planck's law [21, 22], it is possible to demonstrate that $i_b(T) = e_b(T)/\pi = \sigma T^4/\pi$ (Problem 1.1).

The radiation heat transfer rate emitted by a surface is quantified by the empirically based Stefan-Boltzmann law adapted to the gray surface model, as follows [22]:

$$\dot{Q}_{emt} = \varepsilon_s \sigma A_s T_s^4 \tag{1.23}$$

where A_s the surface area; ε_s the surface emissivity, and T_s the surface absolute temperature.
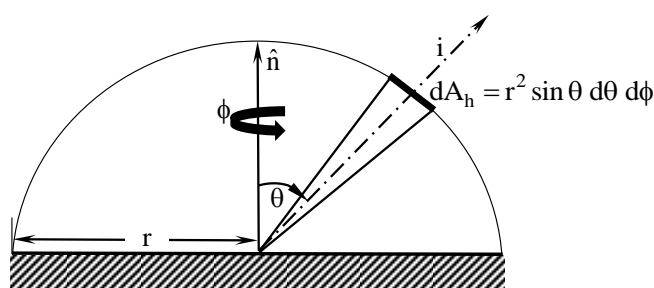

Figure 1.4. The radiation intensity and the hemispherical space above the emitting surface.

A conceptual method to understand and treat thermal radiation problems is to consider a space closed by n surfaces, as shown in Fig. 1.5 left. The method is based on the idea of an appropriately defined closed space, namely the **enclosure**. The analysis starts with the construction of an appropriate enclosure, so that all radiation is completely considered, noting that not all surfaces need to materially exist (e.g., the open end of a duct, an open window) in which case equivalent radiation properties and blackbody temperatures should be assigned to them, corresponding to radiation rates crossing the imaginary surface into the enclosure. It is then clear that only a fraction of the total stream emitted by one surface reaches one of the other surfaces and is possibly absorbed, reflected or transmitted by it. That fraction depends on: i) relative position; ii) surface characteristics (e.g., roughness, cleanliness, shape: convex, flat of concave), and iii) nature of the medium in the space. The heat transfer problem consists of calculating the resulting radiation net heat transfer rate for each surface.
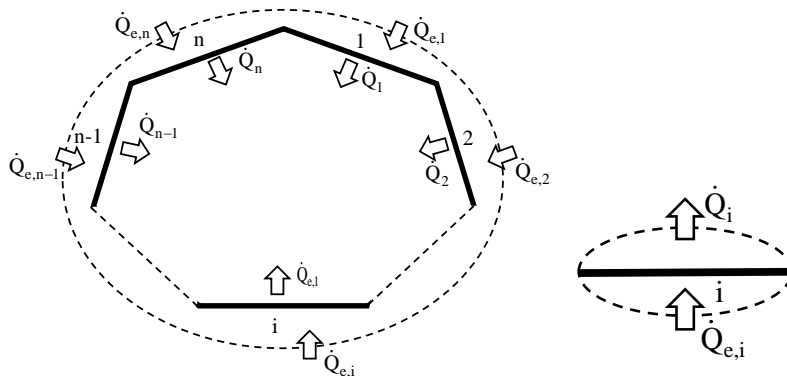

Figure 1.5. The enclosure idea.

Lemma 1.1

In an enclosure with n surfaces, as shown in Fig. 1.5 left, at steady state, the following relation holds:

$$\sum_{i=1}^{n} \dot{Q}_i = 0 \tag{1.24}$$

where $\dot{Q}_i$ is the internal net heat transfer rate in surface i.

Proof:

i) Based on Fig. 1.5 left, the first law of thermodynamics states that:

$$\sum_{i=1}^{n} \dot{Q}_{e,i} = 0$$

where $\dot{Q}_{e,i}$ is the external net heat transfer rate in surface i.

ii) Taking a system consisting of just one surface, as shown in Fig. 1.5 right, the first law of thermodynamics states that:

$$\dot{Q}_{e,i} + \dot{Q}_i = 0$$

Therefore, doing the same for all n surfaces and adding up all Equations, the result is:

$$\sum_{i=1}^{n} \dot{Q}_{e,i} + \sum_{i=1}^{n} \dot{Q}_i = 0$$

iii) After using the result from i), it is concluded that:

$$\sum_{i=1}^{n} \dot{Q}_i = 0$$

∎

The thermal radiation heat transfer rates are calculated for the surfaces that interact with one another. Considering an enclosure, as shown in Fig. 1.5 left, the internal radiation net heat transfer rate for each surface, e.g., a solar collector surface, as shown in Fig. 1.6, is calculated by

$$\dot{Q}_i = \left(H_i - B_i \right) \ A_i \tag{1.24}$$

where H_i is the incident radiation heat flux, i.e., the total radiation heat transfer rate per unit of area striking the surface and coming from all directions; B_i is the radiosity, i.e., the total radiation heat transfer rate per unit of area leaving the surface, and A_i is the exposed surface area.

The objective of the analysis is to determine the radiation net heat transfer rate for each of the surfaces that interact energetically in the enclosure. For that, it is necessary to evaluate the fractions of the emitted heat transfer rates by the surfaces that are intercepted by the others. In order to do that, the concept of **view factor** (or, alternatively, angle factor, shape factor, configuration factor, geometrical factor) was introduced.
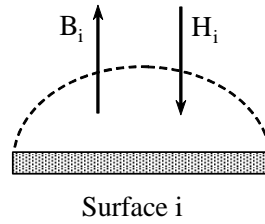

Figure 1.6. Thermal radiation heat fluxes that arrive (H_i) and leave (B_i) a surface.

The view factor is defined as the fraction of the total radiant energy that leaves a given surface and is intercepted by another surface. There are four types of view factor between areas: i) Two infinitesimal areas, $dF_{dA_i-dA_j}$; ii) An infinitesimal and a finite area, $F_{dA_i-A_j}$; iii) A finite and an infinitesimal area, $dF_{A_i-dA_j}$, and iv) Two finite areas, $F_{A_i-A_j}$. Based on the definition, it is clear that the view factor is infinitesimal when the stricken surface is infinitesimal. Only the fourth type is discussed in this book, but the full description of the four types of view factor is available in the work of Sparrow and Cess [22].

The definition of the view factor of the fourth type is summarized as follows:

$$F_{A_i-A_j} = \frac{\text{Radiation rate leaving } A_i \text{ and being intercepted by } A_j}{\text{Radiation rate leaving } A_i \text{ in all directions}} \qquad (1.25)$$

In order to calculate $F_{A_i-A_j}$, consulting Fig. 1.7, dB_i (infinitesimal radiosity) intercepted by dA_j is the emitted and reflected radiation leaving dA_i per unit of area and contained in the solid angle $d\omega_j = dA_j \cos \beta_j / r^2$, in which r is the distance between dA_i and dA_j. Then, using Eq. (1.20) with $de = dB_i$, and assuming diffuse radiation (i_i = constant), Eq. (1.25) is rewritten as follows:

$$F_{A_i-A_j} = \frac{\int_{A_j}\int_{A_i} i_i \cos \beta_i \overbrace{\dfrac{\overbrace{\cos \beta_j \, dA_j}^{d\omega_j}}{r^2}}^{dB_i \text{ intercepted by } dA_j} dA_i}{\int_{A_i}\left[\int_{\phi=0}^{2\pi}\int_{\theta=0}^{\pi/2} i_i \cos \theta \underbrace{\underbrace{\sin \theta \, d\theta \, d\phi}_{d\omega_i}}_{dB_i \text{ in any direction } (\theta,\phi)}\right] dA_i} = \frac{1}{A_i}\int_{A_j}\int_{A_i}\frac{\cos \beta_i \cos \beta_j}{\pi r^2}dA_j dA_i \quad (1.26)$$

which is the general expression to calculate the view factor. Note that the view factor has a clear physical meaning from its definition and from Eq. (1.25), but Eq. (1.26) shows that it depends only on the geometry of the arrangement among the surfaces interacting energetically, as in the case of the enclosure shown in Fig. 1.5.

By switching subscripts i and j in Eq. (1.26), the following reciprocity relation results:

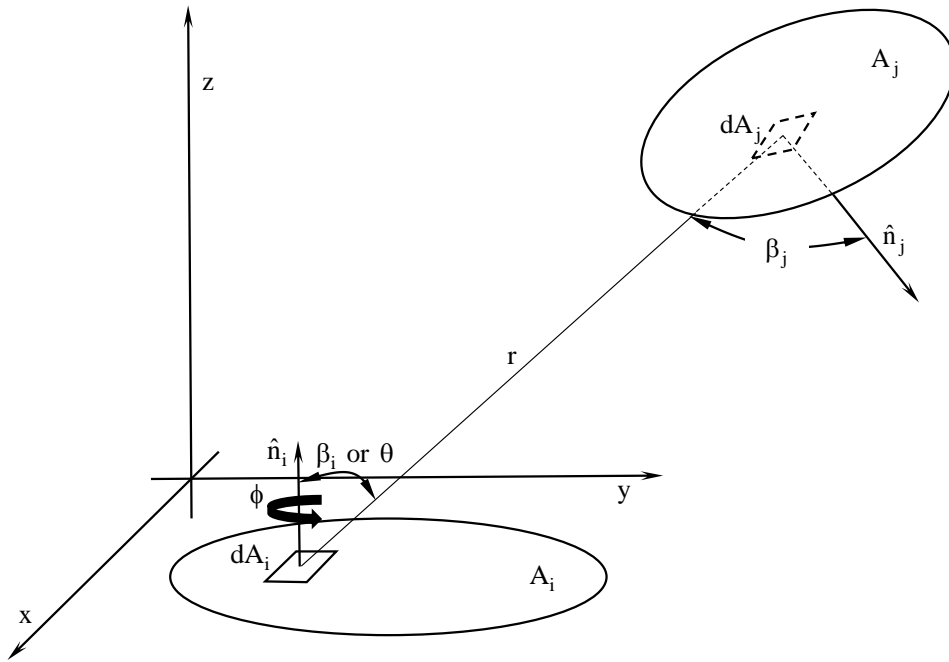$$A_i \, F_{A_i-A_j} = A_j \, F_{A_j-A_i} \qquad (1.27)$$

Figure 1.7. The general relative position of two finite areas A_i and A_j for the calculation of $F_{A_i-A_j}$.

Through the years, the engineering community has developed many expressions for calculating the view factor in geometric situations of practical interest based on Eq. (1.26). Heat transfer books and radiation technical literature make those expressions available in tabular form [22, 25]. However, for novel structures, it will be necessary to calculate the appropriate view factors between the interacting surfaces in the enclosure to obtain the radiation net heat transfer rates in each of them.

An important result of the definition of the view factor and of the first law of thermodynamics (conservation of energy) is known as the **view factor conservation** in an enclosure with n surfaces as the one shown in Fig. 1.5. The following expression summarizes the concept:

$$F_{A_i-A_1} + F_{A_i-A_2} + \cdots + F_{A_i-A_i} + \cdots + F_{A_i-A_n} = 1 \text{ or } \sum_{k=1}^{n} F_{A_i-A_k} = 1 \tag{1.28}$$

Next, assuming gray surfaces (diffuse emitted and reflected radiation; opaque surface, $\tau_i = 0$, and $\varepsilon_i = \alpha_i$) in the enclosure of Fig. 1.5 so that $\rho_i = 1 - \varepsilon_i$, the analysis proceeds with the calculation of the radiosity in each surface, as follows:

$$B_i = \varepsilon_i \sigma T_i^4 + (1 - \varepsilon_i)\, H_i \tag{1.29}$$

Combining Eqs. (1.24) and (1.29), and with some algebra, surface i net heat transfer rate is given by

$$\dot{Q}_i = A_i \frac{\varepsilon_i}{1-\varepsilon_i}(\sigma T_i^4 - B_i) \tag{1.30}$$

Equation (1.30) relates $\dot{Q}_i$ and T_i for all surfaces. Therefore, the method allows for the calculation of all surfaces radiation net heat transfer rates as functions of the surfaces temperatures, as follows:

i) Derive an expression for the incident radiation on each surface:

$$A_i H_i = B_1 A_1 F_{A_1-A_i} + B_2 A_2 F_{A_2-A_i} + \cdots + B_i A_i F_{A_i-A_i} + \cdots + B_n A_n F_{A_n-A_i}$$

$$A_i H_i = \sum_{j=1}^{n} B_j A_j F_{A_j-A_i} \tag{1.31}$$

and using Eq. (1.27), i.e., the reciprocity relation, the result is

$$H_i = \sum_{j=1}^{n} B_j F_{A_i-A_j} \tag{1.32}$$

ii) Substitute Eq. (1.32) in Eq. (1.29) to obtain

$$B_i = \varepsilon_i \sigma T_i^4 + (1 - \varepsilon_i) \sum_{j=1}^{n} B_j F_{A_i-A_j} \tag{1.33}$$

which is a linear system of n equations to be solved for n unknowns, i.e., n radiosities, B_i.

iii) The last step is the calculation of the n radiation net heat transfer rates, $\dot{Q}_i$, based on the calculated B_i, using Eq. (1.30).

Alternatively, all n temperatures could be evaluated as functions of $\dot{Q}_i$ (Problem 1.2). Other possibility is to have a number of surfaces with $\dot{Q}_i$ as functions of T_i, and the remaining surfaces with T_i as functions of $\dot{Q}_i$.

In this section a brief description of the thermal radiation phenomena of radiation exchange between surfaces was presented. Also, thermal radiation could be diffuse, or directional, i.e., with a specific direction of propagation (specular or mirrorlike). Additionally, radiation energy either incident on or leaving from a surface could be split in two components of polarization. One component is polarized parallel and the other perpendicular to the incidence plane (plane that includes the incident ray and the surface normal). It is also useful to approximate radiation problems by defining wavelength bands (e.g., solar collectors or cavities). Finally, attention should be dedicated to radiant energy transfer within media that absorb, emit, and scatter thermal radiation, i.e., the medium around the system under analysis participates of the radiation transfer processes, which could and commonly occur in combination with the other modes of heat transfer (conduction and convection), such as in atmospheric phenomena that are of paramount importance in biological and engineering problems. The physical details of such aspects could be found in the prolific thermal radiation technical literature [21, 22, 26].

Example 1.2) Consider the solar collector and water storage tank system shown in Fig. 1.8. What is the radiation net heat transfer rate on the collector surface exposed to the sun, $\dot{Q}_c$, as a function of the collector temperature, T_c, and system operating and design parameters? In the analysis, assume that the heat loss by convection on the collector surface is negligible in comparison to $\dot{Q}_c$. Derive mathematical expressions to calculate the water temperature in the tank, T_t, when water is not being consumed, and the collector (or serpentine) water output temperature, $T_{sp} = T_c$, based on sun exposed collector area, A_c, radiation heat flux, $\dot{I}$, collector emissivity, ε_c, ambient (or sky) temperature, T_0, collector water mass flow rate, $\dot{m}_{sp}$, liquid water specific heat, c_w, tank walls global heat transfer coefficient, U, and tank walls heat transfer area, A_t.

Solution

i) Based on Fig. 1.6, using the gray surface model, Eq. (1.24), Kirchhoff's law, and considering surface i as the collector surface, the collector net radiation heat transfer rate is calculated as follows:

$$\frac{\dot{Q}_c}{A_c} = H_c - \underbrace{\left[\varepsilon_c \sigma T_c^4 + (1-\varepsilon_c)H_c\right]}_{B_c} = \varepsilon_c\left(H_c - \sigma T_c^4\right)$$

$$\frac{\dot{Q}_c}{A_c} = \varepsilon_c \left(\dot{I} + \sigma T_0^4 - \sigma T_c^4 \right)$$

$$\dot{Q}_c = \left\{ \alpha_c \dot{I} - \varepsilon_c \sigma \left(T_c^4 - T_0^4 \right) \right\} A_c$$
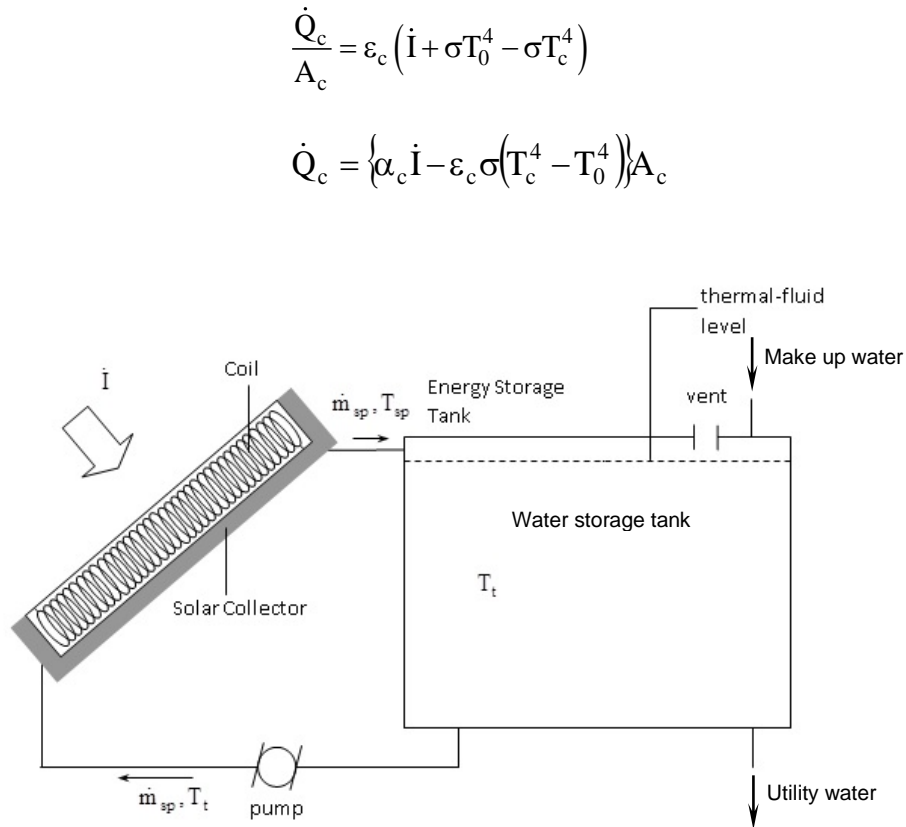

Figure 1.8. Schematic diagram of a solar collector and water storage tank system.

ii) A balance of energy in the solar collector shown in Fig. 1.8 states that:

$$\dot{Q}_c + \dot{m}_{sp} c_w T_t = \dot{m}_{sp} c_w T_c$$

$$\dot{Q}_c = \dot{m}_{sp} c_w (T_c - T_t)$$

iii) A balance of energy in the water storage tank shown in Fig. 1.8 states that:

$$UA_t (T_0 - T_t) + \dot{m}_{sp} c_w (T_c - T_t) = 0$$

therefore

$$T_t = \frac{UA_t T_0 + \dot{m}_{sp} c_w T_c}{\dot{m}_{sp} c_w + UA_t}$$

iv) Combining i) and ii), T_t and T_c are related as follows:

$$\left\{ \alpha_c \dot{I} - \varepsilon_c \sigma \left(T_c^4 - T_0^4 \right) \right\} A_c = \dot{m}_{sp} c_w (T_c - T_t)$$

v) Therefore, combining iii) and iv), T_c is determined by the following nonlinear equation:

$$f(T_c) = \left\{ \alpha_c \dot{I} - \varepsilon_c \sigma \left(T_c^4 - T_0^4 \right) \right\} A_c - \dot{m}_{sp} c_w \left\{ T_c - \frac{UA_t T_0 + \dot{m}_{sp} c_w T_c}{\dot{m}_{sp} c_w + UA_t} \right\} = 0$$

for a given set of operating and design parameters. After T_c is known, T_t is calculated through step iii).

Comment:
Note that, considering a set of operating and design parameters, a sensitivity (or parametric) analysis can be conducted to investigate their impact on resulting tank and collector temperatures (Problem 1.3). ∎

1.4.   THE SECOND LAW OF THERMODYNAMICS

Although the first law of thermodynamics allowed for understanding energy transformations and how to size engineering systems, scientists also noted that not all processes that comply with the energy conservation principle in fact are possible. For example, spontaneous processes are a special class of processes that happen in one particular direction, not in the inverse direction, although energy could be conserved.

The Joule expansion is a classic example in thermodynamics that consists of a thermally isolated container with two compartments separated by a valve (or partition). Initially, a volume of gas is maintained on one side and the other side is evacuated, then the valve is opened so that the gas flows to the other side filling the entire container. The gas internal energy is unaltered in the process. The inverse process would require compressing the gas from one side to the other, which would not happen spontaneously. Further, that would not lead to the original thermodynamic state, because compression would increase the gas internal energy. The return to the original state would only be possible by cooling the compartment, thus heating the surroundings irreversibly.

In all processes briefly discussed in the previous paragraph, energy was conserved, but the first law did not allow for the distinction between the processes that can happen from those that cannot. In simple cases, such as the spontaneous cooling of a hot body placed in contact with a colder environment, it is well known that the body would cool down to eventually reach equilibrium with the temperature of the surroundings, and the inverse process would not happen spontaneously, although the first law could be satisfied. However, when there is a combination of systems interacting energetically, a clear orientation is needed to predict what will result. For that, several scientists proposed the second law of thermodynamics as the principle to provide that guidance [12].

1.4.1. Thermodynamic reservoir

For a full understanding of the second law statements, initially, it is necessary to review the concept of a reservoir in thermodynamics. A reservoir is a particular system in which a specific property remains unchanged despite the energy interactions experienced with other surrounding systems, such as temperature, pressure, and concentration. If temperature remains constant, then it is defined as a thermal reservoir. For example, the planet's atmosphere, oceans, large metal blocks, pure substances undergoing a change of phase at constant temperature and pressure.

1.4.2. Irreversibility

Consider a system undergoing a process starting at a known thermodynamic state. The process is defined as **irreversible** if, after the process finishes, the system and the surroundings original states cannot be reestablished. Otherwise, the process is defined as **reversible**.

In the irreversible process, the system could return to its original state, but the surroundings state would no longer be its original state. Processes that include heat transfer from a hot to a cold body; unconstrained expansion of a gas or liquid; friction; electric resistance; plastic deformation, and other spontaneous events, are irreversible. In sum, all actual processes are irreversible.

There are four such processes that are of particular interest for the study of thermal machines: i) Heat transfer; ii) Friction (mechanical and fluid); iii) Throttling, and iv) Mixing.

i) Heat transfer: this is possibly the most paradoxical one. Essentially, heat transfer happens spontaneously from a higher to a lower temperature, which is the basis for one of the 2nd Law of thermodynamics statements proposed by Clausius [11, 12]. Work input would be necessary for heat transfer to occur from a lower to a higher temperature, such as in a heat pump, that is presented and discussed in Chapter 9. Note that, during a pure heat transfer process, no work is produced between the two temperature levels, and the potential work increases as the temperature gradient increases, thus the work loss increases as well. Hence, it is desirable to reduce temperature differences to a minimum across heat exchangers, but they cannot be zero, otherwise no heat transfer will occur. On the other hand, heat transfer rates by conduction, convection and radiation increase as temperature differences increase. As a result, a balance of such tradeoffs is mandatory for adequate heat exchanger design to avoid loss of efficiency in actual systems;

ii) Friction: for didactical purposes, friction is usually separated in mechanical and fluid. The former refers to heat dissipation caused by mechanical work done by rotating shafts and other moving parts (e.g., translational actuators). It is evident that the same amount of dissipated heat added to the component would not result in shaft rotation, i.e., the process is not reversible. Similarly, the expansion of a fluid in a cylinder or through a turbine experiences internal friction that dissipates a portion of the fluid energy that is therefore not transformed into work, whereas the fluid heats up, which in turn reduces the work output;

iii) Throttling: in this process a fluid expands from a high to low pressure location through a narrow opening (e.g., an orifice, a leakage from a high-pressure pipe). Since no work is done in the process and heat transfer is negligible, considering a control volume that encompasses the high (inlet) and low (outlet) pressure locations, the first law of thermodynamics for open systems, i.e., Eq. (1.11), and steady state operation, $\dfrac{\partial E_{CV}}{\partial t} = 0$, establishes that $h_{in} = h_{out}$, and shows that the process is isenthalpic, namely a Joule-Thompson expansion [13]. Clearly, the flow could not happen from the low to high pressure location, i.e., the process is irreversible, and potential work that could have resulted from the expansion through a piston or turbine indicates such loss (or irreversibility), which increases as the pressure gradient increases. However, throttling is necessary in some thermal machines components (e.g., refrigeration systems).

iv) Mixing: for several purposes, two or more fluids can be mixed, but cannot be unmixed without energy expenditure, therefore irreversible. The higher the temperature mismatch among streams, pressure and concentration gradients, the higher the loss of potential work that is brought by the participant fluids. Examples are the mixtures of fuel and air for combustion, and the mixture of absorbent and refrigerant fluids in heat driven refrigerators.

In the field of thermal machines, irreversibilities are usually classified as **external and internal**. The former happens across the system boundaries, e.g., in a power system, heat transfer at the high- and low-temperature ends, mechanical friction in rotating shafts, and electrical losses. The latter happens inside the system boundaries, mostly due to fluid friction in all components, throttling and mixing.

The effects that make real processes irreversible are termed **irreversibilities**. They are also known as nonidealities or thermodynamic losses, that make actual (irreversible) processes depart from reversible processes that establish the limit of ideal operation. Therefore, the quantification and possible minimization of such unavoidable effects is highly desirable in systems engineering design and operation.

1.4.3. Closed systems

In the history of thermodynamics, many experiments were conceived of systems operating cyclically in contact with one temperature reservoir. Examples are Rumford's experiments that linked the cannon-boring mechanical work to the continuous creation of heat, and Joule's measurements of the mechanical equivalent of heat [27]. Among the tested systems were paddles in a pool of water on one end of a vertical shaft with the other end in the air linked and spun by a rope driven by a weight which resulted in water temperature increase. All such experiments showed that the tested systems received work and rejected heat, never the opposite.

1.4.3.1. The 2nd Law of thermodynamics for a cycle

As a result of the experimental observations, Max Planck [28] and Lord Kelvin [12] in different moments proposed the following second law statement: "It is impossible to construct an engine which will work in a complete cycle and produce no effect except the raising of a weight and the cooling of a heat-reservoir", which would be the inverse of Joule's paddle wheel experiment.

Alternatively, Rudolf Clausius [11] proposed a statement of the second law as follows: "It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body".

In fact, the Clausius and Kelvin–Planck statements are equivalent. The demonstration by showing that the violation of each statement implies the violation of the other is proposed as an exercise (Problem 1.4).

Based on the Kelvin-Planck statement, the cycle net work should not be positive. Therefore, the 2nd Law of thermodynamics for a cycle in contact with one temperature reservoir reads as follows:

$$\oint \delta W \leq 0 \tag{1.34}$$

in which, the 1st Law of thermodynamics for the cycle states that:

$$\oint \delta W = \oint \delta Q \tag{1.35}$$

Therefore, the 2nd Law of thermodynamics for a cycle in contact with one temperature reservoir also stated that:

$$\oint \delta Q \leq 0 \qquad (1.36)$$

In a cycle, the system initial and end states are the same, and the equal sign in Eqs. (1.34) and (1.36) means that the net work and heat exchanged with the surroundings are equal to zero, thus both the system and the surroundings original states are the same. As a result, the equal sign in Eqs. (1.34) and (1.36) means that the cycle is **reversible**. When $\oint \delta W = \oint \delta Q < 0$, the inequality shows that system internal irreversibilities (e.g., friction) convert the work input into internal energy that is rejected by heat transfer to the surroundings, thus the cycle is **irreversible**.

Next, the analysis is extended to cycles operating in contact with two reservoirs. Historically, Sadi Carnot introduced the concept of the reversible cycle in 1824 [13] for a closed system while in communication with two temperature reservoirs. Carnot idealized a heat engine cycle that would be in perfect thermal contact with the two reservoirs, i.e., the heat engine extremities temperatures matched the two reservoirs temperatures. Such assumption implied in very large heat exchangers areas or infinitely slow processes to allow for thermal equilibrium. Hence, the Carnot cycle established the ceiling limit for the heat engine thermal efficiency.

The initial question to be answered is how the Kelvin–Planck statement affects the signs of the two heat transfer interactions of a general (reversible or irreversible) cycle (1), which is schematically shown in Fig. 1.9 (left). Without loss of generality, assume that $W_{(1)} > 0$ (heat engine), but a similar analysis could be done for $W_{(1)} < 0$ (Problem 1.5). There are three possible alternatives: i) $Q_I < 0$ and $Q_{II} < 0$; ii) $Q_I > 0$ and $Q_{II} > 0$, and iii) $Q_I \times Q_{II} < 0$, i.e., with opposite signs.
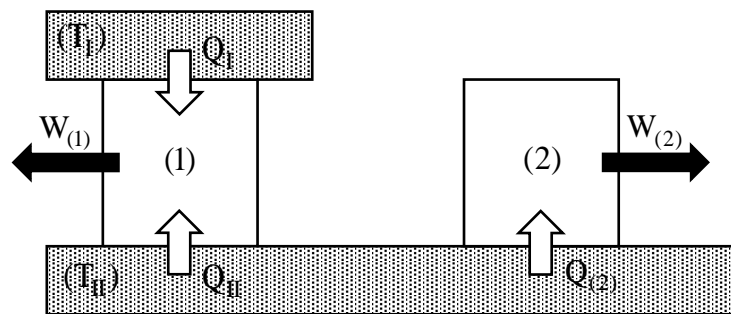

Figure 1.9. Schematic diagram of closed systems that execute a cycle in contact with two (left) and one (right) temperature reservoirs.

The 1st Law of thermodynamics for a cycle states that $Q_I + Q_{II} = W_{(1)}$. The first alternative, i.e., $Q_I < 0$ and $Q_{II} < 0$, leads to $W_{(1)} < 0$, which does not comply with the initial condition $W_{(1)} > 0$ (heat engine), thus it is ruled out.

Cycle (2) in Fig. 1.9 (right) is also assumed to be general (reversible or irreversible), and in contact with only one thermal reservoir, therefore $Q_{(2)} \leq 0$, according to Eq. (1.36). The thermal reservoirs in Fig. 1.9 only exchange heat, and one possibility is to assume that $Q_{II} = -Q_{(2)}$, since $Q_{II} > 0$ in the second alternative. Hence, the (T_{II}) reservoir operates

cyclically, according to the 1st Law of thermodynamics for a cycle, since $Q_{II} + Q_{(2)} = 0$. In conclusion, cycles (1), (2) and (T_{II}) together operate cyclically in contact with the (T_I) thermal reservoir, thus the 2nd Law of thermodynamics for a cycle in contact with one temperature reservoir, Eq. (1.36), establishes that $Q_I \leq 0$, then the second alternative is also ruled out.

As a result, the analysis demonstrated that the third alternative is the only one that complies with the 2nd Law of thermodynamics. In sum, for a system to operate cyclically in contact with two thermal reservoirs, Q_I and Q_{II} must have opposite signs, i.e., $Q_I \times Q_{II} < 0$. Hence, in any system executing a power cycle in contact with two temperature reservoirs, only a portion of the absorbed heat from the hot reservoir is converted to work, and the other part has to be rejected to the cold reservoir, indicating that the thermal efficiency must be less than 100%. Note that this conclusion was obtained without any consideration regarding the cycle internal processes (ideal or not), and substances in the system (e.g., working fluid), therefore applies to all power cycles. Well before the Kelvin-Planck and Clausius statements of the 2nd Law of thermodynamics, Sadi Carnot postulated that all power cycles absorb heat, but must also reject heat to a heat sink, thus efficiency is below 100% [29].

Next, in the schematic diagram shown in Fig. 1.10, two closed systems are drawn, on the left a general cycle (reversible or irreversible) and on the right a Carnot cycle (reversible). The two cycles are in contact with the same two temperature reservoirs, (T_I) and (T_{II}). Let $Q_I > 0$ and $Q_{II} < 0$, since $W \neq 0$ is also assumed. Accordingly, one possible configuration for the Carnot cycle is to take $Q_I + Q_{IC} = 0$. Hence, the (T_I) temperature reservoir operates cyclically, so that cycles (1), (C) and (T_I) together operate cyclically in contact with (T_{II}) thermal reservoir, thus the 2nd Law of thermodynamics for a cycle in contact with one temperature reservoir, Eq. (1.36), establishes that

$$Q_{II} + Q_{IIC} \leq 0 \tag{1.37}$$

Rearranging Eq. (1.37) and dividing by $Q_I = -Q_{IC}$ which are positive numbers, the following result is obtained:

$$\frac{-Q_{II}}{Q_I} \geq \frac{Q_{IIC}}{-Q_{IC}} \quad \text{or} \quad \frac{-Q_{II}}{Q_I} \geq \left(\frac{-Q_{II}}{Q_I}\right)_{rev} \tag{1.38}$$

from which, it is concluded that the positive ratio $\dfrac{-Q_{II}}{Q_I}$ of the general cycle (reversible or irreversible) cannot be smaller than the positive ratio $\left(\dfrac{-Q_{II}}{Q_I}\right)_{rev}$ of the reversible cycle that operates in contact with two temperature reservoirs. Such limiting case is defined by the equal sign in Eq. (1.38).

In fact, the inequality shown in Eq. (1.38) is the 2nd Law of thermodynamics for a cycle in contact with two temperature reservoirs. As it was discussed previously in the text, the smallest limiting value for the positive ratio $\left(\dfrac{-Q_{II}}{Q_I}\right)_{rev}$ was obtained without any consideration regarding the cycle internal processes, and substances in the system (e.g., working fluid), thus

is only a function of the temperatures of the two separate and distinct thermal reservoirs, (T_I) and (T_{II}), as follows:

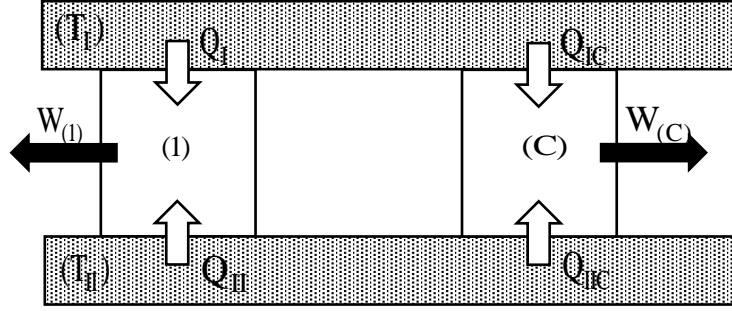$$\left(\frac{-Q_{II}}{Q_I}\right)_{rev} = f(T_I,\ T_{II}) \tag{1.39}$$

Figure 1.10. Schematic diagram of closed systems that execute a cycle in contact with two temperature reservoirs: left – general (reversible or irreversible), and right – ideal (reversible).

Although Eq. (1.39) reveals that $\left(\dfrac{-Q_{II}}{Q_I}\right)_{rev}$ depends only on T_I and T_{II}, $f(T_1,\ T_2)$ is not known. However, considering three distinct reservoirs, (T_I), (T_{II}) and (T_{III}), with $T_I > T_{II} > T_{III}$, two other closed systems could operate cyclically between (T_I) and (T_{III}) with $Q_I > 0$ and $Q_{III} < 0$, and (T_{II}) and (T_{III}) with $-Q_{II} > 0$ and $Q_{III} < 0$. In like manner to Eq. (1.39), for the newly proposed two cycles it is possible to write:

$$\left(\frac{-Q_{III}}{Q_I}\right)_{rev} = f(T_I,\ T_{III})\ \text{and}\ \left(\frac{-Q_{III}}{-Q_{II}}\right)_{rev} = f(T_{II},\ T_{III}) \tag{1.40}$$

In Eq. (1.40), note that dividing the first by the second equation, $\left(\dfrac{-Q_{II}}{Q_I}\right)_{rev}$ is obtained, which is combined with Eq. (1.39). The result is as follows:

$$\left(\frac{-Q_{II}}{Q_I}\right)_{rev} = f(T_I,\ T_{II}) = \frac{f(T_I,\ T_{III})}{f(T_{II},\ T_{III})} \tag{1.41}$$

Since $\left(\dfrac{-Q_{II}}{Q_I}\right)_{rev}$ does not depend on T_{III}, then $f(T_I,\ T_{II})$ is given by:

$$f(T_I,\ T_{II}) = \frac{g(T_I)}{g(T_{II})} \tag{1.42}$$

Noting that Q_I and Q_{II} are the heat exchanges with (T_I) and (T_{II}) reservoirs, respectively, the functions $\phi(T_I) = g^{-1}(T_I)$ and $\phi(T_{II}) = g^{-1}(T_{II})$ are utilized instead of $g(T_I)$ and $g(T_{II})$. Therefore, Eq. (1.39) is rewritten as follows:

$$\left(\frac{-Q_{II}}{Q_I}\right)_{rev} = \frac{\phi(T_{II})}{\phi(T_I)} \text{ or } \left(\frac{-Q_{II}}{Q_I}\right)_{rev} = \frac{T_{II}}{T_I} \tag{1.43}$$

Equation (1.43) is the foundation of the Kelvin and Rankine scales, i.e., a thermodynamic temperature scale, $T \equiv \phi$, which does not depend on any substance properties. Thus, any two temperatures ratio on the Kelvin or Rankine scales is equal to the two heat exchanges at those temperatures ratio, in a closed system executing a reversible cycle in contact with the two thermal reservoirs. Hence, for the Kelvin or Rankine scales, Eq. (1.43) can be generalized with respect to a reference heat reservoir that absorbs Q_0 at T_0 as follows:

$$T = T_0 \left(\frac{Q}{Q_0}\right)_{rev} \tag{1.43}$$

in which $Q = -Q_{II} > 0$ and $Q_0 = Q_I > 0$ are positive numbers, as stated previously in the text. Since $Q > 0$, and the constant T_0 was assigned the value 273.16 K (Kelvin scale) to the temperature at the triple point of water, and 491.69 R (Rankine scale) [30], $T > 0$. The constant T_0 is the temperature at which water in the solid, liquid, and vapor phases are in equilibrium. As $Q \to 0$, $T \to 0$, which is called absolute zero, i.e., the lowest T value in both the Kelvin and Rankine absolute temperature scales.

Finally, combining Eq. (1.43) and Eq. (1.38), the 2nd Law of thermodynamics for a cycle executed by a closed system in contact with two temperature reservoirs is rewritten using the concept of the thermodynamic temperature scale, as follows:

$$\frac{Q_I}{T_I} + \frac{Q_{II}}{T_{II}} \leq 0 \tag{1.44}$$

Similarly, for a cycle executed by a closed system in contact with one temperature reservoir, using Eq. (1.36), replacing the heat transfer integral by Q_I, and dividing by the absolute temperature of the thermal reservoir, the result is given by:

$$\frac{Q_I}{T_I} \leq 0 \tag{1.45}$$

By means of mathematical induction, for a closed system in contact with N temperature reservoirs, it is possible to write:

$$\frac{Q_I}{T_I} + \frac{Q_{II}}{T_{II}} + \frac{Q_{III}}{T_{III}} + \cdots + \frac{Q_N}{T_N} \leq 0 \text{ or } \sum_{k=1}^{N} \frac{Q_k}{T_k} \leq 0 \tag{1.46}$$

Next, an infinite number of thermal reservoirs in contact with the closed system, $N \to \infty$, and with each boundary point crossed by a heat transfer exchange δQ is considered. As a result, for a continuous variation of the system boundary temperature, Eq. (1.46) is rewritten as follows [13]:

$$\oint \frac{\delta Q}{T} \leq 0 \tag{1.47}$$

which is known as Clausius inequality [15, 31].

The equal sign in Eq. (1.47) accounts for reversible cycles, following the same reasoning presented after Eq. (1.38), so that:

$$\oint \frac{\delta Q_{rev}}{T} = 0 \tag{1.48}$$

Recall that a cycle is a special process that starts and ends in the same thermodynamic state, thus for any property, such as temperature, for example, $\oint dT = 0$. Hence, the function revealed by Eq. (1.48) could be understood as a thermodynamic property as follows:

$$dS = \frac{\delta Q_{rev}}{T} \tag{1.49}$$

which was named entropy, S, by Clausius in 1865, noting that Rankine proposed the name thermodynamic function in his previous work [13].

1.4.3.2. The 2nd Law of thermodynamics for a process

Consider a general process from state 1 to state 2, the change in the property entropy is calculated by integrating Eq. (1.49) from state 1 to state 2 as follows:

$$S_2 - S_1 = \int_1^2 dS = \int_1^2 \frac{\delta Q_{rev}}{T} \tag{1.50}$$

Next, consider the cycle showed in Fig. 1.11, with an irreversible and a reversible process, for paths $1 \to 2$, and $2 \to 1$, respectively. Applying Eqs. (1.49) and (1.50), the result is as follows:

$$\oint \frac{\delta Q}{T} = \int_1^2 \frac{\delta Q}{T} + \int_2^1 \frac{\delta Q_{rev}}{T} \leq 0 \tag{1.50}$$

$$S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T} \tag{1.51}$$

In Equation (1.50), the value of the first term on the left hand side of the inequality depends on the path of process $1 \to 2$, therefore it is not a property and was named **entropy transfer** [13], which is always smaller than the entropy change, $S_2 - S_1$, as shown in Eq. (1.51), i.e., the second law of thermodynamics for a process. Rearranging the terms in Eq. (1.51), the

entropy generation or entropy production, S_{gen}, appears as a quantity that is always positive, as follows:

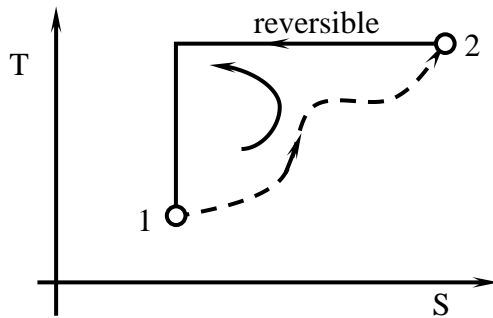$$S_{gen} = S_2 - S_1 - \int_1^2 \frac{\delta Q}{T} \geq 0 \qquad (1.52)$$

Figure 1.11. Illustrative temperature versus entropy diagram of a closed system that executes a cycle between states 1 and 2, with $1 \to 2$ being an irreversible process, and $2 \to 1$ a reversible process.

Note that the entropy generation of a process allows for measuring the distance that any real (irreversible) process $1 \to 2$ is from the corresponding ideal (reversible) one. In fact, Eq. (1.52) is the most popular form of the second law of thermodynamics for a closed system executing a process, and gave the foundation for scientists and engineers to propose the method of entropy generation minimization for engineering systems [32].

Example 1.3) Consider a chemical reactor closed system. Based on the second law of thermodynamics for a closed system, state the physical condition for a chemical reaction to occur spontaneously.

Solution

Assume that state 1 is the instant when the reactor is fed with reactants, and state 2 is the instant when the spontaneous reaction is completed and the products are fully formed. No work is done, and the heat of reaction, $\Delta H = H_2 - H_1$ (enthalpy of products minus enthalpy of reactants), accounts for the total heat exchanged in the process, then Eq. (1.52) states that:

$$\underbrace{S_2 - S_1}_{\Delta S} - \frac{\Delta H}{T} \geq 0$$

or multiplying by T

$$\Delta G = \Delta H - T\Delta S \leq 0$$

where ΔG is the reaction Gibbs free energy change that must be negative for the reaction to happen spontaneously, since the process is irreversible. ∎

1.4.4. Open systems

The derivation of the second law of thermodynamics for an open system executing a process follows similar steps of the same derivation presented in section 1.3.2. for the first law. Therefore, based on the process from t to $t+\Delta t$ of a closed system which is transformed into an open system (or control volume) as follows:

$$S_{closed}(t) = S_{open}(t) + \Delta S_{in} = S_{open}(t) + (s\ \dot{m})_{in}\Delta t \tag{1.53}$$

$$S_{closed}(t+\Delta t) = S_{open}(t+\Delta t) + \Delta S_{out} = S_{open}(t+\Delta t) + (s\ \dot{m})_{out}\Delta t \tag{1.54}$$

The entropy generated in the process for t to $t+\Delta t$ is defined as ΔS_{gen} and calculated with Eq. (1.52), as follows:

$$\Delta S_{gen} = S_{open}(t+\Delta t) - S_{open}(t) - \frac{\dot{Q}}{T}\Delta t + (\dot{m}s)_{out}\Delta t - (\dot{m}s)_{in}\Delta t \geq 0 \tag{1.55}$$

Finally, dividing Eq. (1.55) by Δt, taking the limit when $\Delta t \rightarrow 0$, assuming n heat transfer interactions, with n_{out} outlets and n_{in} inlets, for the control volume shown in Fig. 1.2, the following result is obtained:

$$\dot{S}_{gen,CV} = \frac{dS_{CV}}{dt} - \sum_{i=1}^{n}\frac{\dot{Q}_i}{T_i} + \sum_{i=1}^{n_{out}}(\dot{m}s)_i - \sum_{i=1}^{n_{in}}(\dot{m}s)_i \geq 0 \tag{1.56}$$

1.5. EXERGY ANALYSIS

In section 1.4, it was argued that the first law did not allow for the distinction between the processes that can happen from those that cannot, mainly for a combination of systems interacting energetically. The second law of thermodynamics was then proposed to fulfill such a need. Hence, it makes sense to couple the first and second law analyses aiming at realistic mechanical system design. As a result, the combination of the first and second law of thermodynamics allows for the definition of a physical quantity named **exergy**, which is capable of evaluating the maximum useful work produced by a system that undergoes an ideal process from a given thermodynamic state to a state of equilibrium with the environment, i.e., with no entropy generation. Hence, exergy and energy have the same units, but it is essential to distinguish the two concepts. Traditional engineering methods use only energy for system design. Energy flows in and out of a system through mass flow, heat transfer and work, and is conserved. Exergy is a completely different concept.

Quantitatively, exergy represents the ability to do work - the useful work content - of various streams (mass, heat, work) flowing through the system. As a result, exergy allows common-based comparison of interactions that are quite different in a physical sense. An important benefit is that by considering the exergy currents into and out of the system, it is possible to determine the extent to which the system **destroys** exergy. Therefore, in any process, **exergy** is always destroyed, partially or totally (2nd law of thermodynamics). In sum, exergy is a measure of the departure of a given state with respect to the ambient state.

In a closed system, the nonflow exergy, Ξ, of a mass is given by:

$$\Xi = E - E_0 - T_0(S - S_0) + P_0(V - V_0) \tag{1.57}$$

where subscript 0 refers to the ambient state, also known as the restrict dead state [13, 32].

Next, considering the control volume shown in Fig. 1.2, it should be noted that $\dot{Q}_{CV}$ represents the net heat transfer rate across the system boundary, so that, it could be split into n possible heat transfer interactions, one of them being $\dot{Q}_0$, the heat transfer rate with the ambient temperature reservoir at T_0. Note also that the system volume could vary due to the interaction with the ambient, either doing work on (volume increase) or receiving work (volume decrease) from the environment, $P_0\,dV/dt$. To obtain the useful work (or exergy) rate produced by the system, $\dot{E}_W$, Eq. (1.10) – 1st law should be added to Eq. (1.56) – 2nd law multiplied by T_0. Note that $\dot{Q}_0$ cancels out in the process. The end result is as follows [13]:

$$\dot{E}_W = \dot{W}_{CV} - P_0\frac{dV}{dt} = -\frac{d\left(E - T_0 S + p_0 V\right)}{dt} + \sum_{i=1}^{n}\dot{E}_{Q_i} + \sum_{in}\dot{m}\,e_x - \sum_{out}\dot{m}\,e_x - T_0\,\dot{S}_{gen} \quad (1.58)$$

in which, the first term after the second equal sign is the CV accumulation of nonflow exergy, the second term the heat transfer exergy rate with $\dot{E}_{Q_i} = \left(1 - \dfrac{T_0}{T_i}\right)\dot{Q}_i$, the third term the flow exergy input rate, the fourth term the flow exergy output rate, the fifth term the destroyed exergy rate $\dot{E}_D = T_0\,\dot{S}_{gen}$, and $e_x = (h + v^2/2 + gz) - (h + v^2/2 + gz)_0 - T_0(s - s_0)$ the specific flow exergy, J kg^{-1}, with respect to the ambient.

From Equation (1.58) it is now possible to evaluate the maximum useful work that could be produced by the system. That would happen when the system undergoes an ideal process, i.e., when it is reversible, so that Eq. (1.58) delivers $\left(\dot{E}_W\right)_{rev}$. In such case, $\dot{S}_{gen} = 0$, and the fifth term after the second equal sign in Eq. (1.58) is also zero, $\dot{E}_D = T_0\,\dot{S}_{gen} = 0$, i.e., no exergy destruction rate.

Example 1.4) For a power plant steady flow operation with the classical Rankine cycle between a high temperature T_H and the ambient at T_0, derive expressions to evaluate the exergy destruction rate in each of the four components (boiler, turbine, condenser and pump). Consider states 1 (pump inlet/condenser outlet), 2 (boiler inlet/pump outlet), 3 (turbine inlet/boiler outlet) and 4 (condenser inlet/turbine outlet). The pumping power, input heat transfer rate, turbine power and heat rejection rate to the ambient are $\dot{W}_p$, $\dot{Q}_H$, $\dot{W}_t$, and $\dot{Q}_0$, respectively, and assumed to be positive numbers for simplicity in this example with each component processing a single water stream $\dot{m}_w$.

Solution

The steady flow exergy destruction rate in each component is obtained from Eq. (1.58) by making $d\left(E - T_0 S + p_0 V\right)/dt = 0$ (no variations with respect to time), as follows:

1. Boiler:

$0 = \dot{E}_{Q_H} + \dot{m}_w \, (e_{x,2} - e_{x,3}) - \dot{E}_{D,boiler}$, which is rewritten to show that

$\dot{E}_{D,boiler} = \dot{E}_{Q_H} + \dot{m}_w \, (e_{x,2} - e_{x,3})$

2. Turbine:

$\dot{E}_{W_t} = \dot{W}_t = \dot{m}_w \, (e_{x,3} - e_{x,4}) - \dot{E}_{D,turbine}$, which is rewritten to show that

$\dot{E}_{D,turbine} = \dot{m}_w \, (e_{x,3} - e_{x,4}) - \dot{W}_t$

3. Condenser:

$0 = \dot{m}_w \, (e_{x,4} - e_{x,1}) - \dot{E}_{D,condenser}$, which is rewritten to show that

$\dot{E}_{D,condenser} = \dot{m}_w \, (e_{x,4} - e_{x,1})$

4. Pump:

$\dot{E}_{W_p} = -\dot{W}_p = \dot{m}_w \, (e_{x,1} - e_{x,2}) - \dot{E}_{D,pump}$, which is rewritten to show that

$\dot{E}_{D,pump} = \dot{m}_w \, (e_{x,1} - e_{x,2}) + \dot{W}_p$

Comments:

1. In the pump, exergy is supplied to the circuit as pump power, so that the input flow exergy, $\dot{m}_w e_{x,1}$, is increased to enter the boiler. However, the power to pump an incompressible liquid is small, thus its exergy destruction rate, being negligible in comparison to the turbine exergy destruction rate;

2. The power plant exergy input rate is $\dot{E}_{Q_H} = \left(1 - \dfrac{T_0}{T_H}\right)\dot{Q}_H$ and the net exergy output rate is

$\dot{W}_t - \dot{W}_p$, so that the plant second law (or rational) efficiency is $\eta_{II} = \dfrac{\dot{W}_t - \dot{W}_p}{\dot{E}_{Q_H}}$, and

3. Each component destroyed exergy rate allows for the establishment of an irreversibility ranking among the cycle components. As a result, exergy analysis pinpoints which part of a global system requires improvement so that global efficiency is augmented. ∎

Since there are no possible ideal process in the universe, the maximum useful work that could be produced by the system will never be achieved. However, it is reasonable to state that the best possible system would be the one in which the exergy destruction is minimum, namely, the "unavoidable exergy destruction". Therefore, in practice, systems that operate destroying more exergy than they could, at the unavoidable exergy destruction level, represent the waste of exergy sources, such as from oil, natural gas, coal.

In sum, exergy analysis allows for finding ways to avoid exergy destruction. For that, the method determines the location, type, and "true" magnitude of wasted fuel resources.

The strategy is to search for the optimum allocation of resources and efforts. The method consists of minimizing exergy destruction or irreversibility. In modern thermodynamics, the method is known as Entropy Generation Minimization (EGM), or Thermodynamic

Optimization (TO) [5, 13, 32], through the combination of thermodynamics with principles of heat transfer, fluid mechanics, and other transport phenomena. Thermal machines and any other real device or installation could then be mathematically modeled and optimized by: i) Elaborating a realistic model that includes detailed geometric (design) and operating parameters; ii) Writing the system or process entropy generation rate (objective function) equation as a function of all parameters, and iii) Minimizing entropy generation with respect to one or more parameters of interest. Several physical or general constraints need to be recognized and established for the strict optimization problem formulation [33], e.g., finite sizes, finite periods, material types, shapes.

The following chapters in this book discuss and apply the methodology to thermal machines. Additionally, the objective function that was selected in the previous paragraph as the entropy generation rate could be changed to other of specific interest for the analysis, or even other objective functions included in the optimization problem formulation to treat the problem as one of multi-objective optimization [34].

1.6. EXERGOECONOMIC ANALYSIS

The combination of exergetic analysis and economic principles, namely, exergoeconomic (or thermoeconomic) analysis was proposed to provide information not available through exergetic and economic analyses solely, but crucial to the design and operation of a physically and economically effective system [5]. In this section, the fundamentals of exergoeconomic analysis are presented and discussed.

The conventional economic analysis, also known as techno-economic analysis (TEA) [35], provides a methodology to predict how a product, service or process will succeed economically in the market. Capital cost, operating cost, and revenue are estimated according to technical and financial input parameters [5, 35], which are then varied using modeling and simulation to quantify their impact on economic performance through parametric analyses in graphs and diagrams.

The main goals of industrial cost accounting usually are: i) Finding the actual product or service cost; ii) Providing a rationale for products or services pricing; iii) Allocating and controlling expenses, and iv) Supplying reliable information for decision making. Steady state operation is usually utilized to formulate a system total cost balance as follows [5]:

$$\dot{C}_{P,tot} = \dot{C}_{F,tot} + \dot{Z}_{tot}^{CI} + \dot{Z}_{tot}^{OM} \tag{1.59}$$

in which $\dot{C}_{P,tot}$ is the product total, $\dot{C}_{F,tot}$ the fuel, $\dot{Z}_{tot}^{CI}$ the capital investment, and $\dot{Z}_{tot}^{OM}$ the operating and maintenance cost rates. Exergy containing streams (matter, power or heat transfer) cost rates are usually represented by $\dot{C}$, and $\dot{Z}$ all other cost rates. $\dot{Z}_{tot}^{CI}$ and $\dot{Z}_{tot}^{OM}$ are estimated based on the annual capital investment and operating/maintenance cost divided by the number of system operating hours (days or seconds) per year, respectively. In fact, usually, the capital investment and operating/maintenance costs are combined as follows:

$$\dot{Z} = \dot{Z}_{tot}^{CI} + \dot{Z}_{tot}^{OM} \tag{1.60}$$

1.6.1. Exergetic costs

Exergy measures the true thermodynamic value of matter and energy transfers into and out of a system. Costs must be associated with things that have value. Exergy is used as a basis

for assigning costs in thermal (or industrial) systems in general. The exergetic costs are defined starting from exergy transfer rates associated with system interactions, as follows:

$$\text{Matter flow rate: } \dot{E}_{in} \text{ (input) and } \dot{E}_{out} \text{ (output)} \qquad (1.61)$$

$$\text{Power: } \dot{W} \text{ and Heat transfer rate: } \dot{E}_{Q} \qquad (1.62)$$

$$\dot{C}_{in} = c_{in}\dot{E}_{in} = c_{in}(\dot{m}_{in} \; e_{in}) \; ; \; \dot{C}_{out} = c_{out}\dot{E}_{out} = c_{out}(\dot{m}_{out} \; e_{out}) \qquad (1.63)$$

$$\dot{C}_{W} = c_{W}\dot{W} \; ; \; \dot{C}_{Q} = c_{Q}\dot{E}_{Q} \qquad (1.64)$$

in which c_{in}, c_{out}, c_{W} and c_{Q} are the average costs per unit of exergy, $\$ \, kJ^{-1}$.

1.6.2. Assignment of exergetic costs

Cost balances for each component must be conducted. For the any (k^{th}) system component the sum of cost rates of all outgoing exergy streams equals the sum of cost rates of all incoming exergy streams plus capital investments and operating and maintenance expenses. For example, in a component that receives heat and generates power, the result is as follows:

$$\sum_{out}\dot{C}_{out,k} + \dot{C}_{w,k} = \dot{C}_{q,k} + \sum_{in}\dot{C}_{in,k} + \dot{Z}_{k} \qquad (1.65)$$

in which the total cost of the outgoing exergy currents is equal to the total expenditure to get these streams.

Equation (1.65) represent the exergetic costs account, and could be rewritten as follows:

$$\sum_{out}\left(c_{out}\dot{E}_{out}\right)_{k} + c_{w,k}\dot{W}_{k} = c_{q,k}\dot{E}_{q,k} + \sum_{in}\left(c_{in}\dot{E}_{in}\right)_{k} + \dot{Z}_{k} \qquad (1.66)$$

in which, subscript k refers to the system component k under analysis (control volume). In the analysis, it is assumed that all costs per unit of exergy entering the system are known, and the unknowns are the output costs (matter, power or heat).

In Equation (1.66), all terms must be positive. Ex: compressor, the work would pass to the right hand side, or if the component rejects heat to the environment, the term would go to the left hand side (remember the thermodynamic sign conventions).

(IN PREPARATION FROM HERE TO THE END!)

Example 1.5) ANÁLISE EXERGOECONÔMICA DE UM INCINERADOR DE RESÍDUOS SÓLIDOS URBANOS (RSU) – COMPLETA.

Solution
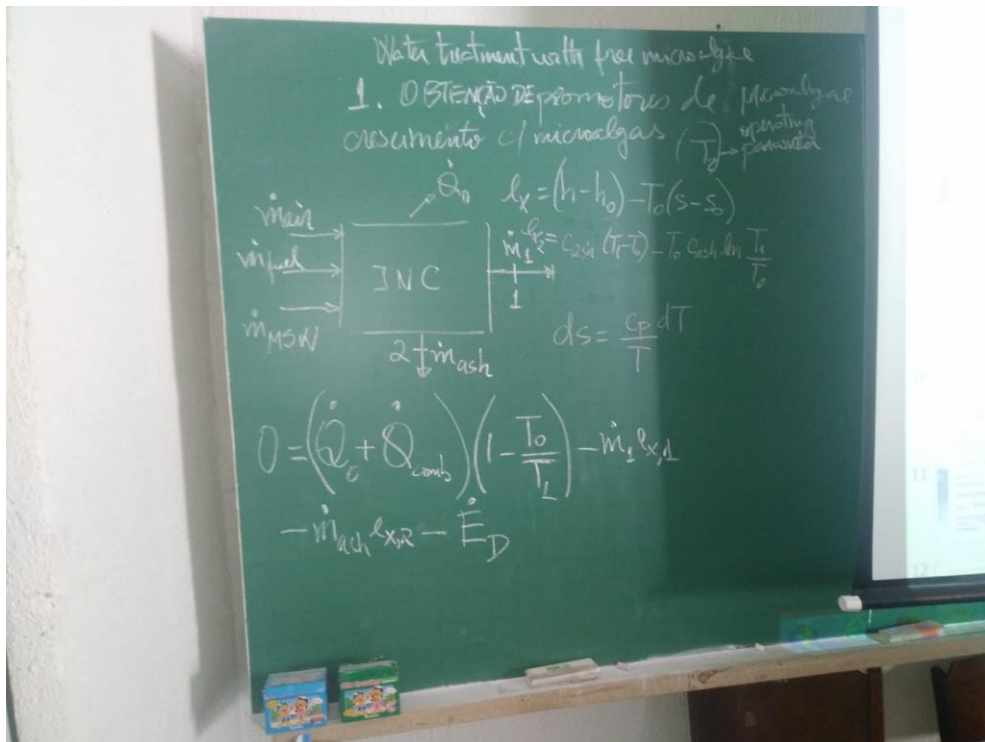
/* Incinerador
****

Hipóteses:

1. Regime permanente
2. Rejeição de calor desprezível, variações de energia cinética e potencial desprezíveis
3. Perdas de carga desprezíveis nas tubulações
4. Produtos da combustão podem ser modelados como ar sendo gás ideal

Análise:

*/

// balanço de massa

z = 1 // fracao molar CH4

x = 0 // fracao molar diesel

y = 0.5 // fracao molar MSW

ndotmsw = 0.5/3600 // kmol de msw/s

ndotch4 = (1 - y) * (1 - x) * z * (ndotch4 + ndotmsw) // kmol de ch4/s

M_CH4 = 16 // Mol de CH4 - kg/kmol

M_msw = 99.72 // Mol de RSU - kg/kmol

rac = 17.24

mdot1 = mdotch + mdotar - mdot2 // kg/s

mdotar = rac * mdotch // kg/s

mdotch4 = ndotch4 * M_CH4 // CH4 mass flow rate - kg/s

mdotmsw = ndotmsw * M_msw // MSW mass flow rate - kg/s

mdotch = mdotch4 + mdotmsw // hybrid fuel mass flow rate - kg/s

mdot2 = 0.04*mdotmsw

// poder calorifico inferior do RSU

LHVmsw = 1300 * 4.189 // kJ/kg

// poder calorifico inferior do CH4

LHVch4 = 11940 * 4.189 // kJ/kg

qcomb = mdotmsw * LHVmsw + mdotch4 * LHVch4

// Balanço de energia

// q0 = 0

- q0 + qcomb = Wdot_fan + mdot1 * hprod + mdot2 * c_ash * T1 // 1a Lei Termodinamica

c_ash = 0.73 // calor específico da cinza kJ/(kg.K)

T1 = T_h("Air", hprod)

// condicoes ambientais

T0 = 298 // K

// Dimensionamento do incinerador

hext = 1 // coef conv natural externa

hint = 500 // coef conv forcada e radiacao interna

tp = 0.1 // m - espessura de parede isolada

kiso = 1 // W/mK - condutividade isolante

D = 1 // m - diametro do incinerador

// pi = 3.14159

// hinc = 2 // m - altura do incinerador

uinv = 1/hext + tp/kiso + 1/hint

u = 1/uinv // W/m2K - coef global transf calor

area = pi * D * D / 2 + pi * D * hinc

q0 = u * area * (T1 - T0) / 1000 // perda de calor

V_inc = pi * D * D * hinc / 4 // Volume do incinerador - m3

V_inc = 1.571 // Volume fixo do incinerador - m3

// Analise exergetica do incinerador

h0_air = h_T("Air",T0)

sprod = s_Tp("Air",T1,p1)

p0 = 1.01325 // bar

p1 = p0 // bar

Delta_p = (p1 - p0) * 1e5 // Air pressure rise (N/m2)

rho_air = 1.225 // air density @ 25 oC (kg/m3)

Wdot_fan = - (mdotar * Delta_p / rho_air) / 1e3 // Fan power (kW)

s0 = s_Tp("Air",T0,p0)

ex1 = (hprod - h0_air) - T0 * (sprod - s0) // exergia específica dos produtos da combustão

ex2 = c_ash * (T1 - T0) - T0 * (c_ash * LN(T1/T0)) // Ash spec exergy (kJ/kg)

Edot1 = mdot1 * ex1 // Incinerator products exergy rate (kW)

Edot2 = mdot2 * ex2 // Incinerator ashes exergy rate (kW)

Edot_qinc = (-q0 + qcomb) * (1 - T0/T1) // Fuel input exergy rate (kW)

Wdot_fan = Edot_qinc - Edot1 - Edot2 - ED_inc // Calculate destroyed exergy rate by the incinerator (kW)

// Analise termoeconomica

// First, evaluate exergetic costs (R$/kJ)

c_ch4_m3 = 4.50 // natural gas cost (R$/m3)

rho_ch4 = 0.657 // NG density (kg/m3)

c_ch4_kg = c_ch4_m3/rho_ch4 // NG cost (R$/kg)

fm_ch4 = mdotch4 / mdotch // NG mass fraction in the fuel (kg_ch4/kg_fuel)

fm_MSW = 1 - fm_ch4 // MSW mass fraction in the fuel (kg_MSW/kg_fuel)

c_ch4 = c_ch4_kg / LHVch4 // NG exergetic cost (R$/kg)

c_msw_kg = - 3.5 // MSW treatment cost (R$/kg)

c_msw = c_msw_kg / LHVmsw // MSW exergetic cost (R$/kJ)

c_F = fm_ch4 * c_ch4 + fm_MSW * c_msw // Hybrid fuel exergetic cost (R$/kJ)

// Next, evaluate nonexergetic costs (R$/kJ)

P_inc = 150e3 // Incinerator price for processing 50 kg/h of MSW

tlife_inc = 10 // Expected incinerator life time (years)

Z_CI_inc = P_inc / tlife_inc // Incinerator capital investment cost rate (R$/year)

Sal_1op = 6e3 // Salary of 1 operator (R$/month)

N_op = 1 // Number of incinerator operators

Parts_replac = 2e3 // Parts replacement cost rate (R$/month)

Z_OM_inc = N_op * Sal_1op * 12 + Parts_replac * 12 // Incinerator OM cost rate (R$/year)

// Exergoeconomic equation

c_elect = 0.78 / 3600 // Electricity cost (R$/kJ)

c_1 * (Edot1 + Edot2) * conv_s_ano = c_F * Edot_qinc * conv_s_ano - c_elect * Wdot_fan * conv_s_ano+ Z_CI_inc + Z_OM_inc

conv_s_ano = 3600 * 24 * 365 // Number of seconds/year

C_1 = c_1 * (Edot1 + Edot2) * conv_s_ano // Products cost per year (R$/year)

Exergoeconomic metrics

Exergy destruction + non-exergetic cost rates

$$\dot{Z}_k \dot{C}_{D,k} = \dot{C}_{D,k} + \dot{Z}_k$$

Relative cost

$$r_k = \left(c_{P,k} - c_{F,k}\right)/c_{F,k} = \left(1 - \varepsilon_k\right)/\varepsilon_k + \dot{Z}_k/\left(c_{F,k} \cdot \dot{E}_{P,k}\right)$$

Exergoeconomic factor

$$f_k = \left(100\%\right) \cdot \left(\dot{Z}_k\right)/\left(\dot{Z}_k + c_{F,k} \cdot \dot{E}_{D,k}\right)$$

Relation between product and fuel exergy rates

$$\varepsilon_k = \left(100\%\right) \cdot \dot{E}_{P,k}/\dot{E}_{F,k}$$

Exergy destruction ratio

$$y_{D,k} = \left(100\%\right) \cdot \dot{E}_{D,k}/\dot{E}_{F,tot}$$

EXERGOECONOMIC STRATEGY

Priorities for component analysis/optimization:
1) First, choose to analyze the component with the greater sum $\dot{Z}_k \dot{C}_{D,k}$.
2) Among those above, improve the component with a high-cost relative difference, r_k.
3) Verify, with the exergoeconomic factor, f_k, if the component requires better efficiency or lower costs.
4) Investigate the component with relatively low exergetic efficiency (ε_k) or high exergy destruction rate ($\dot{E}_D$), or high exergy destruction ratio (y_D).

(CHAPTER 1 ENDS HERE!)

(STOPPED HERE ON SUNDAY, SEPTEMBER 3, 2023 @ 7:36 PM)