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## **Chapter I – Thermodynamics: Concepts and Applications**

The concepts of Thermodynamics are extremely important on the application for thermal systems design. As they present heat transfer process by conduction on the heat source and sink, evaporation and condensation of the working fluid, the entire cycle that those devices perform can be well explained by the laws of thermodynamics.

The Laws of Thermodynamics could be applied to determine the better geometry that a capillary evaporator or a condenser should present, as well as they could be used to design optimization. Parasite heat transfer problems in capillary evaporators and two-phase reservoirs, especially in loop heat pipes, could be minimized. Furthermore, interfacial processes presented and discussed in Chapter IV are highly dependent on the thermodynamic equilibrium that those devices present during the working fluid evaporation process in the porous wick. Such interface equilibrium conditions, which are highly dependent on the correct operation of capillary evaporators,

are the main factors that lead to a successful design and its optimization.

The Laws of Thermodynamics presented here are seen in every textbook related to this subject, which are the basic tools for any research and application where heat and mass transfer are involved. Conditions for the thermal equilibrium and energy transfer in processes are discussed as in other books that present this approach on thermodynamics phenomenon, whether they are related to the fundamentals of specific applications.

### ***1.1. Basic Concepts***

As thermodynamics is a science applied to conservation of energy, it is particular involved in the changes related to it. Energy must always be conserved, which could be modified from a initial to a final state, however, the total quantity of energy must remain the same, as it cannot be destroyed. In any application where the laws of thermodynamics can be used, the so-called energy balance can be applied, which are related to the application of the First and Second Laws of Thermodynamics.

In the case of the First Law of Thermodynamics, the processes are treated using an expression that describes the energy conservation. In this case, the energy from a source can be modified and used for another destination. This is the case of chemical energy stored in fuels that is transformed in mechanical energy that runs the internal combustion engines. Another classical example is the potential energy, where the height difference on the water reservoir can be transformed in mechanical energy that will result in electricity generation. Therefore, the relations between the transformed energy can be well established.

In the case of the Second Law of Thermodynamics, the *details* of the energy are analyzed, which represent both its quantity and its quality. In this case, the processes occur on the direction of the decreasing on the energy quality, which means that all processes are irreversible due to losses present in any process that could be re-

lated to friction between mechanical parts or even during the two-phase flow of a substance, inefficient combustion process, etc. As irreversible processes are a reality present in any process, the *entropy* generation that quantifies how irreversible a process is will give a better representation of the energy quality.

From the processes that any system is suitable as far as its analysis is a concern upon applying the Laws of Thermodynamics, it is always necessary to consider and remember the concepts involved in two important variables in this analysis: heat and work. *Heat* is any form of energy transferred as a result of chemical process, friction between mechanical parts, etc and released in a form of increase or decrease of temperature. In its classical form, *heat* is the energy transferred by atomic ways. *Work* is any form of energy associated to the motion or transfer, being mechanical, electrical, etc [1]. Following the same direction, *work* is also associated with the displacement of a system's boundary, when forces are acting on order to promote such interaction [2]. Heat and work are placed on the same side of the First Law of Thermodynamics as these two terms represent equivalency between each other because they appear as not distinguishable as far as energy interactions are a concern. This statement was established in the early times when the thermodynamics was being introduced as a course for physicists and engineers [2], which is well accepted and is still used in today's courses.

Heat and Work are important parts on the role of the thermodynamics interaction between the system and the environment. Of course, a complete analysis of the thermodynamic behavior cannot put aside the irreversibilities that any system presents as no perfect machine was or will be ever built. In this case, it is very convenient to mention that the irreversibilities are related to the entropy generation that will be better discussed in item 2.3.3 but it can be firstly introduced as the most important parameter that describes the quality of the energy being analyzed. It is correct to link the heat transfer interaction with entropy transfer, being clear that work does not present such an interaction [2]. However, how these parameters interact with the system under analysis can be well established upon evaluating the First Law of Thermodynamics, whether for a closed or an open system.

When applying the First and Second Laws for a cycle, being a vapor compression or for energy generation (Rankine), it is important to perform the so called *Exergy Analysis* in which the quality and the quantity of the available energy will be transformed. In fact, upon designing a thermal system it is highly advisable to perform such analysis so potential errors and problems can be mitigated and the designer can have more degrees of freedom to manipulate the design so it can meet the requirements.

### 1.2. Ideal Gases

To evaluate a given process, it is convenient to treat them as ideal gases with a specific formulation for this. Upon using an ideal gas, the evaluation must be made based on the Equation of State, which is:

$$Pv = RT \quad (1.1)$$

and the Van der Waals relation is

$$P = \frac{(\bar{R} / \bar{M})T}{v - b} - \frac{a}{v^2} \quad (1.2)$$

where

$$a = \frac{27(\bar{R} / \bar{M})^2 T_c^2}{64P_c}, \quad b = \frac{(\bar{R} / \bar{M})T_c}{8P_c} \quad (1.3)$$

The other important relations that must be used on this analysis are related to the internal energy ( $u$ ), enthalpy ( $h$ ) and specific heats ( $c_p$ ), such as:

$$\begin{aligned} \Delta h &= \Delta u + W \\ h &= u + Pv \end{aligned} \quad (1.4)$$

resulting in  $h = u + RT$  (T in Kelvin). Evaluating the specific heats, they can be written as follows:

$$\begin{aligned} h &= u + RT \\ dh &= du + RdT \end{aligned} \tag{1.5}$$

As  $dh=c_p dT$  and  $du=c_v dT$ , results in  $c_p=c_v+R$ . Another important relation is the ration between the specific heats used to evaluate the processes from one state to another, which is defined as  $k=c_p/c_v$ .

### ***1.3. The First Law of Thermodynamics***

The First Law of Thermodynamics defines the change that energy can present for a system under development from an initial to a final state. All energies involved in this development, being heat or work, can be described as the system interaction with the phenomena that is under progress within its boundaries. This analysis only establishes the quantity of the energy interaction that has undergoing within the boundaries and how they develop towards the equilibrium. Thus, it is possible to quantify the amount of energy required for a system to go from an initial to a final state.

The system under analysis can be taken as two distinguished types: closed and open. The *closed system* does not present mass transfer across its boundaries and thus only the *internal energy* change can be evaluated. The internal energy is directly related to the sum of all microscopic forms of energy. The *open system* analysis requires a more complete approach as mass is allowed to cross the system's boundaries. In this case, the average change on the energy within the system should be evaluated in terms of *enthalpy* as well as the other types of energies that might be interacting with the system, such as the kinetic and potential energies. A more detailed explanation related to the First Law of Thermodynamics application in each type of system is presented below.

### 1.3.1. Application for Closed Systems

In a closed system, the total quantity of energy can only be changed from heat and/or work to an overall evolution of the internal energy. As mass cannot cross the boundary of the system, the interaction between the sources of energy and the internal energy is very close, which will give the proper condition from an initial to a final state. With a fixed amount of mass, any change on the system's temperature or pressure will be a result of the internal energy variation as it develops from an initial to a final state (Fig. 1.1).

Fig. 1.1. Forms of energy on a closed system.

However, if work has been produced at the boundaries due to the evolution from one state to another (Fig. 1.2), with a direct influence of the internal pressure and volume, the system can be analyzed in terms of the enthalpy change according to the following thermodynamic relation

$$dh = dU + d(PV). \quad (1.6)$$

Upon evaluating the energy interaction in this closed system, the First Law of Thermodynamics can be represented as

$$dQ - dW = dE, \quad (1.7)$$

where the total amount of energy that interacts with the system, also called as the total net increase or decrease in the total energy of the system, can be represented as

$$dE = dU + dKe + dPe. \quad (1.8)$$

**Fig. 1.2. Work being generated at the closed system boundary.**

In a closed system, the kinetic energy variation is negligible as there is no mass flow across the boundaries and the potential energy can also be neglected because no height difference is present in such an analysis. Therefore, the net increase or decrease in the total energy can be summarized as

$$dE = dU = m c_v dT \quad (1.9)$$

which represents the total variation of the internal energy of a system that develops a path from an initial to a final state.



Other important thermodynamic relations can be widely used when evaluating a closed system, especially when ideal gases behavior is under investigation. In the case where work is generated at the closed system boundary, the relationship presented by Eq. (1.6) can be described as

$$dH = dU + RdT, \quad (1.10)$$

where the definitions for the enthalpy ( $dH$ ) and internal energy ( $dU$ ) can be used as

$$dh = c_p dT \quad (1.11)$$

$$du = c_v dT \quad (1.12)$$

resulting in the thermodynamic relation

$$c_p = c_v + R. \quad (1.13)$$

One example can be presented here, which has a more classical approach for solving a Thermodynamic problem for a closed system, for the sake of concepts application. Considering a rigid adiabatic volume with an ideal gas, divided in three smaller volumes by rigid and diathermal membranes, being each volume with a given pressure, temperature and a proportional mass of the gas, present equilibrium state, closed at the top by a piston (Fig. 1.3a). Upon breaking the membranes, this system will find another equilibrium state until the pressure is equalized once again and a final temperature is reached (Fig. 1.3b).

At the beginning, the Ideal Gas equation can be used as

$$PV = mRT. \quad (1.14)$$

At the final state, the Energy balance is done resulting in

$${}_1Q_2 = (E_2 - E_1) + {}_1W_2. \quad (1.15)$$

**Fig. 1.3. Rigid adiabatic volume.**

At state 1, the entire system is in equilibrium. At the final state, one can say that the final temperature and pressure are uniform and  $P_2 = P_{1_A}$  that is given by the pressure applied by the piston on the system.

Since the left hand side does not exist and the energy terms associated with this process are related only with the variation of the internal energy, Eq. (1.15) resumes to

$$U_2 - U_1 + {}_1W_2 = 0. \quad (1.16)$$

At the beginning, the internal energy presented in the volume was composed by

$$U_1 = u_{1_A} \frac{m}{3} + u_{1_B} \frac{m}{3} + u_{1_C} \frac{m}{3} = \frac{m}{3} (u_{1_A} + u_{1_B} + u_{1_C}) \quad (1.17)$$

and  $u_{1_A} = u_{1_B} = u_{1_C}$  are dependent of the temperature. From Eqs. (1.11) and (1.12), the term  $U_2 - U_1$  from Eq. (1.16) can be written as

$$U_2 - U_1 = m \int_{T_1}^{T_2} c_v dT = m c_v (T_2 - T_1). \quad (1.18)$$

The work generated by the piston on the system in a isobaric process is given by

$${}_1W_2 = P_{1_A} (V_2 - V_1), \quad (1.19)$$

where

$$V_1 = V_{1_A} + V_{1_B} + V_{1_C} = \frac{m}{3} \frac{RT_1}{P_{1_A}} + \frac{m}{3} \frac{RT_1}{P_{1_B}} + \frac{m}{3} \frac{RT_1}{P_{1_C}} \quad (1.20)$$

and

$$V_2 = \frac{mRT_2}{P_{1_A}}. \quad (1.21)$$

Rearranging Eqs. (1.18) to (1.21) into Eq. (1.16), after some manipulation, results in

$$\frac{T_2}{T_1} = \frac{1 + \frac{1}{3} \left( \frac{R}{c_v} \right) \left( 1 + \frac{P_{1_A}}{P_{1_B}} + \frac{P_{1_A}}{P_{1_C}} \right)}{1 + R/c_v}. \quad (1.22)$$

The above equation gives the relation between the initial and final temperatures at which the systems will be subjected to, showing that the evolutions from an initial equilibrium state to a final will only depend on the ideal gas behavior, being dependent on the pressures.

### 1.3.2. Application for Open Systems

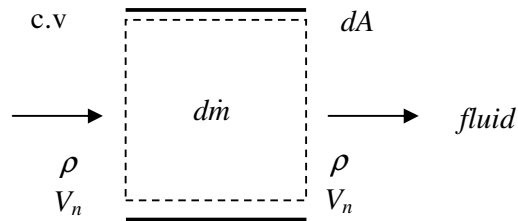
For open systems (Fig. 1.4), mass is allowed to go across the system's boundaries and usually the energies associated with kinetic and potential energies cannot be neglected as done for closed systems. However, the potential energy is frequently neglected due to the requirement of a height difference for this variable is taken into consideration. As mass flow across the system's boundaries, the average change on the enthalpy associated with the process taking place must also be carefully considered.

**Fig. 1.4. Representation of an open system.**

As mass is allowed to flow across the system's boundaries, in this case, the Conservation of Mass must be properly observed. Since the system under analysis presents at least one inlet and one outlet, the Conservation of Mass must be evaluated as the balance of the total mass that enters and leaves the system's boundaries being equal to the net change in mass within the system, i.e.

$$\sum \dot{m}_i - \sum \dot{m}_o = \sum \dot{m}_{system} . \quad (1.23)$$

When analyzing the flow across an infinitesimal control volume (c.v.) with known cross-section area and the fluid's properties (Fig. 1.5), the mass balance can be evaluated from the following relation



**Fig. 1.5. Infinitesimal control volume in an open system.**

$$\int_A d\dot{m} = \int_A \rho V_n dA . \quad (1.24)$$

The Conservation of Mass can also be represented in terms of the Euler Coordinates as follows

$$\int_{\forall(t)} \frac{\partial \rho}{\partial t} d\forall + \int_{S(t)} \rho \vec{V} \cdot \hat{n} dS = 0, \quad (1.25)$$

where the above relation can be extended, considering that  $\vec{V} = \vec{V}_{cs} + \vec{V}_r$  to

$$\int_{\forall(t)} \frac{\partial \rho}{\partial t} d\forall + \int_{S(t)} \rho (\vec{V}_{cs} + \vec{V}_r) \cdot \hat{n} dS = 0. \quad (1.26)$$

Upon applying the Leibnitz rule to the Eq. (1.26), the Conservation of Mass in the integral form can be written as

$$\frac{d}{dt} \int_{CV(t)} \rho d\forall + \int_{CS(t)} \rho \vec{V}_r \cdot \hat{n} dS = 0. \quad (1.27)$$

For the open system, the energy components can be represented as

$$E = \int_{\forall(t)} \rho e d\forall, \quad (1.28)$$

where

$$e = u + \frac{V^2}{2} + gz \quad (1.29)$$

and thus considering that the First Law of Thermodynamics could be applied to the open system as

$$\dot{Q} = \frac{dE}{dt} + \dot{W}, \quad (1.30)$$

the following relation could be used upon applying the Reynolds transport theorem

$$\dot{Q} = \int_{\forall(t)} \frac{\partial(\rho e)}{\partial t} d\forall + \int_{CS(t)} \rho e \vec{V} \cdot \hat{n} dS + \dot{W} . \quad (1.31)$$

After applying the Leibnitz rule to the above relation, with the proper evaluation of the velocity vector on the second right hand term, the First Law of Thermodynamics for an open system can finally be written as

$$\dot{Q} = \frac{d}{dt} \int_{\forall(t)} \rho e d\forall + \int_{CS(t)} \rho e \vec{V}_r \cdot \hat{n} dS + \dot{W} . \quad (1.32)$$

This relation represents the overall energies that are affecting the entire system with proper consideration of the mass that flow across the boundaries. Physically, this relation indicates that the total amount of energy that cross the system's boundaries as heat or work plus the balance of the total energy of mass that enters and leaves the control volume is equal to the net change in energy of the control volume. Equation (1.32) is applied in each component of any two-phase passive thermal control device, being the evaporator, condenser or two-phase reservoir to evaluate their influence on the system's behavior.

Thermodynamics deal with energy transfer by the use of a substance, where its mass flow carries energy in the form of heat or work from a source to a sink. It is thus important to correctly define a substance as a homogeneous fluid that has its characteristics related to its saturation temperature, such as water, acetone, ammonia, etc. Thermodynamics defines such properties as intensive (dependent on mass) or extensive (not dependent on mass).

The substance is treated from its State of Equilibrium. In a given state, the substance presents its properties with fixed values. If any variation on such properties takes place, then the substance is found in another state. In the equilibrium conditions, all substance's potentials present no variation.

Each substance can be treated from their conditions of saturation given by P-v or P-T curves, as shown by Fig. 1.6.

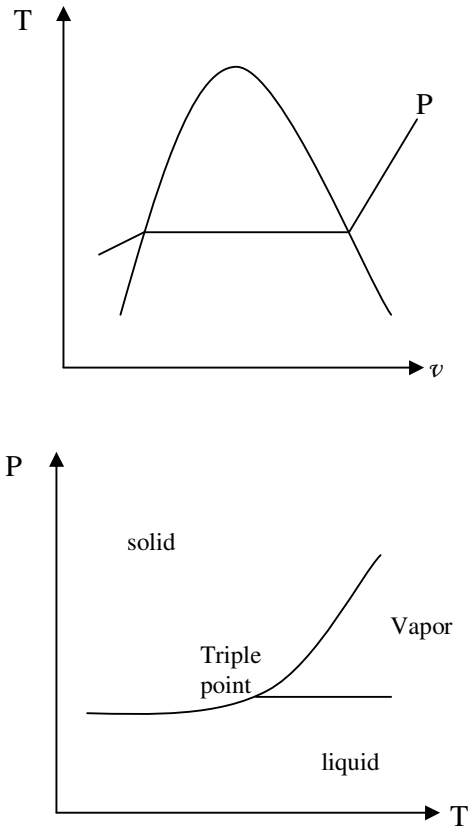


Fig. 1.6. Thermodynamics states of a given substance.

From this analysis, it is possible to identify processes where phase change happens in substances, such as what takes place in a vapor bubble in a liquid medium. For such case, the Energy Conservation equation, or the First Law of Thermodynamics, can be used either for a closed system, where no mass cross the system's boundary, or an open system, where mass is crossing the boundaries of the system. On the first case, the internal energy ( $u$ ) of the system

must be evaluated, as the volume does not change ( $du = c_v dT$ ). In an open system, there is a change of energy at a given pressure ( $dh = c_p dT$ ), which is related to the system's enthalpy. Either one, the process evaluation shows the substance's change from one initial state to a final state taking place in the control volume, as presented by Fig. 1.7a, for a closed system and Fig. 1.7b for an open system.

As an example, upon evaluation the heat transfer process in a bubble, it is known that the entire process takes place at the interface where the liquid in contact with this interface evaporates, transferring mass to the interior of the bubble, which continuously grows.

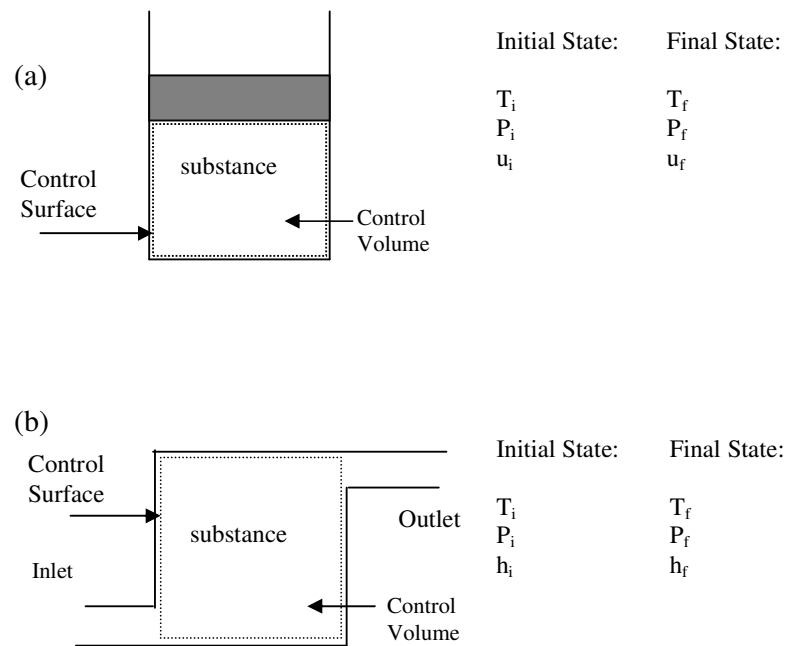


Fig. 1.7. Process evaluation from an initial to a final state.

Figure 1.8 presents an example of interfacial interaction between vapor and liquid phases, where it is possible to describe the



vapor bubble growth by means of the Thermodynamics Laws application.

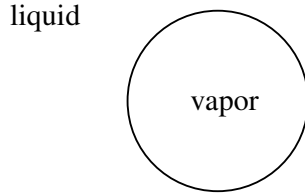


Fig. 1.8. Interfacial interaction between phases.

$$P_v - P_l = \frac{2 \sigma}{\Phi_b} \quad (1.33)$$

In this process, the 1<sup>st</sup> Law of Thermodynamics does apply, such as:

$$\delta Q - \delta W = \delta U + \delta E_c + \delta E_p, \quad (1.34)$$

$$\delta Q - \delta W = \delta H + \delta E_c + \delta E_p, \quad (1.35)$$

where Eq. (1.34) is related for a *Closed System* and Eq. (1.35) for an *Open System*, and

$$H = U + PV. \quad (1.36)$$

In the case of closed systems, only the internal energy variation is considered, as there is no mass transfer by the system's boundaries, in such a way that there is no variation on the kinetic and potential energy. In this case, the First Law of Thermodynamics can be written as  $\delta Q - \delta W = \delta U$ .

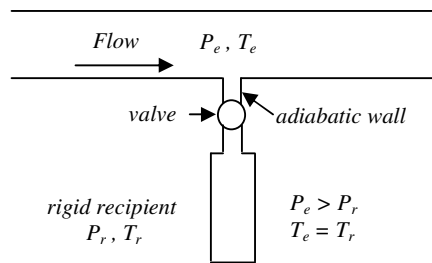
In the case of open systems, as there is mass flow by the system's boundaries, their analysis are related to the kinetic (such as the case of converging and diverging nozzles) and potential (such as the case of hydropower generation) energies variations. As there is mass

flow across the boundaries, the First Law of Thermodynamics can be simply described as:

$$\dot{Q} - \dot{W} = \dot{m} \left[ (h_o - h_i) + \left( \frac{V_o^2 - V_i^2}{2} \right) + g(z_o - z_i) \right]. \quad (1.37)$$

Perhaps one of the most important processes that it is applied to thermal systems design is the one related to charging the system with a given working fluid. This is a common practice for vapor compression cycles as well as heat pipes and loop heat pipes. Since a working fluid needs to be transferred from its recipient (bottle, tank, etc) to the internal volume of the system that is under vacuum<sup>1</sup>, such a procedure can be performed upon evaluating it as a *Uniform Regime*.

For the *Uniform Regime* the properties as considered uniform throughout the system. Considering the example presented by Fig. 1.9, where a recipient with rigid walls is connected to a line where a fluid is flowing at a given pressure and temperature, one can say that the fluid must present: a uniform state and the inlet conditions at the bottle are constant, considering adiabatic walls and no mass content at the beginning.



**Fig. 1.9. Uniform Regime representation.**

<sup>1</sup> The levels of vacuum vary from an application to another. Usually, for a vapor compression cycle, vacuum levels of  $10^{-1}$  mbar are already acceptable; however, for heat pipes and loop heat pipes applications, vacuum levels of  $10^{-4}$  mbar are the minimum acceptable along with the proper outgassing of the working fluid and the related procedure for non-condensable gas generation that will be properly addressed on Chapter 5.

For the presented problem and its respective control volume, the Mass Conservation equation can be written as

$$\frac{d}{dt} \int_{C^{\forall}(t)} \rho d\forall + \int_{SC(t)} \rho \vec{V}_r \cdot \hat{n} dS = 0, \quad (1.38)$$

which reduces to

$$\frac{dm}{dt} - \dot{m}e = 0 \quad (1.39)$$

as  $e$  is the energy quantity transported by the flow. The Energy Conservation equation can be presented as

$$\dot{Q}_{C^{\forall}} = \frac{d}{dt} \int_{C^{\forall}(t)} \rho u d\forall + \int_{CS(t)} \rho h \vec{V}_r \cdot \hat{n} dS + \int_{CS(t)} \rho \vec{V}_{CS} \cdot \hat{n} dS + \dot{W}_{C^{\forall}}. \quad (1.40)$$

Since adiabatic walls are considered on this application, the left hand side term vanishes. Once the recipient is made of rigid walls, the third right hand side term also vanishes, and as no work is generated, the fourth right hand side term is equal to zero.

For *Uniform State* of the fluid inside the recipient, the following relations can be written for the first and second right hand terms respectively, as

$$\frac{d}{dt} \int_{C^{\forall}(t)} \rho u d\forall = \frac{d}{dt} (\dot{m}u), \quad (1.41)$$

and

$$\int_{CS(t)} \rho h \vec{V}_r \cdot \hat{n} dS = \dot{m}h_i. \quad (1.42)$$

where  $h_i$  stands for the enthalpy of the fluid at the inlet. The combination of Eqs. (1.41) and (1.42) in Eq. (1.40) results in

$$\frac{d}{dt}(mu) - mh_i = 0. \quad (1.43)$$

Integrating Eq. (1.43), the resultant equation is

$$(m_2u_2 - m_1u_1) - (m_2 - m_1)h_i = 0, \quad (1.44)$$

which is the general equation for *Uniform State*. In the condition where the recipient is under vacuum,  $m_1 = 0$  and  $u_2 = h_e$ .

In the condition where an ideal gas is used

$$u_2 = h_2 - P_2v_2 = h_2 - RT_2. \quad (1.45)$$

Rearranging Eq. (1.45), the temperature  $T_2$  at the end of the filling process can be calculated as

$$T_2 = \frac{c_p}{c_p - R} T_i = \gamma T_i. \quad (1.46)$$

It is important to mention that the process is presented to be completely detached from time. Also, the variation process of  $\gamma$  is instantaneous and takes place as soon as the valve is opened and mass flows into the rigid volume. Once again mentioning the process of transferring the working fluid to a heat pipe or a loop heat pipe, as these devices need to be completely under vacuum prior to be charged, the equilibrium temperature between the bottle and the device is instantaneous. Thus, if an absolute pressure transducer is presented in the device, it is possible to observe that the pressure inside the heat pipe or the loop heat pipe will jump from zero to its saturation pressure according to the local temperature instantly, which is a good method to evaluate whether a leak is present or not.

The following example is intended to better demonstrate the conditions of a *Uniform State* application, which is a very common practice of filling/evacuation processes for many thermal systems.

**Example 1.1:** Consider a tank filled with nitrogen gas at a pressure of 687 kPa and temperature of 298 K (tank A). This tank is con-

connected by a line to a much smaller tank (tank B), which is at atmospheric pressure and 298 K. The smaller tank has a valve at the line that connects it to the bigger tank (valve A); another valve is located at its outlet, which connects to a line that serves a given process (valve B), as presented by Fig. 1.10. Since the smaller tank needs to be filled with nitrogen, valve A will be opened while valve B will remain closed; then, to release the nitrogen to the process, valve B will be opened while valve A remains closed. Calculate the final temperature at both filling and evacuation processes in tank B and how many times valves A and B need to be opened and closed until reaching equilibrium.

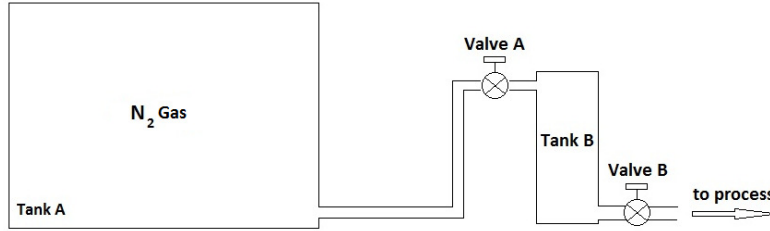


Fig. 1.10. Representation for Example 1.1.

The properties of  $N_2$  gas at tank A can be obtained as  $c_p = 1.0416$  kJ/kg.K,  $c_v = 0.7448$  kJ/kg.K,  $R = 0.2968$  kJ/kg.K. This is a typical *Uniform State* problem, when considering that the volume of tank A is much bigger than tank B, so during the process of opening and closing the valves, the properties in tank A will remain constant. From the initial (1) to final (2) states of the filling process, when valve A is open while valve B is closed, Eq. (1.44) can be applied for this problem as

$$(m_{B_2} u_{B_2} - m_{B_1} u_{B_1}) - (m_{B_2} - m_{B_1}) h_i = 0 \quad (1.47)$$

leading to

$$m_{B_2} (u_{B_2} - h_i) - m_{B_1} (u_{B_1} - h_i) = 0. \quad (1.48)$$

Using Eqs. (1.4), (1.5) and (1.14), Eq. (1.48) results in

$$\frac{P_{B_2} V_{B_2}}{RT_{B_2}} (h_{B_2} - RT_{B_2} - h_i) = \frac{P_{B_1} V_{B_1}}{RT_{B_1}} (h_{B_1} - RT_{B_1} - h_i). \quad (1.49)$$

Since  $V_{B_2} = V_{B_1}$  because tank B has a rigid volume, Eq. (1.49) can be manipulated as follows

$$\frac{P_{B_2}}{T_{B_2}} [T_{B_2} (c_p - R) - c_p h_e] = \frac{P_{B_1}}{T_{B_1}} [T_{B_1} (c_p - R) - c_p h_e], \quad (1.50)$$

$$\frac{P_{B_2}}{T_{B_2}} c_p T_i = P_{B_2} (c_p - R) - \frac{P_{B_1}}{T_{B_1}} [T_{B_1} (c_p - R) - c_p T_i], \quad (1.51)$$

$$T_{B_2} = \frac{P_{B_2} (c_p T_i)}{P_{B_2} (c_p - R) - \frac{P_{B_1}}{T_{B_1}} [T_{B_1} (c_p - R) - c_p T_i]}. \quad (1.52)$$

Rearranging Eq. (1.52), the equation to predict the temperature of tank B for the *filling process* is

$$T_{B_2} = \frac{KT_i}{1 + \frac{P_{B_1}}{P_{B_2}} \left[ K \left( \frac{T_i}{T_{B_1}} \right) - 1 \right]}. \quad (1.53)$$

For the evacuating process, when tank B is already filled with nitrogen gas and valve A is closed while valve B remains open (state 3), the conditions when  $\dot{m}_i = 0$  and  $\dot{m}_o = -dm/dt$  do apply since mass is leaving the volume. This, the Conservation of Mass equation is written as

$$\frac{dU}{dt} + \dot{m}_o h_o = 0 \quad (1.54)$$

and

$$\dot{m}_o + \frac{dm}{dt} = 0. \quad (1.55)$$

Combining Eqs. (1.54) and (1.55) results in

$$\frac{d}{dt}(mu) - h_o \frac{dm}{dt} = 0. \quad (1.56)$$

Working on Eq. (1.56), its development leads to the following:

$$mdu + udm - h_o dm = 0, \quad (1.57)$$

$$mdu + (h_o - pv - h_o)dm = 0, \quad (1.58)$$

$$mc_v dT - RTdm = 0, \quad (1.59)$$

which results in the following differential equation

$$\frac{dT}{T} = \frac{R}{c_v} \frac{dm}{m}. \quad (1.60)$$

Integrating Eq. (1.60) leads to

$$\ln\left(\frac{T_{B_3}}{T_{B_2}}\right) = \frac{R}{c_v} \ln\left(\frac{m_3}{m_2}\right). \quad (1.61)$$

Manipulating Eq. (1.61) and applying the Thermodynamic relations for ideal gases, the equation for the temperature at the *evacuation process* can be written as

$$T_{B_3} = T_{B_2} \left(\frac{P_{B_3}}{P_{B_2}}\right)^{\frac{\gamma-1}{\gamma}}, \quad (1.62)$$

where

$$\gamma = \frac{c_p}{c_p - R}. \quad (1.63)$$

Upon applying the initial conditions at the filling process and calculating the conditions after the evacuation of tank B, the temperatures at each state can be found as presented by Table 1.1, indicating that after the 8<sup>th</sup> operation, the temperatures are stabilized.

**Table 1.1. Temperatures calculation for the filling and evacuation processes.**

Operation	Filling Temperature (K)	Evacuating Temperature (K)
1	393.70	227.98
2	371.53	215.15
3	366.29	212.11
4	364.98	211.36
5	364.66	211.17
6	364.57	211.12
7	364.55	211.11
8	364.54	211.10
9	364.54	211.10

Example 1.2: This is a really interesting application of *Uniform State* and *Ideal Gas* theories, especially for evacuating a vessel with a gas, where the temperature could drop dramatically and become very dangerous. For a well-insulated vessel made from carbon steel filled with nitrogen gas, estimate the bulk gas temperature of the vessel gas for the first 2 minutes, assuming the following characteristics: inside wall area: 9.290 m<sup>2</sup>; volume: 0.7788 m<sup>3</sup>; wall thickness ( $e$ ): 8.38 mm; wall specific heat: 0.419 J/kg K; wall density: 8.46 x 10<sup>3</sup> kg/m<sup>3</sup>; initial pressure: 137.9 bar; initial temperature: 241.5 K; rate of pressure decay: vessel pressure is reduced by a factor of 2 every 1.6 minutes. For the sake of calculations, assume the heat transfer coefficient is 45.4 W/m<sup>2</sup> K for all vessel pressures in excess of 69 bar and 34.1 W/m<sup>2</sup> K for pressures less than 69 bar.

Using Fig. 1.9 as the schematics for this problem, the nitrogen gas properties for the initial conditions are as follows:



$c_p=1.0416 \text{ kJ/kg K}$ ;  $c_v=0.7448 \text{ kJ/kg K}$ ;  $R=0.2968 \text{ kJ/kg K}$ . The Conservation of Mass and Energy are, respectively:

$$\dot{m} + \frac{dm}{dt} = 0 \quad (1.64)$$

$$\frac{d}{dt}(mu) + \dot{m}h = h(T_g - T)A. \quad (1.65)$$

At the vessel wall, we have:

$$\frac{dU_g}{dt} = 0, \quad (1.66)$$

$$m_g c_g \frac{dT_g}{dt} = h A (T - T_g). \quad (1.67)$$

Applying Eq. (1.64) in Eq. (1.65), yields:

$$\frac{d}{dt}(mu) - \frac{dm}{dt}h = -hA(T - T_g). \quad (1.68)$$

Then, applying Eq. (1.68) in Eq. (1.67), after rearranging, results in

$$\rho_g e_g A_g c_g \frac{dT_g}{dt} = \frac{dm}{dt}h - \frac{d}{dt}(mu). \quad (1.69)$$

With the proper manipulation, Eq. (1.69) can be lead to

$$\rho_g e_g A_g c_g \int_1^2 d(T_g) = - \left[ mc_v \int_1^2 dT - RT \int_1^2 dm \right]. \quad (1.70)$$

Using the *Ideal Gas* relation and applying to the above equation, the final temperature can be calculated as

$$T_2 = T_1 - \frac{P_2 V_2}{\rho_g e_g A_g c_g} \left(1 - \frac{c_v}{R}\right) + \frac{P_1 V_1}{\rho_g e_g A_g c_g} \left(1 - \frac{c_v}{R}\right). \quad (1.71)$$

After 2 min, the pressure will be reduced by 2.5 times. Thus, the final pressure will be 55.16 bar. Applying the number in Eq. (1.71), the final temperature will be  $T_2=206.34 \text{ K}$ .

#### ***1.4. Second Law of Thermodynamics – Association with Irreversibilities***

Every thermodynamic process present irreversibilities, as losses will take place despite how good the project is. Those losses are directly related to heat generation caused by friction and/or chemical reactions, for example. On the same way, some thermal applications could not be real without the existing losses, such as the case of a domestic refrigerator. In this analysis, a thermodynamic system is considered operating between two thermal reservoirs, being called heat source and heat sink. Those reservoirs could be admitted as a source to supply or absorb energy without variation of its temperature (example: lakes, oceans, air, etc). It can also be considered as a thermal reservoir systems that operate under two-phase conditions, as during the phase change, the system supplies or absorbs a great amount of energy at a constant temperature.

As a given quantity of energy will be taken from a source and transferred to another, it is convenient to treat those quantities during a process. Imagine that a thermal system is in contact with two reservoirs as shown by Fig. 1.11. The quantity of energy taken from the source (high temperature reservoir) is used to activate the thermal system generating work ( $W_{\text{net}}$ ) and the resulting energy is transferred to the low temperature reservoir ( $Q_L$ ). In this case, the performance achieved during the process can be calculated as:

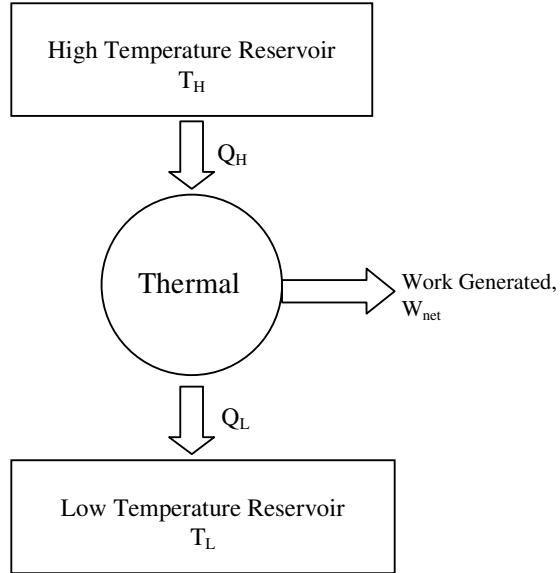


Fig. 1.11. Thermodynamic process between two thermal reservoirs.

$$\dot{W}_{net} = \dot{Q}_H - \dot{Q}_L, \quad (1.64)$$

where

$$\eta_T = \frac{\dot{W}_{net}}{\dot{Q}_H} \quad (1.65)$$

or

$$\eta_T = 1 - \frac{\dot{Q}_L}{\dot{Q}_H}. \quad (1.66)$$

To evaluate the irreversibilities that exist in any thermodynamic process, the Second Law also applies as

$$\delta S \geq \frac{\delta Q}{T} \quad (1.67)$$

once all processes occur at the direction on the decreasing quality of energy. In an irreversible process, the entropy generated represents how irreversible the process is. For such, the Second Law can be defined as represented by the following relation for a closed system:

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} + \dot{S}_{gen}, \quad (1.68)$$

where  $S_{gen} \geq 0$ .

In an open system, where there is flow across the system's boundaries, the entropy generation can be determined by the relation:

$$\frac{dS_{CV}}{dt} = \int_1^2 \frac{\delta Q}{T} + \int_1^2 \dot{m}_i s_i - \int_1^2 \dot{m}_o s_o + \dot{S}_{gen} \quad (1.69)$$

Other Thermodynamic relations are very important for an evaluation of the entire process. The first one is the *Clausius-Clapeyron* relation

$$\left( \frac{dP}{dT} \right)_{sat} = \frac{s_{lv}}{v_{lv}} = \frac{h_{lv}}{T v_{lv}} \quad (1.70)$$

and the *Gibbs-Duhem* equation for a multi-component system

$$\sum_{i=1}^n x_i d\mu_i = -s dT + v dP \quad (1.71)$$

being  $x_i$  the mass fraction of each component  $i$ . For a pure substance, this can be reduced to

$$d\mu = -s dT + v dP \quad (1.72)$$

These concepts can be freely used to treat any heat transfer process, being single or two-phase, when there is mass transfer and consequently an evolution for the system from an initial to a final state. However, depending on the selected mode of analysis, other ways of representing the conservation equations are necessary.

It is important to mention that there are other thermodynamic relations for the Second Law, which are applied for processes involving ideal gases and mixtures, which is especially important for combustion applications. Generally, these relations can be represented as follows:

$$TdS - PdV = dU \quad (1.73)$$

$$dS = \frac{dU}{T} + P \frac{dv}{T} \quad (1.74)$$

$$dS = \frac{dH}{T} + v \frac{dP}{T} \quad (1.75)$$

For an evaluation during a process, we have:

$$s_2 - s_1 = \int_1^2 c_v(T) \frac{dT}{T} + R \ln \frac{v_2}{v_1} \quad (1.76)$$

or

$$s_2 - s_1 = \int_1^2 c_p(T) \frac{dT}{T} - R \ln \frac{P_2}{P_1}. \quad (1.77)$$

On an isentropic process, the following relations are valid:

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{v_1}{v_2}\right)^{k-1}, \quad (1.78)$$

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{P_2}{P_1}\right)^{(k-1)/k} \quad (1.79)$$

or

$$\left(\frac{P_2}{P_1}\right) = \left(\frac{v_1}{v_2}\right)^k. \quad (1.80)$$

Usually, the application of the Second Law of Thermodynamic involves the so-called *entropy* that is frequently avoided, as it is considered a complicated property to be understood. In fact, this property can be directly related to the degree of irreversibilities or the incapacity of the system to return to its initial state after completing a cycle, without spending any energy or generating heat.

Of course, the application of this property depends on the methodology used by the designer, as the combination of the First and Second Laws of Thermodynamics will give both the quantity and quality of the energy in a cycle.

### ***1.5. The Combination of the First and Second Laws of Thermodynamics: The Destruction of the Exergy***

The combination of the First and Second Laws of Thermodynamics are important for any cycle where the designer can evaluate the best operational conditions in order to obtain the higher thermal efficiency possible. Aligned with this methodology, it is inevitable mentioning the *Exergy* which is the energy availability in a system. Such term is usually employed in power generation systems operating in a cycle and is extremely important basically for the evaluation and

prediction of the costs for such energy. Since *Exergy* is related to the available maximum work between two systems, it can and should be used by designers to properly answer the following questions:

- a. Is there enough energy sources to be transformed in work?
- b. The thermal efficiency is the highest possible for this configuration or the project can be improved?
- c. The costs involved with the design and manufacturing of the equipments needed to build the cycle are worth spending in regard to the available energy that will be produced?
- d. The operation costs are reasonable?
- e. How long it will take to have a return on the investment?

These are tough questions to be answered and will require a joint effort between designers, management and investors. However, since the need for new energy sources and innovative forms of power generation are growing, quick answers must be found.

Such an analysis has become extremely important for new lines of energy generation based on renewable resources such as biomasses. The application of biomasses in power generation can be either as a fuel for typical Rankine cycles or used for gasification purposes in combined cycles, on a so called BIG-GTCC (Biomass Integrated Gasification-Gas Turbine Combined Cycle). This last case presents an integrated configuration where a gasifier produces a gas from biomass resources and uses it in a gas turbine to generate electricity; a heat recovery system uses the waste heat to power a Rankine cycle and thus a combined configuration is obtained for maximum power generation. Since the complexity is enhanced in this case, an optimized *Exergy* analysis must be performed in order to properly address the investments in equipments and operation.

This session will briefly present the approach that needs to be taken in order to verify the *Exergy* relation on a system, which can be applied for any power generation cycles based on thermal energy. Such analysis was derived based on the one presented by Bejan [2].

### **1.5.1. Availability in Closed Systems**

For a Closed System, when it is considered that no mass is crossing its boundaries, the Energy and Entropy balances are, respectively

$$E_2 - E_1 = \int_1^2 \delta Q - W \quad (1.81)$$

and

$$S_2 - S_1 = \int_1^2 \left( \frac{\delta Q}{T} \right) + S_{gen} . \quad (1.82)$$

Upon combining Eqs. (1.81) and (1.82) and multiplying them by the temperature at the source  $T_o$ , the following equation can be obtained which deals with the potential energy available in the cycle as

$$E_2 - E_1 - T_o(S_2 - S_1) = \int_1^2 \delta Q - T_o \int_1^2 \left( \frac{\delta Q}{T} \right) - W - T_o S_{gen} . \quad (1.83)$$

As the change on the energy's availability can be determined by the relation

$$A_2 - A_1 = (E_2 - E_1) + P_o(V_2 - V_1) - T_o(S_2 - S_1), \quad (1.84)$$

where  $P_o$  and  $T_o$  are determined by the conditions at the medium. Thus Eq. (1.83) can be rewritten as

$$(A_2 - A_1) - P_o(V_2 - V_1) = \int_1^2 \left( 1 - \frac{T_o}{T} \right) \delta Q - W - T_o S_{gen} \quad (1.85)$$

or

$$(A_2 - A_1) = \int_1^2 \left( 1 - \frac{T_o}{T} \right) \delta Q - [W - P_o(V_2 - V_1)] - T_o S_{gen} . \quad (1.86)$$

The left hand side term is related to the available change on the medium for the process to take place. The combination of the first and second right hand side terms refer to the available transfers and the third right hand term is the destruction of the availability in



the medium, which is directly related to the entropy generation and thus with the irreversibilities of the cycle.

Based on Eq. (1.86) it is also possible to evaluate the availabilities present in a cycle during its operation in regard to the combination of *Exergy*, which has to deal with the one given by heat and work, respectively, as

$$I_H = \int_1^2 \left(1 - \frac{T_o}{T}\right) \delta Q, \quad (1.87)$$

$$I_W = [W - P_o(V_2 - V_1)], \quad (1.88)$$

as well as the availability destruction given by

$$I_D = T_o S_{gen}. \quad (1.89)$$

For the sake of cycle analysis,  $I_D > 0$  results that irreversibilities are present in the system, which is the expected case for any thermal system operating in real conditions;  $I_D = 0$  results that no irreversibilities are present in the system.

Following the above mentioned analysis, the Energy balance for Closed and Open Systems shall be written, respectively, as follows

$$\frac{dA}{dt} = \sum_i \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i - \left(\dot{W} - P_o \frac{dV}{dt}\right) - \dot{I}, \quad (1.90)$$

$$\begin{aligned} \frac{dA_{CV}}{dt} = \sum_i \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i - \left(\dot{W}_{CV} - P_o \frac{dV_{CV}}{dt}\right) + \\ + \sum_i \dot{m}_i a_{f_i} - \sum_o \dot{m}_o a_{f_o} - \dot{I}_{CV}, \end{aligned} \quad (1.91)$$

where the availability in the flow can be defined as

$$a_f = h - h_o - T_o(s - s_o) + \frac{V^2}{2} + gz. \quad (1.92)$$

Equation (1.91) describes how the availability presented in the flow performs the transformations in the system according to the destruction rate (combination of the First and Second Laws). The left hand side of Eq. (1.91) represents the change rate on the availability, the first through the fourth right hand side terms deal with the transfer availability rate and the fifth right hand side is the destruction rate.

Upon designing a cycle to generate power from thermal sources, it is inevitable to consider the *thermal efficiency*. Considering that the thermal efficiency based on a Carnot Cycle (Eq. 1.93) is the highest level that can be reached as it is based on reversible states, the designer can have a guiding value for the entire cycle's efficiency as

$$\eta_C = 1 - \frac{T_L}{T_H}, \quad (1.93)$$

where the temperatures  $T_L$  and  $T_H$  should be taken as absolute temperatures. Upon considering the steady state model of a process presented in Fig. 1.12, the Energy Balance can be described as

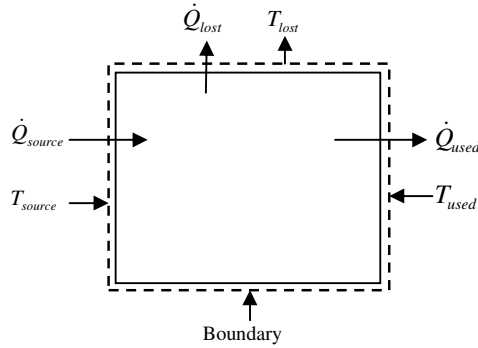


Fig. 1.12. Model for Exergy efficiency.

$$\frac{dE}{dt} = (\dot{Q}_{source} - \dot{Q}_{used} - \dot{Q}_{lost}) - \dot{W}. \quad (1.94)$$

Since the left hand side term vanishes and there is no work generation, Eq. (1.94) can be rewritten as

$$\dot{Q}_{source} = \dot{Q}_{used} + \dot{Q}_{lost} \quad (1.95)$$

and the *Exergy* analysis can be derived as

$$\begin{aligned} \frac{dA}{dt} = & \left[ \left(1 - \frac{T_o}{T_{source}}\right) \dot{Q}_{source} - \left(1 - \frac{T_o}{T_{used}}\right) \dot{Q}_{used} - \left(1 - \frac{T_o}{T_{lost}}\right) \dot{Q}_{lost} \right] - \\ & - \left[ \dot{W} - P_o \frac{dV}{dt} \right] - \dot{i}. \end{aligned} \quad (1.96)$$

Once the left hand side term vanishes as well as the term related to the variation of volume with time ( $dV/dt$ ) and taking into account Eq. (1.95), then

$$\left(1 - \frac{T_o}{T_{source}}\right) \dot{Q}_{source} = \left(1 - \frac{T_o}{T_{used}}\right) \dot{Q}_{used} + \left(1 - \frac{T_o}{T_{lost}}\right) \dot{Q}_{lost} + \dot{i}. \quad (1.97)$$

As the source energy ( $\dot{Q}_{source}$ ) is used ( $\dot{Q}_{used}$ ) or lost ( $\dot{Q}_{lost}$ ), the thermal efficiency can be determined as

$$\eta = \frac{\dot{Q}_{use}}{\dot{Q}_{source}}. \quad (1.98)$$

Then, the effectiveness of the process can be defined as

$$\varepsilon = \frac{\left(1 - \frac{T_o}{T_{used}}\right) \dot{Q}_{use}}{\left(1 - \frac{T_o}{T_{source}}\right) \dot{Q}_{source}} \quad (1.99)$$

where combining Eq. (1.98) and Eq. (1.99) results in

$$\varepsilon = \eta \frac{\left(1 - \frac{T_o}{T_{used}}\right)}{\left(1 - \frac{T_o}{T_{source}}\right)}. \quad (1.100)$$

It is also possible to evaluate the quantity of work lost in an open system by using inefficient forms of converting the available energy into work or by correctly evaluating the governing laws. Considering the representation of an open system as shown by Fig. 1.13 and its related variables, the Energy Balance can be written as

$$\frac{dE}{dt} = \sum_{i=0}^n \dot{Q}_i - \dot{W} + \sum_{inlet} \dot{m} h_0 - \sum_{outlet} \dot{m} h_0, \quad (1.101)$$

where

$$h_0 = h + \frac{V^2}{2} + gz. \quad (1.102)$$

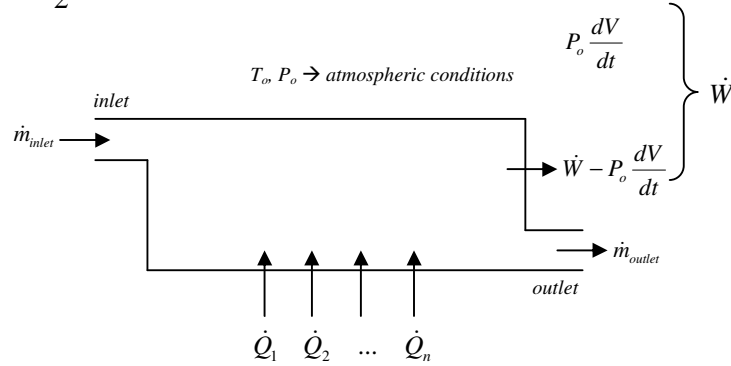


Fig. 1.13. Exergy analysis for an open system.

The entropy generation can be described as

$$\dot{S}_{gen} = \frac{dS}{dt} - \sum_{i=0}^n \frac{\dot{Q}_i}{T_i} - \sum_{inlet} \dot{m} s - \sum_{outlet} \dot{m} s \geq 0. \quad (1.103)$$

Combining Eqs. (1.102) and (1.103) the resulting equation

$$\begin{aligned} \dot{W} = & -\frac{d}{dt}(E - T_o S) + \sum_{i=1}^n \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i + \sum_{inlet} \dot{m}(h_0 - T_o s) - \\ & - \sum_{outlet} \dot{m}(h_0 - T_o s) - T_o \dot{S}_{gen} \end{aligned} \quad (1.104)$$

describes the parameters for the open system to operate at its maximum availability, in regard to the quantity and quality of the energy available to be transformed into work. The first four right hand side terms describe the maximum limit for the work generated, in case  $\dot{S}_{gen} > 0$ . For a reversible system, Eq. (1.104) can be written as

$$\begin{aligned} \dot{W}_{rev} = & -\frac{d}{dt}(E - T_o S) + \sum_{i=1}^n \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i + \\ & + \sum_{inlet} \dot{m}(h_0 - T_o s) - \sum_{outlet} \dot{m}(h_0 - T_o s). \end{aligned} \quad (1.105)$$

Thus, it can be said that

$$\dot{W} = \dot{W}_{rev} - T_o \dot{S}_{gen} \quad (1.106)$$

or

$$\dot{W}_{rev} - \dot{W} = T_o \dot{S}_{gen} \geq 0. \quad (1.107)$$

In this case, for reversible processes,  $\dot{W}_{rev} \geq \dot{W}$ . In the case when the atmospheric conditions with pressure  $P_o$  exchanges work with the system, the fraction of work  $\dot{W}$  that is transferred to the atmosphere is  $P_o dV/dt$ , being the remaining the available work rate represented as

$$\begin{aligned} \dot{E}_W = \dot{W} - P_o \frac{dV}{dt} = -\frac{d}{dt}(E + P_o V - T_o S) + \sum_{i=1}^n \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i + \\ + \sum_{inlet} \dot{m}(h_0 - T_o s) - \sum_{outlet} \dot{m}(h_0 - T_o s) - T_o \dot{S}_{gen}. \end{aligned} \quad (1.108)$$

At the limit of reversibility, the maximum value for the available work will be

$$(\dot{E}_W)_{rev} = \dot{W}_{rev} - P_o \frac{dV}{dt} \quad (1.109)$$

or

$$\begin{aligned} (\dot{E}_W)_{rev} = -\frac{d}{dt}(E + P_o V - T_o S) + \sum_{i=1}^n \left(1 - \frac{T_o}{T_i}\right) \dot{Q}_i + \\ + \sum_{inlet} \dot{m}(h_0 - T_o s) - \sum_{outlet} \dot{m}(h_0 - T_o s). \end{aligned} \quad (1.110)$$

The terms in Eq. (1.110) have the following physical meanings: the left hand side term is the maximum available work for mechanical power; the first right hand side term is the exergy accumulation without flow; the second right hand side term is the exergy transfer done by heat transfer; the third right hand side term is the exergy carried by the inlet mass flow rate; the last right hand side term is the exergy carried by the outlet mass flow rate. All the terms related to Eq. (1.110) can be simplified by an equation that deals with the total work lost in regard to the available work, thus

$$\dot{W}_{lost} = (\dot{E}_W)_{rev} - \dot{E}_W = (\dot{E}_W)_{lost}. \quad (1.111)$$

The presented analysis is extremely useful for a power generation cycle, where heat and work must be treated as useful sources of energy and its correct evaluation of the quantity and quality become important for both technical and economical point of views.

The designer must be aware of such an analysis in order to correctly predict the net efficiency and performance of the power cycle under study, as well as perform its optimization.

### ***1.6. Summary of Fundamental Equations of Conservation***

The following is a summary of the basic and most important analysis that needs to be performed when evaluating a cycle's design. Upon making an analysis based on Equations of Conservation on the integral form, they can be briefly represented as follows:

a. Conservation of Mass:

$$\frac{d}{dt} \int_{CV} \rho \, dV + \int_{CS} \rho \, \vec{V}_R \cdot \hat{n} \, dS = 0; \quad (1.112)$$

b. Conservation of Momentum:

$$\sum \vec{F}_{Ext} = \frac{d}{dt} \int_{CV} \rho \, \vec{V} \, dV + \int_{CS} \rho \, \vec{V} \vec{V}_R \cdot \hat{n} \, dS; \quad (1.113)$$

c. Conservation of Energy:

$$\dot{Q}_{CV} = \frac{d}{dt} \int_{CV} \rho \, e \, dV + \int_{CS} \rho \left( h + \frac{V^2}{2} + g \, z \right) \vec{V}_R \cdot \hat{n} \, dS + \dot{W}_{CV}. \quad (1.114)$$

On the same way, evaluating how a system evolves from one state to another using the differential formulation, the following relations can be written.

a. Conservation of Mass:

$$\frac{d\rho}{dt} + \rho \nabla \cdot \vec{V} = 0; \quad (1.115)$$

b. Conservation of Momentum:

$$\rho \frac{d\vec{V}}{dt} = \nabla \cdot \tau + \rho \vec{g}; \quad (1.116)$$

c. Conservation of Energy:

$$\rho \frac{du}{dt} = \tau \nabla \vec{V} - \nabla \cdot \vec{q}. \quad (1.117)$$

### 1.6.1. Evaluation of Systems

Taking the subject related to a vapor bubble in a liquid medium (Fig. 1.14), it is possible to freely analyze it with respect to the heat transfer occurring on the border between vapor and liquid. In the case of a vapor bubble that continuously grows due to the liquid evaporation on its boundary, let us evaluate what would be the growth rate of the bubble.

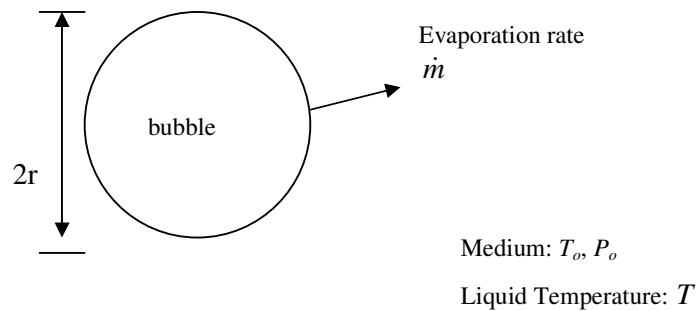


Fig. 1.14. Schematics of a bubble growth and the surrounding conditions.

The First Law based on the Integral Analysis can be written as



$$\dot{Q}_{CV} = \frac{d}{dt} \int_{CV} \rho e dV + \int \rho h \vec{V}_R \cdot \hat{n} dS + \dot{W}_g, \quad (1.118)$$

$$\dot{Q}_{CV} = \frac{d}{dt} (mu)_b + h_v \frac{dm_b}{dt} + \dot{W}_b, \quad (1.119)$$

$$\dot{Q}_{CV} = m_b cp \frac{dT}{dt} - h_v \dot{m}_s + p \frac{dV}{dt}, \quad (1.120)$$

where

$$\dot{W}_b = p \frac{dV}{dt} = \dot{m}_s h_l, \quad (1.121)$$

thus having:

$$\dot{Q}_{CV} = m_b cp \frac{dT}{dt} - h_v \dot{m}_s + h_l \dot{m}_s = m_b cp \frac{dT}{dt} + m_s h_{lv}. \quad (1.122)$$

As  $\dot{Q}_{CV} = k A (T_b - T_l)$ , the relation derives to

$$k A (T_v - T_l) = m_v cp \frac{dT}{dt} + m_s h_{lv}, \quad (1.123)$$

$$m_v cp \frac{dT}{dt} = k A (T_v - T_l) - m_s h_{lv}, \quad (1.124)$$

knowing that  $\dot{m}_b = \rho V_b$ , the above relation becomes:

$$\frac{dT}{dt} = \frac{kA(T_b - T_l) - m_s h_{lv}}{\frac{4}{3} \pi r^3 \rho_v cp_v}. \quad (1.125)$$

Note that the above relation deals with the bubble growth in respect to time, being able to evaluate its behavior as the evaporation occurs at the interface.

### 1.6.2. Conditions of Equilibrium

The conditions of equilibrium occur when there are no modifications on the phases of the substance. If there is still variation on the temperature and, consequently, on the substance's properties, the equilibrium has not been reached and the process analysis becomes a bit more complicated.

To correctly evaluate this process, let us consider the equilibrium conditions in a mixture of a simple compressible substance in a rigid container with thermal insulation. In this case, the work performed on this system is

$$\delta W = PdV . \quad (1.126)$$

Any spontaneous change on the state of the mixture shall satisfy the Second Law and be consistent with the conditions imposed to the system, where:

$$dV = 0; dU = 0; dS \geq 0 . \quad (1.127)$$

Therefore, the conditions of equilibrium will exist if:

$$dF = 0, \quad (1.128)$$

$$dG = 0, \quad (1.129)$$

$$dU = 0, \quad (1.130)$$

where  $G$  is the Gibbs relation defined as  $G = H - TS$  and  $F$  is the Helmholtz relation defined as  $F = U - TS$ .

When the above relations present variations less than zero, then the process occurs naturally. One example to evaluate if the above conditions result in the equilibrium of a system is to evaluate the two-phase mixture in a container, where its condition could be described by the relation:

$$G = n' g'(T, P) + n'' g''(T, P), \quad (1.131)$$

under this condition,  $dn' = -dn''$ , thus:

$$dG = (g' - g'') dn'. \quad (1.132)$$

To exist equilibrium,  $dG = 0$ . Thus,  $g' = g''$  is a valid relation.

***INCLUIR: NOTAS DE AULAS COM PROBLEMAS DO MODELL, EXERGIA E EXERCÍCIOS***

### ***1.7. Thermal Efficiency and Fundamental Discussion on Heat and Work***

Perhaps one of the most intriguing discussions on Thermodynamics is related to the concept of energy involving heat and work. As presented before, heat and work are forms of energy that can be converted one to another, being possible to quantify them by using the First Law of Thermodynamics and check their quality upon using the Second Law of Thermodynamics.

However, such a definition was never too simple and in the beginning of the investigations on thermal cycles many questions were involved in order to better understand the behavior of heat and work.

The great mind behind the definitions that we have today is named Sadi Carnot (1796-1832), who died very early in his life at the age of 36. Even though he was so young when he died, his contributions to Thermodynamics are enormous and impact everyone's life until today. On his book called "*Réflexions sur la puissance motrice du feu et sur les machines propres à développer cette puissance*" [4] he draws the lines related to the theory involved in Thermodynamics especially the ones dealing with heat and work and the first thoughts about reversible and irreversible processes.

It is out of the scope of this book to discuss the findings of Carnot but it is inevitable to point some comments regarding the concepts that he had to courage to write, especially because he was an engineer and not a physicist involved with pure science. Perhaps this is why his findings were not even considered when he published his book, but were well accepted after his death and are still being used today form the basis of Thermodynamics.

There some articles written about this book and how his ideas were disseminated throughout the years. A very good reference for reading is a paper published by Erlichson [5] who explains very carefully the concepts and findings of Carnot. In Carnot's book he mentions the word *caloric* that has been considered by many as the first definition of *entropy*, but one should be careful not to follow this idea. The way I understand is that *caloric* is used to justify the amount of energy available/carried/transferred by a fluid from a high temperature to a low temperature reservoir to generate work. My understanding about it might be not entirely correct, but this is the way I found to suit me better and to continue on the development of this concept on me. There can be found some parallels about this "concept" on the first translation of Carnot's *Réflexions* done by Thruston [6]. My approach on finding answers about some questions.

The confusion generated by the conversion of heat into work, and work into heat is natural and has haunted many people during the years, especially when trying to come up with the thermal efficiency of a cycle. The basic is that the higher the high temperature reservoir and the lower the low temperature reservoir are the highest will be the thermal efficiency of a given thermal cycle. Of course,

the maximum thermal efficiency that can be reached would be if the low temperature reservoir could reach zero Kelvin. Even in Space conditions this is not possible as the lowest temperature registered so far is 4 K in deep Space. Since it is only possible to go to the lowest temperature that the environment allows, the thermal efficiency will be always lower than 100%, also because of irreversibilities.

There are indeed some tendencies regarding the conversion of heat into work and backwards because of confusions regarding ideal and real conversions. A suitable understanding about it is that it is impossible to convert 100% of heat into work, mainly because of irreversibilities involved with the heat generation (incomplete combustion for example) and the irreversibilities in work generation (mainly by friction) - part of the heat will be converted into work and some will be rejected as heat to the environment. However, since work generation implies irreversibilities that generate heat, all work can be converted into heat with 100% efficiency - let's say it is possible to lock an engine while being plugged into the power outlet and the energy that would be used to generate work will be converted into heat with 100% efficiency. Other examples can be used to give basis to this argument, since everything that is irreversible generates heat.

That would be against the argument of Carnot if we were not dealing with the so undesired irreversibilities. Remember that Carnot always look at a cycle with reversible paths (2 adiabatics and 2 isothermals) that could be used in either way as necessary. That's why it might be confusing sometimes. Usually, when performing an analysis of a cycle, the calculation of the maximum thermal efficiency needs to be done following the Carnot's concept based on the highest and lowest temperatures. Then you can be sure that no matter what it is done, the cycle will never present higher thermal efficiency than the one given by a Carnot cycle because it assumes that everything is reversible. When calculating the real thermal efficiency for that very same cycle, the heat and work generated and/or applied are used. This thermal efficiency will of course be lower than the one calculated using Carnot's concept because heat and work *carry all the irreversibilities that a cycle can give - friction, incomplete combustion, parasitic heat transfer, etc.*

Anyhow, one should consider that heat should be heat anyway, but there is the type of heat that is used to generate work and the heat that, during work generation, is dissipated to the environment due to the irreversibilities in the machine. Treating as a form of energy, heat is heat. As far as it can be analyzed, there are no other options for what work could go to besides being transformed in heat.

Such discussions are important to solidify concepts related to the Laws of Thermodynamics, as they will guide any thermal system design no matter how simple or complicated it might be.

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