8. Exergy

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1. Introduction

In this chapter the concept of Exergy will be presented. Through the use of both First and Second Law, the significance of both quantity and quality of energy become essential in energy analysis encountered in engineering applications. Exergy was developed from early concepts presented as *Available Energy* at MIT in the 1940's. The term Available Energy was gradually replaced by *Exergy* first in Europe and then in North America over the past thirty years.

> *All calories are equal, but some are worth more than others.*

A well known utility company sells energy in two forms: electricity and steam.[1] One thousand kJ of steam energy costs about half as much as one thousand kJ of electrical energy. How does this company, and many others just like it justify such a discrepancy of cost for the same thing? Cost analysis holds a distant second place or is often ignored in everyday experiences and cost analysis goes beyond the actual monetary value of energy for it affects the rate of depletion of finite energy reserves, the production of carbon dioxide resulting from fossil fuel combustion, and the overall impact of energy on the environment.

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[1] This illustrative example was paraphrased from Sussman, M. V., "Availability (Exergy) Analysis", Milliken House (1980).

The true cost of energy for a process depends on both the <u>quantity</u> and <u>quality</u> of energy.

The quantity of energy used in a process is calculated by straight forward accounting techniques based upon the principle that energy is never created nor destroyed (the First Law of Thermodynamics). First Law analysis makes no distinction between the energy entering a system and the energy leaving. There is a significant difference in the quality of energy. A gauge or measure of quality is needed to assess the energy value.

This gauge for assessing the quality of energy is the fraction of energy that can be converted into work. In the utility company illustration above, the energy in electrical form can be conveniently and (in an ideal world without friction) completely turned into work with an electric motor. The energy in steam form must be channeled through a thermodynamic cycle with corresponding thermodynamic efficiency losses which of course can be significant.

Exergy, also called free energy or available energy, is that portion of any transferred energy either to or from the system that is available to perform thermodynamic work.

Exergy is that portion of energy that can be converted into useful work.

Exergy is subject to irreversible loss in the course of such work. Since first-law energy is always conserved, it is evident that exergy is an expendable, second-law concept of energy.

2. Exergy Concepts

In order to fully understand and derive the concept of exergy it is necessary to define (or redefine) heat and work within the framework of the Second Law. Here, the Carnot cycle becomes a nice visual tool to understand how irreversible heat transfer processes can be thought of in terms of useful work.

2.1 Heat Exergy

Consider a closed thermodynamic system is at some temperature and pressure above the ambient condition, the environment. The system has internal energy indicative of the translation, rotation, and electronic states of the atoms and molecules that compose the substance within the system. These atoms and molecules will continue to translate, rotate, and possess energy electronically as the system is brought into equilibrium to the surrounding environment, hence the system in equilibrium with the surroundings will continue to possess internal energy. It is only at absolute zero (the Third Law) that all energy ceases to exist and the internal energy is zero. The availability of heat (exergy of heat) is that amount energy that can be transferred to the environment through heat transfer to the point where the system is in

equilibrium with its surroundings. This energy is available. Energy within the system when the system is in equilibrium with its surroundings is unavailable.

To extract the energy from a system the system undergoes a process. Consider a system at T_2, p_2 above the surroundings at T_o, p_o undergoing an isothermal heat transfer process to p_3.
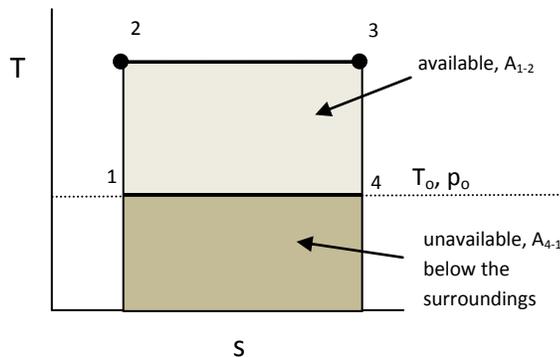
The energy transferred in the form of heat above T, $p_{ambient}$ is available. It can be used to operate an ideal cycle, a Carnot cycle. The energy transferred in the form of heat below is unavailable.

$$W|_{Carnot} = Q_2^3 - Q_4^1$$

$$W|_{Carnot} = \int_2^3 T dS - \int_4^1 T_o dS$$

This work is, by definition, the availability of heat, $X|_{heat}$. The work produced by the idealized Carnot cycle could be used to turn a shaft. It is completely available whereas the energy transferred in the heat rejection process by the Carnot cycle cannot be used. This heat energy is unavailable since the temperature of this rejected heat is at T_o.
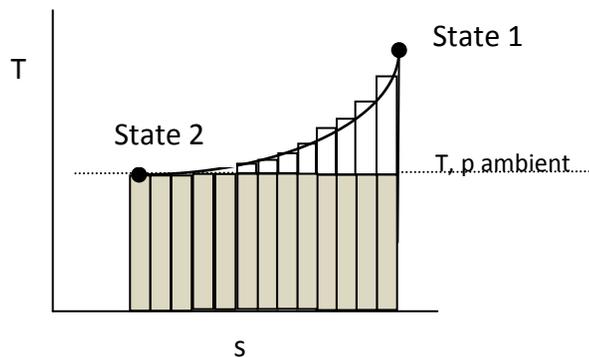
$$X|_{heat} = \int_2^3 T dS - \int_4^1 T_o dS$$

Or

$$X|_{heat} = Q|_{reversible} + \int_4^1 T dS$$

Since $X|_{heat}$ is a function of two thermodynamic properties T and s then $X|_{heat}$ is a thermodynamic property.

The exergy (available energy) of a system is a property.

Consider next a reversible transfer of heat not at constant temperature as shown below.

Work is more valuable than heat since the production of work from heat must incorporate, in thermodynamics, a cycle. Here a series of infinitesimal Carnot cycles can be used to extract the heat and produce W, or exergy, $X|_{heat}$.

For each infinitesimal Carnot cycle, in differential form,

$$\partial X|_{heat} = \partial Q|_{reversible} - T_o dS$$

Example 1.

A rigid tank contains 5 kg of air at 300 kPa and 90 C. Determine the exergy within the tank.

Solution

The maximum energy that could be extracted in the form of heat is

2.2 Work Exergy

In a thermodynamic sense, work, which is energy in transition, exists in several forms. Fundamentally work is defined as a force exerted through a distance, W = F x d, which can represent a mechanical frictionless linear sliding mechanism or a rotating shaft. This work can perpetuate forever if no irreversibilities are present, therefore this work is completely available and can be transformed into other forms of mechanical work again provided the transformation is completely reversible. In the case of moving boundary work such as that encountered in a piston-cylinder arrangement (or diaphragm, flexible container, etc.) the work

required displacing the atmosphere must be taken into account when accounting for the available work.
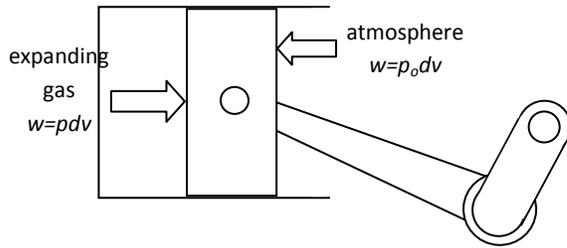
The work required to displace the atmosphere is an irreversibility or lost work during the process. Thus the availability of work in this case is:

$$\Delta X|_{work} = W_{reversible} - \int p_o \, dV$$

Since in the case of a rotating shaft or linearly translating mechanism the dv term is zero then Equation xx is a general case statement for the availability of work.

3. Exergy of a System

The property Exergy is the work potential of a system in a specified environment, usually the atmosphere. Exergy is the maximum amount of work that can be obtained from a system as the system is bought into equilibrium with its surroundings which is referred to as the dead state. Only thermo-mechanical exergy is considered here. Energy from chemical reactions and other forms (such as nuclear, etc.) are not considered here.

The total exergy is that exergy that can be extracted through heat and work processes, hence:

$$\Delta X|_{system} = \Delta X|_{heat} - \Delta X|_{work}$$

Substituting from above

$$\Delta X|_{system} = (Q|_{reversible} - T_o \int dS) - (W_{reversible} - \int p_o \, dV)$$

And rearranging

$$\Delta X|_{system} = Q|_{reversible} - W_{reversible} - T_o \int dS + \int p_o \, dV$$

Introducing the First Law

$$Q - W = \Delta E$$

Eliminates Q and W yielding

$$\Delta X|_{system} = \Delta E - T_o \int dS + \int p_o \, dV$$

Expanding

$$\Delta X|_{system} = \Delta U - T_o \int dS + \int p_o \, dV + m\frac{V^2}{2} + mgz$$

Here V is the velocity of the system relative to the reference frame of the environment and z is the height of the system relative to the reference frame of the environment (where $z_0 = 0$ usually the ground).

3.1 Closed System Exergy

Integrating the above between the state of the system and the dead state yields

$$X = (U - U_0) + p_0(V - V_{0)} + T_0(S - S_0) + m\frac{V^2}{2} + mgz$$

On a unit mass basis the closed system (no mass transfer) exergy is

$$\phi = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{V^2}{2} + gz$$

Where $\phi = \frac{X}{m}$

It is important to note that the exergy of a system is either positive or zero, never negative. Recall by definition exergy is the maximum theoretical useful work obtained from a system, hence it must be either positive or zero. It is also important to note that a system can exist (of course) at temperatures and pressures _lower_ than the environment but that there is a capacity to extract useful work from this potential difference through a Carnot cycle hence the exergy is again positive.

3.2 Open System or Flow Exergy

A flowing fluid (encountered in open system analyses) has an additional form of energy called the flow energy which can be thought of as essentially the boundary work of an element in flow done on the next adjacent element upstream. Thus the flow exergy is equivalent to the exergy

associated with this boundary work in excess of that of boundary work against the atmosphere. Thus

$$x|_{flow} = pv - p_0v = v(p - p_0)$$

Note that conceptually we have replaced the pressure term in the earlier defined flow energy *pv* with the pressure difference *p-p₀* in our definition of flow exergy. *v(p-p₀)*.

The total exergy of a flow stream is then the above term added to the exergy of a non-flowing fluid

$$x_{flowing\ fluid} = x_{non-flowing\ fluid} + x_{flow}$$

Thus

$$x_{flowing\ fluid} = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{v^2}{2} + gz + v(p - p_0)$$

Which, upon combining like terms, reduces to

$$x_{flowing\ fluid} = (u + pv) - (u_0 + p_0v_0) - T_0(s - s_0) + \frac{v^2}{2} + gz$$

And using the definition of entropy *h=u+pv* and using the symbol $x_{flowing\ fluid} = \psi$ we define the flow (or stream) exergy.

$$\psi = (h - h_0) - T_0(s - s_0) + \frac{v^2}{2} + gz$$

Compare the above with that of the closed system defined in the previous step.

$$\phi = (u - u_0) + p_0(v - v_0) - T_0(s - s_0) + \frac{v^2}{2} + gz$$

Exergy Change for a Process

The exergy change of a closed system during any process from state 1 to state 2 is simply the difference between exergy levels

$$X_2 - X_1 = \Delta X = (U_2 - U_1) + p_0(V_2 - V_1) + T_0(S_2 - S_1) + m\frac{V_2{}^2 - V_1{}^2}{2} + mg(z_2 - z_1)$$

Or on a unit mass basis

$$\phi_2 - \phi_1 = \Delta\phi = (u_2 - u_1) + p_0(v_2 - v_1) + T_0(s_2 - s_1) + \frac{V_2{}^2 - V_1{}^2}{2} + g(z_2 - z_1)$$

where

$$\chi = m\phi$$

and

$$\Delta\chi = m(\phi_2 - \phi_1)$$

In a similar fashion, the exergy change of an open system (control volume) during any process from state 1 to state 2 is simply the difference between exergy levels

$$\Delta\psi = (h_2 - h_1) - T_0(s_2 - s_1) + \frac{V_2^2 - V_1^2}{2} + g(z_2 - z_1)$$

4. Effectiveness

The term effectiveness can now be defined and is of value in exergy analysis. Effectiveness compares the ratio of a thermodynamic process to that of an ideal thermodynamic process or cycle. Effectiveness can be thought of as a second law efficiency.

4.1 Effectiveness of a Process.

The effectiveness for a process is simply defined

$$\epsilon = \frac{increase\ in\ exergy\ for\ the\ process}{decrease\ of\ exergy\ for\ the\ process}$$

4.2 Effectiveness of a Cycle

Similarly for a cycle, the effectiveness can be defined in the same manner for all processes comprising a thermodynamic cycle and like the above can be thought of as a second law efficiency

$$\epsilon = \frac{increase\ in\ exergy\ over\ the\ complete\ cycle}{decrease\ of\ exergy\ over\ the\ complete\ cycle}$$

Irreversibility

$$I = \mathrm{X}_{loss} - \mathrm{X}_{gain}$$

Exergy Functions

As exergy is a property, then several exergy functions may be formulated by the application of other thermodynamic property functions and data. Exergy functions are Legendre transformations of the internal energy. For processes involving a system at constant pressure p and temperature T, the Gibbs free energy, $G = H - TS$, is the most useful because, in addition to subsuming any entropy change due merely to heat, it does the same for the pdV work needed to "make space for additional molecules" produced by various processes. (Hence its utility to solution-phase chemists, including biochemists.) The Helmholtz exergy has a special theoretical importance since it is proportional to the logarithm of the partition function for the canonical ensemble in statistical mechanics. (Hence its utility to physicists; and to gas-phase chemists and engineers, who do not want to ignore pdV work.)

The historically earlier Helmholtz free energy is defined as $A = U - TS$, where U is the internal energy, T is the absolute temperature, and S is the entropy. Its change is equal to the amount of reversible work done on, or obtainable from, a system at constant T; thus its appellation "work content" and the designation A from *Arbeit*, the German word for work. Since it makes no reference to any quantities involved in work (such as p and V), the Helmholtz function is completely general: its decrease is the maximum amount of work which can be done *by* a system, and it can increase at most by the amount of work done *on* a system.

Historically, these energy terms have been used inconsistently. In physics, *free energy* most often refers to the Helmholtz free energy, denoted by A, while in chemistry, *free energy* most often refers to the Gibbs free energy.

Problems

Use $T_0 = 298$ K and $p_0 = 100$ kPa for the following problems.

1. Two kilograms of air at 700 kPa and 800 C are constrained in a stationary piston cylinder arrangement. The air expands adiabatically to 150 kPa and 350 C.

a. Determine the exergy of the air in both kJ/kg and kJ at the initial state.

b. Determine the exergy of the air in kJ/kg and kJ after expansion.

c. Determine the change of exergy for the process.

d. If 125 kJ of work are produced determine the effectiveness of this process.

e. Determine the loss of exergy (the irreversibility).

2. Three kilograms of water at 400 C and 4 MPa are contained in stationary a piston cylinder arrangement. The water expands adiabatically to 200 C and 200 kPa.

a. Determine the exergy of the water in both kJ/kg and kJ at the initial state.

b. Determine the exergy of the water in kJ/kg and kJ after expansion.

c. Determine the change of exergy for the process.

d. If 125 kJ of work are produced determine the effectiveness of this process.

e. Determine the loss of exergy (the irreversibility).

3. A large iron block at 500 C is removed from a furnace and cools to 200 C.

a. Determine the exergy of the block in both kJ/kg and kJ at the initial state.

b. Determine the exergy of the block in kJ/kg and kJ after expansion.

c. Determine the change of exergy for the cooling process.

d. Determine the effectiveness of this cooling process.

e. Determine the loss of exergy (the irreversibility).

4. Nitrogen at 600 kPa and 400 C flows into a small turbine and exits at 120 kPa and 100 C. The mass flow rate of the nitrogen is 5 kg/s. Neglect the kinetic and potential energy of the flow.

a. Determine the exergy of the Nitrogen in both kJ/kg and kJ/s at the initial state.

b. Determine the exergy of the Nitrogen in kJ/kg and kJ/s after expansion.

c. Determine the change of exergy for the expansion process.

d. Determine the effectiveness of this expansion process if 200 kJ/s of work is produced.

e. Determine the loss of exergy (the irreversibility).

5. Water at 8 MPa and 600 C flows into a steam turbine with a mass flow rate of 20 kg/s and exits at 140 kPa and 150 C. Neglect the kinetic and potential energy of the flow.

a. Determine the exergy of the water in both kJ/kg and kJ/s at the initial state.

b. Determine the exergy of the water in kJ/kg and kJ/s after expansion.

c. Determine the change of exergy for the expansion process.

d. Determine the effectiveness of this expansion process if 200 kJ/s of work is produced.

e. Determine the loss of exergy (the irreversibility).

6. The driver of a 4000 lbm automobile traveling at 60 mph applies the brakes slowing the auto down to a dead stop. During this process the brake lining temperature abruptly reaches a maximum value of 200 C.

a. Determine the exergy of the automobile in both kJ/kg and kJ/s at the initial state.

b. Determine the exergy of the automobile in kJ/kg and kJ/s after braking to zero velocity.

c. Determine the change of exergy for the process.

d. Determine the effectiveness of this process if the braking energy is discarded to the atmosphere.

e. Determine the effectiveness of this process if the braking energy is stored in batteries by a braking generator instead of friction brakes.

f. Determine the effectiveness of this process if the braking energy is transferred to a Carnot cycle.

g. Determine the loss of exergy (the irreversibility) for all three cases above.