

Availability and Irreversibility

1.0 Overview

A critical application of thermodynamics is finding the maximum amount of work that can be extracted from a given energy resource. This calculation forms the benchmark against which the performances of real, less efficient energy systems are evaluated.

In basic thermodynamics we often use Carnot cycles as indicators of the maximum work that can be extracted by heat engines. Carnot cycles are, however, often unrealistic and overly restrictive since they are limited to cycles that operate between two constant temperature reservoirs. In general, power cycles do not operate between two reservoirs. Let us illustrate this point by a simple example. Figure 1 illustrates how a Rankine cycle is customarily fit between two reservoirs for simple analysis. Here, the actual cycle efficiency can be compared to the Carnot efficiency between the same two reservoirs.

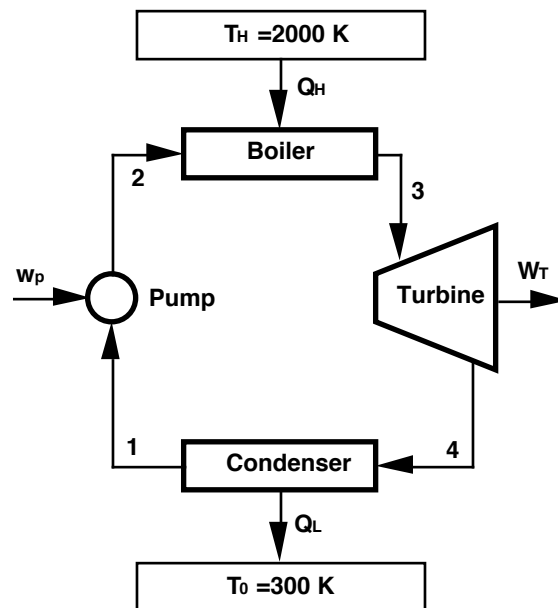


Figure 1. Idealized Rankine cycle operating between two temperature reservoirs.

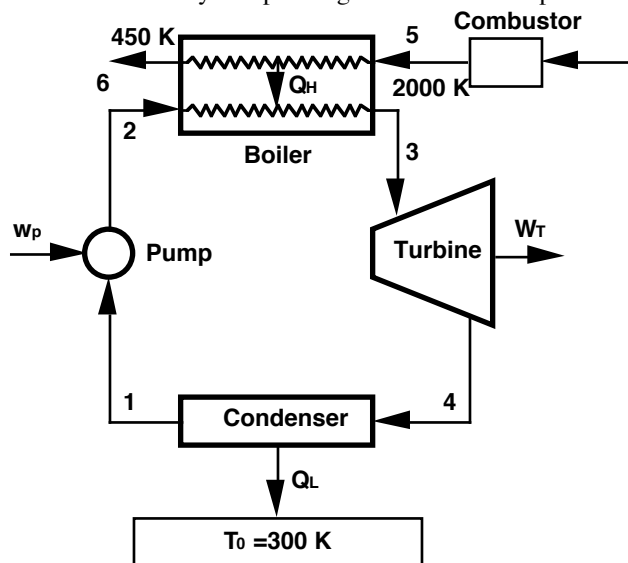


Figure 2. Realistic Rankine cycle based on the boiler acting as a heat exchanger.

However, the heat source in the boiler is not a constant temperature reservoir, but instead a hot combustion product gas that cools as it gives up its heat to the steam, as illustrated in Figure 2. This requires us to develop a somewhat more general benchmark for the maximum work possible, something more appropriate than the Carnot cycle. Fortunately, this is a relatively simple thing to do.

The general idea is that any stream of material that is out of thermal and/or mechanical equilibrium with the environment (such as the 2000 K air stream in Figure 2) represents a source of useful work. The key result from the second law is:

"The maximum work that can be extracted from such a stream occurs when the stream is *reversibly* brought into *thermal and mechanical equilibrium* with the environment."

In other words, if the air stream in Figure 2 (at 100 kPa and 2000 K) is brought by some process reversibly to 100 kPa and 300 K, we will have wrung as much work as we possibly can from the air stream. Once it is at 300 K and 100 kPa, there is no more ΔT or ΔP available to drive any process, and the air is said to be in the "dead state". The correct way to think of the air is as a resource. If our process involves irreversibility, then we do not get as much work out going to the dead state. If we stop short of the dead state (*e.g.*, at 450 K as shown in Figure 2), then there is still ΔP or ΔT left to make more work. Almost everything we deal with in energy systems can be thought of in this way:

- A gallon of gasoline is out of chemical equilibrium with the environment. The maximum work is achieved by reversibly converting it to CO_2 and H_2O at 300 K and 100 kPa (thermal, mechanical, and chemical equilibrium with the environment).
- Steam extracted from a geothermal well is out of thermal equilibrium with the environment. The maximum work is achieved by converting the steam reversibly to 300 K and 100 kPa.
- A supply of compressed air at 1 MPa and 300 K will provide maximum work if it is reversibly converted into a stream of air at 100 kPa and 300 K.

Fortunately, these calculations are easy to perform and do not require you to know any of the details of the process.

We will make use of these concepts to develop two further ideas:

1. We will find the maximum amount of work that can be achieved for a fluid going between any two points (*e.g.*, air going from 1000 K, 1 MPa to 500 K, 400 kPa).
2. We will find an expression for the lost work potential for any process. This is termed the "irreversibility", and it corresponds to how much more work you would achieve if the same process were done reversibly.

2.0 Maximum Work Potential, or Availability

Consider a fluid stream at T_1, P_1 , where the environment is at T_0, P_0 . We hypothesize some generic process that takes the fluid stream to T_0 and P_0 reversibly. Although we do not need to specify such a process to do the calculation, it may be more comforting to give some kind of an example, so let's do so now.

Example 1. An air stream is at 1 MPa, 400 K. Specify a reversible process to take it to the dead state, and find the maximum amount of work that can be extracted. For simplicity, assume constant specific heats at room temperature.

We will do the process in two steps. The first is to use a reversible, adiabatic turbine to take the air to room temperature, but with a pressure that is still above ambient. The second process is to use a constant temperature turbine to expand the air to 100 kPa while absorbing heat from the surroundings. This is shown in the following figure:

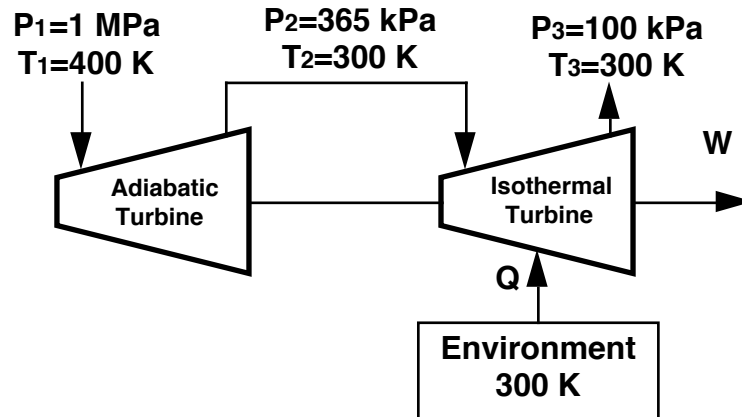


Figure 3. A totally reversible process for taking air at 1 MPa, 400 K to the dead state.

The first turbine is adiabatic and reversible, while the second is internally reversible, and involves only isothermal heat transfer with the environment. Thus the entire process is totally reversible. We get P_2 via an isentropic relation:

$$P_2 = P_1 \left[\frac{T_2}{T_1} \right]^{k/(k-1)} = (1000 \text{ kPa}) \left[\frac{300 \text{ K}}{400 \text{ K}} \right]^{1.4/0.4} = 365 \text{ kPa}$$

For the second turbine, an entropy balance for steady-state operation is

$$s_2 - s_3 + \frac{q_0}{T_0} + \sigma_{cv} = 0$$

so for reversible operation we have:

$$q_0 = T_0 (s_3 - s_2)$$

We can get Δs from the relations in the thermodynamics text:

$$s_3 - s_2 = -R \cdot \ln(P_3/P_2) = -(0.287 \text{ kJ/kg-K}) \cdot \ln(100/365) = 0.371 \text{ kJ/kg-K}$$

So $q_0 = 111.5 \text{ kJ/kg}$. The first law on the second turbine is:

$$q_0 - w_2 = h_3 - h_2$$

But since $\Delta T = 0$, then $\Delta h = 0$ and $q_0 = w_2$. The maximum work (or availability) for this process is then the sum of the work from the two turbines:

$$W_{\max} = C_p(T_1 - T_2) + w_2 = (1.005 \text{ kJ/kg-K}) \cdot (400 - 300 \text{ K}) + 111.5 \text{ kJ/kg} = 212 \text{ kJ/kg}$$

So this tells us that the maximum amount of work that can possibly be extracted from an air stream at 400 K and 1 MPa is 212 kJ for every kg of air processed. The calculation can be repeated for air at any inlet temperature and pressure.

As I promised, this calculation can be set up without needing to know the details of the process. We want to take a stream from P_1 and T_1 to P_0 and T_0 via a totally reversible process. This will look like the following figure:

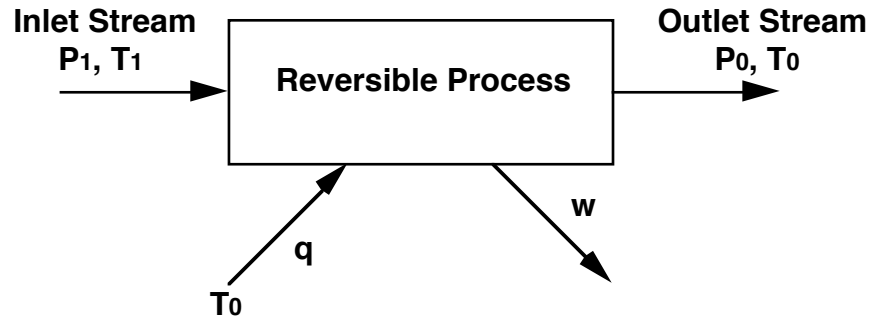


Figure 4. A generic totally reversible process leading to the dead state. The process may involve isothermal heat transfer with the surroundings.

Here, the heat transfer is with the environment. The first law for the process is:

$$W = q + (h_1 - h_0) \quad (1)$$

An entropy balance on the steady-state process is:

$$s_0 - s_1 + \frac{q_0}{T_0} + \sigma_{cv} = 0 \quad (2)$$

so for a reversible process:

$$q_0 = -T_0(s_1 - s_0) \quad (3)$$

Substituting into the first law (Eq. 1) finally yields:

$$W_{\max} = (h_1 - h_0) - T_0(s_1 - s_0) \quad (4)$$

This is then the expression calculating the maximum work attainable for taking a stream that is out of equilibrium with the environment to the dead state, and it can be applied to any material. Let's check our calculation from the first example:

Example 2. Find the maximum amount of work that can be extracted from the air stream from Example 1.

First we find Δs for the process:

$$s_1 - s_0 = C_p \ln \left[\frac{T_1}{T_0} \right] - R \ln \left[\frac{P_1}{P_0} \right] = (1.005 \text{ kJ/kg} \cdot \text{K}) \ln \left[\frac{400}{300} \right] - (0.287 \text{ kJ/kg} \cdot \text{K}) \ln \left[\frac{1000}{100} \right] = -0.372 \text{ kJ/kg} \cdot \text{K}$$

Replacing Δh with $C_p\Delta T$ in Equ. 4 gives:

$$w_{\max} = C_p(T_1 - T_0) - T_0(s_1 - s_0) = (1.005 \text{ kJ/kg-K}) \cdot (400 - 300 \text{ K}) - (300 \text{ K}) \cdot (-.372 \text{ kJ/kg-K}) = 212 \text{ kJ/kg}$$

This matches the answer from Example 1!

Example 3. You have a flow of steam from a geothermal field at 200 kPa, 600°C, and 5 kg/s. Find the maximum amount of work that can be extracted from this resource. The environment is at 20°C and 100 kPa.

Here the dead state will be liquid water at 100 kPa and 20°C. We will approximate the liquid water state as that of saturated liquid at 20°C. This is then just a table lookup with the values inserted in Eq. 4:

$$w_{\max} = (h_1 - h_0) - T_0(s_1 - s_0) = (3704.0 - 83.96 \text{ kJ/kg}) - (293 \text{ K}) \cdot (8.777 - 0.2966 \text{ kJ/kg-K}) = 1135.3 \text{ kJ/kg}$$

Including the mass flow rate yields a maximum possible power output of 5.68 MW.

3.0 Maximum Work between any two States

In Section 2.0 we worked out the way to find the maximum work that could be extracted by reversibly bringing a stream into thermal and mechanical equilibrium with the environment. The next step is to get the maximum work that can be extracted between any two states, such as steam starting at 1000 kPa, 600°C and ending at 100 kPa, 150°C. This is a simple extension of what we did in Section 2.0. See the figure below for the idea:

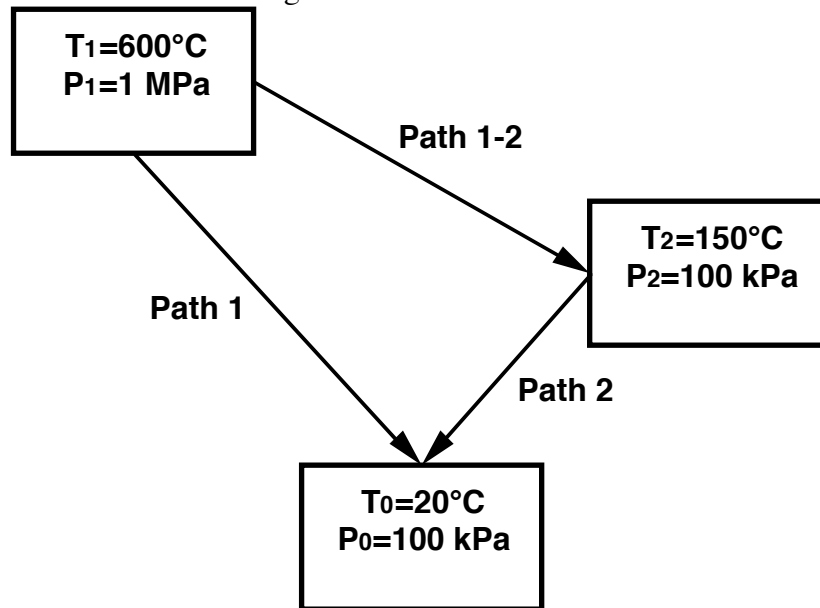


Figure 5. Illustration of two process pathways for reaching the dead state from T_1 and P_1 . One pathway is via T_2 and P_2 .

Each of the paths involves the generation of reversible work and a reversible heat interaction with the environment. We know that all reversible paths connecting the same two endpoints give the same q and w , so:

$$w_1 = w_2 + w_{1-2}, \text{ or } w_{1-2} = w_1 - w_2 \quad (5)$$

Since both Paths 1 and 2 represent maximum work potentials going to the dead state, we can take their difference to get w_{1-2} .

$$w_{1-2} = [h_1 - h_0 - T_0(s_1 - s_0)] - [h_2 - h_0 - T_0(s_2 - s_0)] \quad (6)$$

or,

$$w_{1-2} = h_1 - h_2 - T_0(s_1 - s_2) \quad (7)$$

This equation can be used to calculate the maximum work that can be obtained for a stream going between any two arbitrary states.

Example 4. Find the maximum work that can be obtained from a flow of steam that goes between 1000 kPa, 600°C and 100 kPa, 150°C.

This is just a table lookup for values going into Eq.7:

$$w_{1-2} = h_1 - h_2 - T_0(s_1 - s_2) = (3697.9 - 2776.4 \text{ kJ/kg}) - (293 \text{ K}) \cdot (8.0290 - 7.6134 \text{ kJ/kg-K}) = 799.7 \text{ kJ/kg}$$

So this is the maximum work that can be realized for steam passing between these two states.

At this point the following logical question often comes up: "Why does the environmental temperature, T_0 , figure into this calculation? It does not seem intuitively obvious why this plays a part."

In fact, T_0 does play a part. If we go back to Example 1, the fully reversible process was constructed by first expanding the fluid isentropically until it reached T_0 , and then performing an isothermal expansion (while exchanging heat with the environment) until P_0 was reached. The same idea follows here. To illustrate, let's construct a reversible process for Example 4.

Example 5. Find a reversible process for Example 4 and evaluate the reversible work manually.

This will require a three-stage process which is best illustrated by the T-s diagram shown in Figure 6. The first step is isentropic expansion to 20°C, which results in a two-phase mixture (1-2). The second is isothermal heat extraction from the two-phase mix to the environment, which will condense some of the vapor to liquid, and decrease the steam quality (2-3). The pressure here is the saturation pressure at 20°C, which is 2.339 kPa. The third step is isentropic compression to 100 kPa and 150°C (3-4). All three steps are totally reversible. Since all three processes involve T_0 , the results will depend on T_0 as indicated by Eq. 7.

To carry out the calculation, state 2 will be specified by $T_2 = 20^\circ\text{C}$ and $s_2 = s_1 = 8.029 \text{ kJ/kg-K}$ (where s_1 is from the table for 600°C and 1000 kPa). Entering the tables, we find state 2 is a two-phase mix with $x_2 = 0.924$ and $h_2 = 2350.9 \text{ kJ/kg}$. Working backwards from state 4, we have $T_3 = 20^\circ\text{C}$ and $s_3 = s_4 = 7.6134 \text{ kJ/kg-K}$ (where s_4 is from the table for 150°C and 100 kPa). This also results in a two-phase mix for state 3, with $x_3 = 0.874$ and $h_3 = 2228.8 \text{ kJ/kg}$. From the tables, $h_1 = 3697.9 \text{ kJ/kg}$ and $h_4 = 2776.4 \text{ kJ/kg}$. The total work will be the work released by the expansion from 1-2, minus the work required for the recompression (3-4), or:

$$w_{\text{max}} = (h_1 - h_2) - (h_4 - h_3) = (3697.9 - 2350.9) - (2776.4 - 2228.8) = 799.4 \text{ kJ/kg}$$

This is the same answer as Example 4 within rounding. Note that T_0 played a part in each of the three reversible segments.

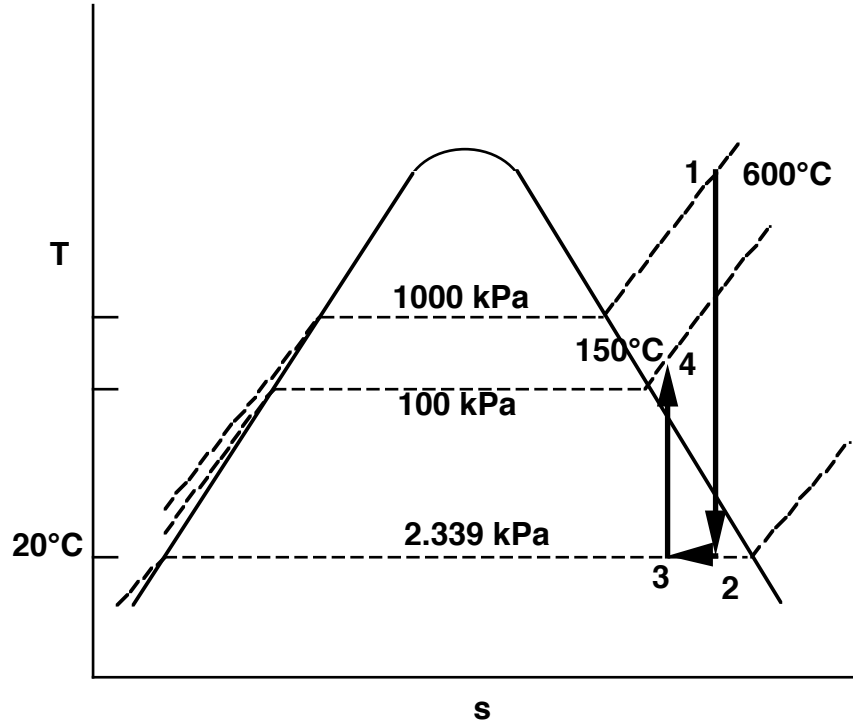


Figure 6. A T-s diagram for the totally reversible expansion of steam from 600°C, 1 MPa to 150°C, 100 kPa.

4.0 Lost Work or Irreversibility

In introductory thermodynamics, we often use the Carnot cycle efficiency to see how close a real cycle comes to an ideal. This does not tell us what part of the real cycle has the most inefficiency associated with it. Irreversibility calculations actually allow us to assign the blame for the difference between ideal and real cycles to specific parts of the cycle. For example, in a Brayton cycle, we can find whether most of the inefficiency is associated with the heat addition step or the heat rejection step. The lost work, or irreversibility, is the amount of potential work that is lost due to irreversibilities in specific parts of a cycle.

Let's consider the heat addition step in a Brayton cycle. Let's assume we heat air from 540 to 1600 K via contact with a thermal reservoir that is at 2000 K:

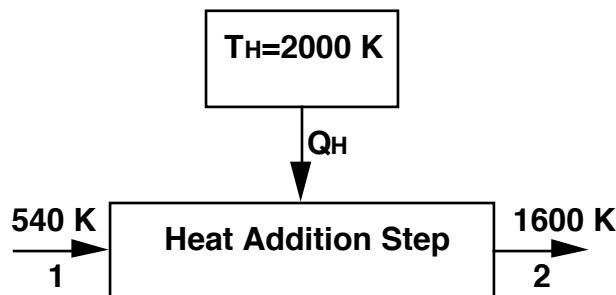


Figure 7. A simple representation for the heat addition step in a Brayton cycle.

We know there is irreversibility associated with this since we are transferring heat across a finite ΔT . The question for a cycle calculation is how much work potential are we losing due to this.

To do this, we need to construct a system with the following three attributes:

1. The system must convert the air at state 1 into state 2.
2. The system must remove the original amount of Q_H from the high temperature reservoir.
3. The entire process must be done totally reversibly.

The following figure shows one process for achieving this.

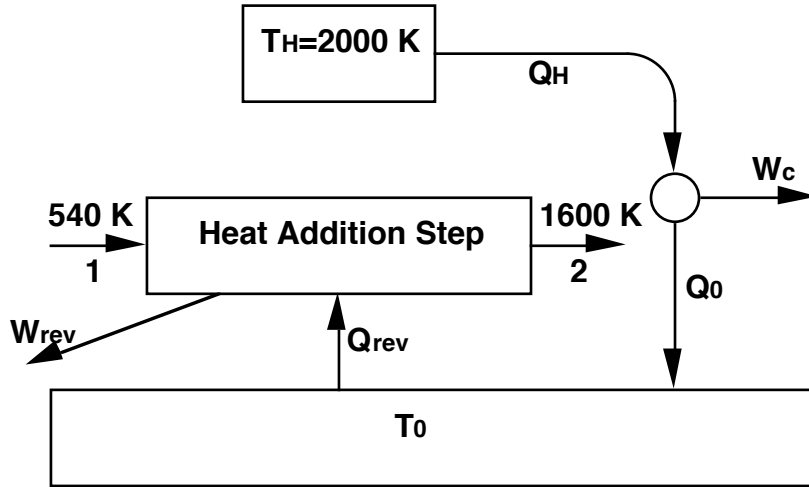


Figure 8. A totally reversible means of achieving the Brayton cycle heating and debiting the same amount of Q_H from the high temperature reservoir.

The heat addition step is now isolated from the high temperature reservoir. The maximum work that can be produced from heat addition step is w_{rev} , which can be calculated via the methods from Section 3 (Eq. 7):

$$W_{rev} = h_1 - h_2 - T_0(s_1 - s_2) \quad (7)$$

Now we need to reversibly debit the original amount of Q_H from the high temperature reservoir. This is easiest to do via a Carnot cycle, which gives:

$$W_c = Q_H \left[1 - \frac{T_0}{T_H} \right] \quad (8)$$

Adding these two together gives the maximum work that can be extracted from this situation, which is equivalent to the work that is lost by doing it the original, irreversible way:

$$W_{lost} = h_1 - h_2 - T_0(s_1 - s_2) + Q_H - \frac{T_0}{T_H} Q_H \quad (9)$$

But the first law on the original process says that $Q_H = h_2 - h_1$, so the Q_H and Δh terms cancel, and we are left with:

$$W_{lost} = i = T_0 \left[s_2 - s_1 - \frac{Q_H}{T_H} \right] \quad (10)$$

It is customary to express the sign of Q_H with respect to the reservoir instead of to the process. With this reversal of sign in mind, the final equation becomes:

$$W_{\text{lost}} = i = T_0 \left[s_2 - s_1 + \frac{Q_H}{T_H} \right] = T_0 S_{\text{gen}} \quad (11)$$

where the sign of Q_H is now referenced to the reservoir by definition.

Example 6. Find the lost work associated with the heat addition step outlined above using Eq. 11.

Since there is no pressure change across the heater,

$$s_2 - s_1 = s_2^o - s_1^o = 3.52364 - 2.29906 \text{ kJ/kg-K} = 1.22458 \text{ kJ/kg-K}$$

We get Q_H from the first law on the system:

$$Q_H = h_2 - h_1 = 1757.57 - 544.35 = 1213.22 \text{ kJ/kg-K}$$

In the final equation, Q_H will be negative since it flows out of the reservoir. The irreversibility is then:

$$i = (300 \text{ K}) \cdot [1.22458 + (-1213.22/2000)] = 185.4 \text{ kJ/kg}$$

5.0 Some Applications

Let's apply Eq. 11 to the simple Rankine cycle shown in Figure 1. Assume the condenser operates at 20 kPa, that state 1 is a saturated liquid, that the boiler pressure is 10 MPa, and that the boiler outlet temperature is 500°C. Assume the turbine efficiency is 87% but the pump is isentropic.

Using the usual Rankine cycle analysis procedures, we find:

Point 1:	$h_1 = 251.40 \text{ kJ/kg}$	$s_1 = 0.832 \text{ kJ/kg-K}$	
Point 2:	$h_2 = 261.55 \text{ kJ/kg}$	$s_2 = 0.832 \text{ kJ/kg-K}$	
Point 3:	$h_3 = 3373.7 \text{ kJ/kg}$	$s_3 = 6.5966 \text{ kJ/kg-K}$	
Point 4:	$h_4 = 2328.47 \text{ kJ/kg}$	$s_4 = 7.066 \text{ kJ/kg-K}$	$x_4 = 0.881$

From this we get:

$$Q_H = h_3 - h_2 = 3112.15 \text{ kJ/kg}$$

$$Q_L = h_4 - h_1 = 2077.07 \text{ kJ/kg}$$

$$W_{\text{net}} = Q_H - Q_L = 1035.08 \text{ kJ/kg}$$

$$\eta_{\text{cycle}} = W_{\text{net}} / Q_H = 0.332$$

Next we will get the irreversibility associated with each process in the cycle using Equ. 11.

$$i_{1-2} = 0$$

$$i_{2,3} = (300 \text{ K}) \cdot [6.5966 - 0.832 + (-3112.15/2000)] = 1262.56 \text{ kJ/kg}$$

$$i_{3,4} = (300 \text{ K}) \cdot [7.066 - 6.5966] = 140.82 \text{ kJ/kg}$$

$$i_{4,1} = (300 \text{ K}) \cdot [0.832 - 7.066 + (+2077.07/300)] = 206.87 \text{ kJ/kg}$$

One way to think of the maximum possible cycle efficiency is to add the actual cycle work to all the lost work (irreversibilities) and divide by Q_H . If we do that we get:

$$\eta_{\max} = (1035.08 + 1262.56 + 140.82 + 206.87)/(3112.15) = 0.8500$$

If we compare this with the Carnot efficiency for an engine operating between the same two reservoirs, we get:

$$\eta_{\text{Carnot}} = 1 - T_0/T_H = 1 - (300)/(2000) = 0.8500$$

So the irreversibility calculation gives the same result as the Carnot calculation! The difference is that the irreversibility calculation takes the overall inefficiency and divides it between the various components. This allows the designer to decide where to most profitably focus cycle improvements.

One way to think about this is that the total work potential [=Qin*(Carnot efficiency)] must equal the net work plus all the irreversibilities. The following is a table showing this:

<u>Component</u>	<u>Percent of Total Availability</u>
Net Work	39.13
Pump	0.0
Heat Addition	47.73
Turbine	5.32
Heat Rejection	7.82

So the second law efficiency (fraction of total possible work realized) is 39.13%

Next, let's apply the same analysis to the more realistic configuration shown in Figure 2. All the properties associated with states 1-4, as listed above, stay the same, as do Q_H , W_{net} , $i_{3,4}$ and $i_{4,1}$. The only difference is the heat exchanger. The first law on the exchanger is:

$$\dot{m}_a (h_5 - h_6) = \dot{m}_s (h_3 - h_2)$$

This is rearranged to give the ratio of air flow to steam flow:

$$\frac{\dot{m}_a}{\dot{m}_s} = \frac{(h_3 - h_2)}{(h_5 - h_6)} = \frac{(3373.7 - 261.55)}{(2252.1 - 451.80)} = 1.729 \text{ kg air/kg steam}$$

Now, we get the availability of the air stream at 2000 K from Equ. 4:

$$W_{\max} = (2252.1 - 300.19 \text{ kJ/kg}) - (300 \text{ K}) \cdot (3.7994 - 1.70203 \text{ kJ/kg-K}) = 1322.70 \text{ kJ/kg air}$$

So this is the maximum amount of work that can be extracted from the 2000 K air stream on a kg-air basis. Now we convert W_{net} from the previous calculation to a kg-air basis for comparison:

$$W_{\text{net,air}} = W_{\text{net,steam}} / (1.729 \text{ kg air/kg steam}) = 1035.08 / 1.729 = 598.66 \text{ kJ/kg-air}$$

This means our process is losing $1322.7 - 598.66 = 724.05 \text{ kJ/kg-air}$ of work potential. Let's see where it is going.

The irreversibilities associated with the turbine and the heat rejection step stay the same, although we need to adjust them to a kg-air basis:

$$i_{3,4} = 81.45 \text{ kJ/kg-air}$$

$$i_{4,1} = 119.65 \text{ kJ/kg-air}$$

The irreversibility associated with the heat addition step requires that we modify Eq. 11 to account for two inlets and two exits. Note that no heat crosses the boundary of the heat exchanger. On a kg-air basis:

$$i_{\text{heatexchanger}} = T_0 \cdot [(s_6^0 - s_5^0) + \left(\frac{\dot{m}_s}{\dot{m}_a} \right) (s_3 - s_2)] = (300\text{K}) \cdot [2.11161 - 3.7994 + (6.5966 - 0.832) / 1.729]$$

$$= 493.88 \text{ kJ/kg-air}$$

The final issue is the availability lost to the system associated with the exhaust of the air at 450 K (*i.e.*, above the ambient). More work could theoretically be extracted by taking this stream reversibly to the dead state. The availability of this stream can be obtained from Eq. 4:

$$W_{\text{max}} = (h_6 - h_0) - T_0(s_6 - s_0) = (451.8 - 300.19 \text{ kJ/kg}) - (300 \text{ K}) \cdot (2.11161 - 1.70203 \text{ kJ/kg-K})$$

$$= 28.74 \text{ kJ/kg-air}$$

Now we can add all the irreversibilities and lost availability and see if they sum to the total lost work of 724.05 kJ/kg-air :

$$i_{\text{total}} = 81.45 + 119.65 + 493.88 + 28.74 = 723.72 \text{ kJ/kg-air}$$

So within rounding we have accounted for all the lost work in detail. Now let's look at how the total availability of the resource represented by the 2000 K air is allocated:

Element	Percent of Availability
Net work recovered	45.27
Irreversibility for high-T heat exchange	37.35
Irreversibility for heat rejection	9.05
Turbine irreversibility	6.16
Irreversibility for hot air exhaust	2.17

So we see that the biggest problem is in the boiler heat transfer process, due to the large ΔT between the air and steam. The second law efficiency ($W_{\text{net}}/W_{\text{max}}$) is 45.27% for this more realistic cycle. This is a much more meaningful number than the 39.06% based on the existence of a high temperature reservoir as a heat source, since no such reservoir really exists.

6.0 Summary

Energy resources can generally be thought of as streams that are out of thermal or mechanical equilibrium with the environment. The maximum possible work (availability) is achieved when

these streams are brought into equilibrium with the environment (the dead state) in a reversible way. For a process that moves between a state 1 and 2, neither of which is the dead state, the maximum possible work is realized by constructing a totally reversible path connecting the two. Simple equations for calculating both of these are available, and they do not require you to specify the process.

One can calculate the amount of work potential that is lost for any real operation (irreversibility). The sum of all these irreversibilities and the actual work recovered must equal the availability of the resource stream that drives the process. This allows one to evaluate the relative importance of each of the irreversibilities within a complex process, something that is valuable when deciding where you want to invest design effort and capital. Simple equations are available for calculating irreversibility for the common situations of adiabatic flow systems, heat exchangers, or flow systems involving heat exchange with a single reservoir. These cover all the situations normally encountered in analyzing energy systems.