Chapter Three

TheoreticalFramework

3.1. EQUILIBRIUM THERMODYNAMICS

Equilibrium or classical thermodynamics deals essentially with the study ofmacroscopic properties of matter at equilibrium. Here it is sufficient to characterize it as atime-independent state, like a column of air at rest in absence of any flux ofmatter, energy, charge, or momentum. By extension, equilibrium thermodynamicshas also been applied to the description of reversible processes: theyrepresent a special class of idealized processes considered as a continuumsequence of equilibrium states.

Since time does not appear explicitly in the formalism, it would be moreappropriate to call it thermo-statics and to reserve the name thermodynamicsto the study of processes taking place in the course of time outside equilibrium.However, for historical reasons, the name “thermodynamics” is widelyutilized nowadays, even when referring to equilibrium situations. We shallhere follow the attitude dictated by the majority but, to avoid any confusion,we shall speak about equilibrium thermodynamics and designate beyondequilibriumtheories under the name of non-equilibrium thermodynamics.

More clearly equilibrium thermodynamics is a section of macroscopic physics whose originalobjective is to describe the transformations of energy in all its forms.

3.2. FIRST LAW EFFICIENCY

First law efficiency or known as Carnot efficiency is one of the important factors for evaluating the performance of heat engines.It represents Carnot cycle efficiency.

First law efficiency determined by the following equation:

$$\eta_I = 1 - \frac{T_2}{T_1} \qquad \ldots\ldots\ldots(3-1)$$

Where:

T_1≡Temperature of source thermal reservoir (**K**).

T_2≡Temperature of sink thermal reservoir (**K**).

The above equation represents the efficiency of Carnot heat engine is the best known reversible engine. This is the highestefficiency a heat engine operating between the two thermal energy reservoirsat temperatures T_1 and T_2 canhave.

All irreversible (i.e. actual) heat engines operating between these temperature limits (T_1 and T_2) have lower efficiencies. An actual heat engine cannot reach this maximumtheoretical efficiency value because it is impossible to completely eliminateall the irreversibilities associated with the actual cycle.

The thermal efficiencies of actual and reversible heat engines operatingbetween the same temperature limits compare as follows:

$$\eta_{th} \begin{cases} < & \eta_I \quad \text{irreversible heat engine} \\ = & \eta_I \quad \text{revesible heat engine} \\ > & \eta_I \quad \text{impossible heat engine} \end{cases} \qquad \ldots\ldots\ldots(3-2)$$

3.3. SECOND LAW EFFICIENCY

Second-law efficiency (also known as the exergy efficiency or rational efficiency) computes the efficiency of a process taking the second law of thermodynamics into account, is defined as the ratio of the actualthermal efficiency to the maximum possible (reversible) thermal efficiencyunder the same conditions

$$\eta_{II} = \frac{\eta_{th}}{\eta_{th,rev}} \quad \ldots\ldots\ldots(3-3)$$

Where

η_{th}≡The actual thermal efficiency.

$\eta_{th,rev}$≡The maximum possible (reversible) thermal efficiency.

The destruction of exergy is closely related to the creation of entropy and as such any system containing highly irreversible processes will have low energy efficiency. As an example the combustion process inside a power stations gas turbine is highly irreversible and approximately 25% of the exergy input will be destroyed here.

3.4. NON-EQUILIBRIUM THEORY

Equilibrium thermodynamic deals with ideal processes taking place at tooslow rate, in arbitrary processes are only compare the initial and final state of equilibrium, but the processesthemselvescannot be described, to deal with the cases of more realistic we must study the system in a state of non-equilibrium.

Non-equilibrium thermodynamics borrows most of the concepts and tools from equilibrium thermodynamics but transposed at a local scale because non-equilibrium states are usually inhomogeneous. The objective is to cope with non-equilibrium situations where basic physical quantities like mass, temperature, pressure, etc. are not only allowed to change from place to place, but also in the course of time.This theory has been very useful in dealing with a wide variety of practical problems.

The relevance of transport equations, which play a central role in non-equilibrium thermodynamics – comparable, in some way, to equations of state in equilibrium thermodynamics – justifies some preliminary considerations. Transport equations describe the amount of heat, mass, electrical charge, or other quantities which are transferred per unit time between different systems and different regions of a system as a response to non-homogeneity in temperature $\boldsymbol{T}$, molar concentration $\boldsymbol{c}$, electric potential $\boldsymbol{\varphi_e}$. Historically, the first incursions into this subject are allotted to Fourier, Fick, and Ohm, who proposed the nowadays well-known laws:

$$\boldsymbol{q = -\lambda \nabla T \quad (Fourier's\ law) \qquad \ldots\ldots\ldots (3-4)}$$

$$\boldsymbol{J = -D \nabla c \quad (Fick's\ law) \qquad \ldots\ldots\ldots (3-5)}$$

$$\boldsymbol{I = \sigma_e \nabla \varphi_e (Ohm's\ law) \qquad \ldots\ldots\ldots (3-6)}$$

Where

$\boldsymbol{q}$≡ The heat flux (amount of internal energy per unit time and unit area transported by conduction).

$\boldsymbol{J}$≡ The diffusion flux (amount of matter, expressed in moles, per unit time and unit area transported by diffusion).

$\boldsymbol{I}$≡ The flux of electric current (electric charge transported per unit time and unit area).

$\boldsymbol{\lambda, D\ and\ \sigma_e}$≡ The heat transfer coefficient, diffusion coefficient, and electric conductivity, respectively.

The knowledge of these various transport coefficients in terms of temperature, pressure, and mass concentration has important consequences in material sciences and more generally on our everyday life.

3.5. REVERSIBLITY AND IRREVERSIBLITY

The second law of thermodynamics shows that there is no heat enginecan have a thermal efficiency of 100%. As we know that the highest thermal efficiency is the efficiency of the Carnot cycle which consists of ideal processes or that so-called “reversible processes”.

A reversible process is defined as a process that can be reversed withoutleaving any trace on the surroundings. That is, both the systemand the surroundings are returned to their initial states at the end of thereverse process. This is possible only if the net heat and net work exchangebetween the system and the surroundings is zero for the combined (originaland reverse) process.

As well as the reversible process can be defined as the process that occurs it changes in some properties of the system without entropy production (i.e. dissipation of energy).

The second law of thermodynamics often leads to expressions that involveinequalities. An irreversible (i.e., actual) heat engine, for example, is lessefficient than a reversible one operating between the same two thermalenergy reservoirs. Another important inequality that hasmajor consequences in thermodynamics is the Clausius inequality. It wasfirst stated by the German physicist R. J. E. Clausius (1822–1888), one ofthe founders of thermodynamics, and is expressed as:

$$\oint \frac{\delta Q}{T} \leq 0 \qquad \dots\dots\dots(3-7)$$

That is, the cyclic integral of dQ/T is always less than or equal to zero. Thisinequality is valid for all cycles, reversible or irreversible. Any heat transfer to or from a systemcan be considered to consist of differential amounts of heat transfer. Then thecyclic integral of dQ/T can be viewed as the sum of all these differentialamounts of heat transfer divided by the temperature at the boundary.

3.6 IRREVERSIBLITIES

The factors that cause an irreversible process calledirreversiblities. They include friction, unrestrained expansion, mixing of two fluids, heattransfer across a finite temperature difference, electric resistance, inelasticdeformation of solids, and chemical reactions. The presence of any of theseeffects renders a process irreversible.Some of these factors will be discussed in a concise manner.

Friction is a form familiar of irreversibility and which is associated with bodies in motion. When two bodies in contact are forced to move relative to each other (i.e. a piston in a cylinder, shown in Fig. 3.1, a friction force that opposes the motion develops at the interface of these two bodies, and some work is needed to overcome this friction force. The energy supplied as work is finally converted to heat during the process and is transferred to the bodies in contact, as reflected by a temperature rise at the interface.

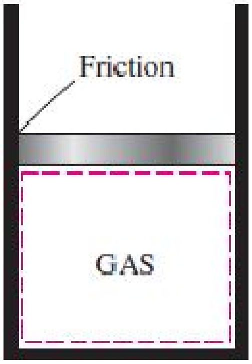

Fig. 3.1: Friction between piston and cylinder walls cause irreversible process

When the direction of the motion is reversed, the bodies are restored to their original position, but the interface does not cool, and heat is not converted back to work. Instead, more of the work is converted to heat while overcoming the friction forces that also oppose the reverse motion. Since the system (the moving bodies) and the surroundings cannot be returned to their original states, this process is irreversible. Therefore, any process that involves friction is irreversible. The larger the friction forces involved, the more irreversible the process is.

Friction does not always involve two solid bodies in contact. It is alsoencountered between a fluid and solid and even between the layers of afluid moving at different velocities. A considerable fraction of the powerproduced by a car engine is used to overcome the friction (the drag force)between the air and the external surfaces of the car, and it finallybecomes part of the internal energy of the air. It is not possible to reversethis process and recover that lost power, even though doing so would notviolate the conservation of energy principle.

Another example of irreversibility is the unrestrained expansion of agas separated from a vacuum by a membrane, as shown in Fig. 3.2.

Fig. 3.2: Unrestrained expansion

Whenthe membrane is ruptured, the gas fills the entire tank. The only way torestore the system to its original state is to compress it to its initial volume,while transferring heat from the gas until it reaches its initial temperature.From the conservation of energy considerations, it can easily be shown thatthe amount of heat transferred from the gas equals the amount of work doneon the gas by the surroundings. The restoration of the surroundings involvesconversion of this heat completely to work, which would violate the secondlaw. Therefore, unrestrained expansion of a gas is an irreversible process.

A third form of irreversibility familiar to us all is heat transfer through afinite temperature difference. Consider a can of cold soda left in a warm room, as shown in Fig. 3.3.

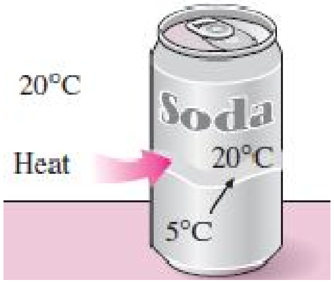

Fig. 3.3: Heat transfer through a finite temperature difference

Heat is transferred from the warmer room air to thecooler soda. The only way this process can be reversed and the sodarestored to its original temperature is to provide refrigeration, whichrequires some work input. At the end of the reverse process, the soda will berestored to its initial state, but the surroundings will not be. The internalenergy of the surroundings will increase by an amount equal in magnitudeto the work supplied to the refrigerator. The restoration of the surroundingsto the initial state can be done only by converting this excess internal energycompletely to work, which is impossible to do without violating the secondlaw. Since only the system, not both the system and the surroundings, canbe restored to its initial condition, heat transfer through a finite temperaturedifference is an irreversible process.

3.7 ENDOREVERSIBLE THERMODYNAMICS

As we mentioned earlier that the equilibrium thermodynamics deals with ideal processes without friction at a very slow speed, in these processes often used Carnot efficiency (Eq. 3 – 1), which showed how much heat can be converted to work in any heat engine receives heat from the high temperature thermal reservoir and pronounces the heat to the low temperature thermal reservoir. But cannotensurefrom a perfect heat transfer from the source thermal reservoir to the heat engine or from the heat engine to the sink thermal reservoir.

There are a number of variables in thermodynamic processes that must be determined to be dealing with the process of heat transfer between the heat engine and heat reservoirs are more realistic.

But determination of these variables requires familiar with the conditions surrounding the system and defines the realistic boundary, well it must be carried out this processes at finite time.All of this represents a big challenge; this challenge has inspired scientists to conduct a wide range of research in this area.

3.8 ENDOREVERSIBLE SYSTEM (NOVICOV ENGINE)

As a simple introductory example we consider the Novicovengine, this engine as shown in Fig. 3.4is a continuously operating, reversible Carnot engine with the internaltemperatures $\boldsymbol{T_{iH}}$ and $\boldsymbol{T_{iL}}$. It is in direct contact with the external low temperature heatbath at $\boldsymbol{T_L}$ and is coupled to an external high temperature heat bath at $\boldsymbol{T_H}$ through a finiteheat conductance$\boldsymbol{K}$.

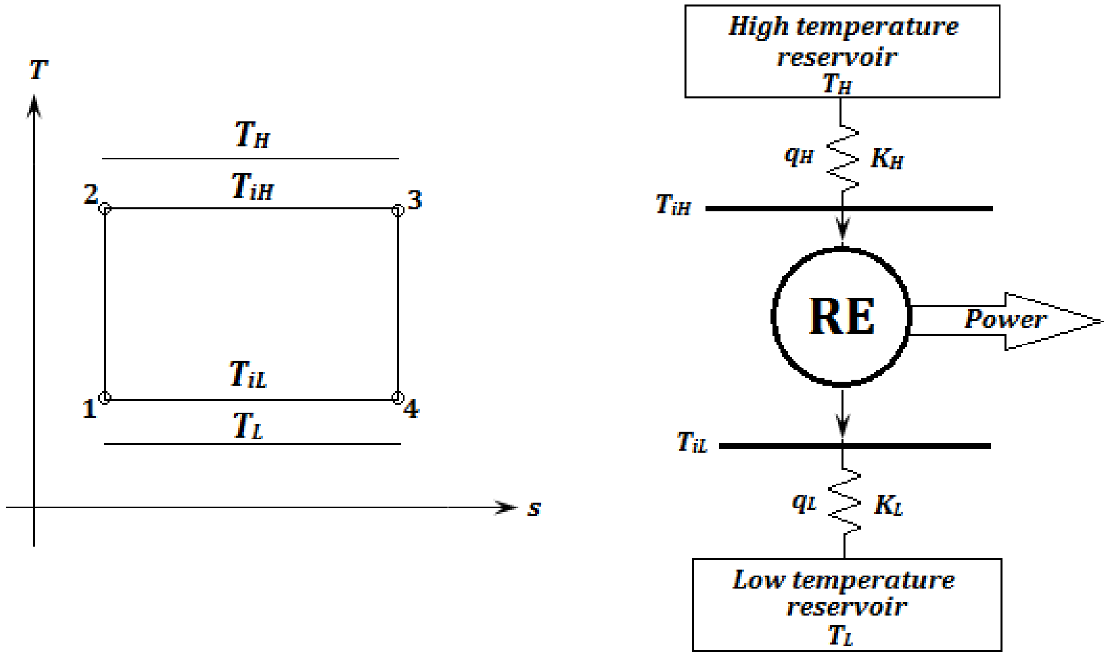

Fig. 3.4:Model of the endoreversibleNovicov engine with finite heatconduction $K_H$to the high temperature thermal reservoir and finite heatconduction K_L to the low temperature thermal reservoir(*left*). T- sdiagramof a Carnot cycle with a temperature difference to the high temperature and low temperaturethermal reservoir (*right*).

One of the assumptions they made was Newtonian heat conductance, i.e. the linear dependence of heat flux on the temperature difference between sink (source) and the working material. According to the reference [11], if the input energy during the isothermal expansion stage is q_H, it lasts for t_1 seconds, the temperature of the working material is T_{iH}, and K_H is a constant then

$$q_H = K_H t_1 (T_H - T_{iH}) \qquad \dots\dots\dots(3-\ 8)$$

Similarly, for the isothermal compression stage with the output energy q_L, duration t_2, the temperature of the working material T_{iL}, and the constant K_L we have

$$q_L = K_L t_2 (T_{iL} - T_L) \qquad \dots\dots\dots(3-\ 9)$$

In addition, as the engine operates reversibly the entropy fluxes to and from the enginehave to cancel

$$\mathbf{0} = \frac{q_H}{T_{iH}} - \frac{q_L}{T_{iL}} \quad \rightarrow \quad \frac{q_H}{T_{iH}} = \frac{q_L}{T_{iL}} \qquad \ldots\ldots\ldots(3-10)$$

If the total cycle duration is proportional to isothermal stages duration with constant γ, the output power of the engine is:

$$P = \frac{q_H - q_L}{\gamma(t_1 + t_2)} \qquad \ldots\ldots\ldots(3-11)$$

Assuming that $x = T_H - T_{iH}$and $y = T_{iL} - T_L$, the previous four equations together give:

$$P = \frac{K_H K_L xy(T_H - T_L - x - y)}{\gamma\big(K_L T_H y + K_H T_L x + xy(K_H - K_L)\big)} \qquad \ldots\ldots\ldots(3-12)$$

The output power reaches its maximum when ∂P/∂x = ∂P/∂y = 0. These conditions lead to:

$$\left.\begin{aligned} K_L T_H y(T_H - T_L - x - y) &= x\big(K_L T_H y + K_H T_L x + xy(K_H - K_L)\big) \\ K_H T_L x(T_H - T_L - x - y) &= y\big(K_L T_H y + K_H T_L x + xy(K_H - K_L)\big) \end{aligned}\right\} \quad \begin{aligned} &\ldots\ldots\ldots(3-13a) \\ &\ldots\ldots\ldots(3-13b) \end{aligned}$$

From these two equations we than have:

$$y = \sqrt{\frac{K_H T_L}{K_L T_H}}\,x \qquad \ldots\ldots\ldots(3-14)$$

Which is then used to eliminate y from equation (3 – 13a) to give the following quadratic equation for $\frac{x}{T_H} = \mu$.

$$\left[1 - \frac{K_H}{K_L}\right]\mu^2 - 2\left[\sqrt{\frac{K_H T_L}{K_L T_H}} + 1\right]\mu + \left[1 - \frac{T_L}{T_H}\right] = 0 \quad \ldots\ldots\ldots(3-15)$$

Since $\mu < 1$the physically relevant solution of this equation is readily shown to be:

$$\boldsymbol{\mu = \frac{x}{T_H} = \frac{1 - \sqrt{T_L/T_H}}{1 + \sqrt{K_H/K_L}}} \qquad \dots\dots\dots(\mathbf{3-16})$$

From equation (3 – 14) it follows that

$$\boldsymbol{\frac{y}{T_L} = \frac{\sqrt{T_H/T_L} - 1}{1 + \sqrt{K_L/K_H}}} \qquad \dots\dots\dots(\mathbf{3-17})$$

The efficiency of the engine at maximum power ($\boldsymbol{\eta_{Pmax}}$) is given by:

$$\boldsymbol{\eta_{Pmax} = 1 - \frac{T_{iL}}{T_{iH}} = 1 - \frac{T_L + y}{T_H - x}} \qquad \dots\dots\dots(\mathbf{3-18})$$

By substituting $\boldsymbol{x}$ and $\boldsymbol{y}$ in equation (3 – 18) we get:

$$\boldsymbol{\eta_{Pmax} = 1 - \sqrt{\frac{T_L}{T_H}}} \qquad \dots\dots\dots(\mathbf{3-19})$$

The efficiency in equation (3 – 19) is called Novicov’s efficiency.