

Chapter 7

Entropy

In the preceding chapter we obtained a number of important results by applying the second law to cyclic processes associated with heat engines and reversed heat engines operating with one and two thermal reservoirs. The concept of a reversible process, though an idealization of real processes, provided a means to find the upper limit of the efficiency of heat engines operating with two heat reservoirs. The maximum efficiency, called the Carnot-cycle efficiency, is a unique function of the two reservoir temperatures. This led to the development of the thermodynamic temperature scale. Finally, we generalized these results for cyclic systems experiencing heat interactions with any number of thermal reservoirs.

In this chapter we shall extend the application of the second law to closed systems undergoing any process, reversible or otherwise. The main outcome of this effort is the emergence of a new system property called entropy which has a broad significance and very wide applications.

7.1 The Clausius Inequality and Entropy

To apply the second law to a system that executes a cycle exchanging heat over a range of temperatures we consider the arrangement shown in Fig. 6.16. The cycle executed by the system S could be internally reversible or irreversible but the heat interactions between the various thermal reservoirs and the system are *reversible*. This is the main difference between the present development and the analysis in Sec. 6.5.5. For external reversibility the temperature T_i of the secondary

reservoir must be equal to the temperature T of the system where heat is received during the process. Since we expect the temperature T to change during the process, we need to have a series of secondary reservoirs with the associated heat engines to achieve reversible heat transfer. Under these new conditions we can rewrite Eq. (6.49) as

$$\sum \frac{\Delta Q_{si}}{T_i} \leq 0 \quad (7.1)$$

where ΔQ_{si} is the heat flow from the reservoir whose temperature T_i is equal to the temperature T of the system at the location where heat is received.

Considering an infinitesimal heat transfer δQ at temperature T , we can express Eq. (7.1) in the cyclic integral form

$$\oint_{cyclic} \frac{\delta Q}{T} \leq 0 \quad (7.2)$$

Equation (7.2), which now involves only the heat input to the system and the temperature of the system at the location where heat is received, is called the *Clausius inequality*.

As we discussed in Sec. 6.5.3 the equality signs in Eqs. (7.1) and (7.2) apply when the cycle executed by the system is *internally reversible* and the inequality is for *irreversible* cycles. For internally reversible processes the temperature T of the system is uniform because the process occurs quasi-statically. However, for internally irreversible processes there could be temperature gradients within the system because the process is not necessarily quasi-static. For this situation, the term T in Eq. (7.2) is the temperature at the location on the boundary where the heat input δQ enters the system as indicated in Fig. 6.16.

7.1.1 Entropy – A thermodynamic property

Consider a closed system executing a *reversible* cycle 1-A-2-B-1 shown in Fig. 7.1. Applying Eq. (7.2) with the equality sign we have

$$\int_{1A}^2 \frac{\delta Q}{T} + \int_{2B}^1 \frac{\delta Q}{T} = 0 \quad (7.3)$$

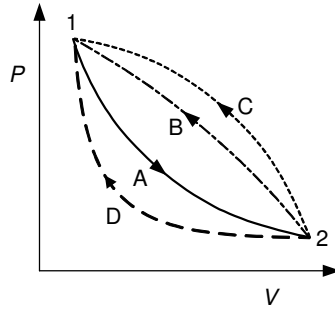


Fig. 7.1 P-V diagram of process

We now envisage an alternative reversible process, 2-C-1 that returns the system from states 2 to 1 thus completing the cycle. Applying Eq. (7.2) to the cycle 1-A-2-C-1 we obtain

$$\int_{1A}^2 \frac{\delta Q}{T} + \int_{2C}^1 \frac{\delta Q}{T} = 0 \quad (7.4)$$

Subtracting Eq. (7.3) from Eq. (7.4)

$$\int_{2B}^1 \frac{\delta Q}{T} = \int_{2C}^1 \frac{\delta Q}{T} \quad (7.5)$$

Since the process C was selected arbitrarily, it follows from Eq. (7.5) that the quantity, $(\delta Q/T)$ is *path-independent*. It is, therefore, a property of the system which depends only on state 1 and state 2. Hence we have

$$\int_2^1 \frac{\delta Q}{T} = S_1 - S_2 \quad (7.6)$$

This new property, denoted by S in Eq. (7.6), is called the *entropy* of the system. It is an *extensive* property that depends on the mass of the system. We recall that the internal energy of a system arose as a consequence of the first law. In a similar manner, the application of the

second law has predicted the existence of this new property but offers no additional information on its physical meaning. Later in this chapter we shall briefly discuss the microscopic interpretation of entropy.

We now select an *irreversible* process D, shown in Fig. 7.1, to return the system from state 2 to state 1. This choice makes the cycle 1-A-2-D-1 *internally irreversible*. Applying Eq. (7.2) with the inequality sign we have

$$\int_{1A}^2 \frac{\delta Q}{T} + \int_{2D}^1 \frac{\delta Q}{T} < 0 \quad (7.7)$$

From Eqs. (7.4) and (7.7) it follows that

$$\int_{2C}^1 \frac{\delta Q}{T} > \int_{2D}^1 \frac{\delta Q}{T} \quad (7.8)$$

From Eqs. (7.8) and (7.6) we have

$$S_1 - S_2 > \int_{2D}^1 \frac{\delta Q}{T} \quad (7.9)$$

For an infinitesimal change of state we can write the differential form of the above relations as

$$dS = \left(\frac{\delta Q}{T} \right)_{rev} \quad (7.10)$$

$$dS > \left(\frac{\delta Q}{T} \right)_{irr} \quad (7.11)$$

It is noteworthy that in Eq. (7.10), T is the system temperature, which is uniform for *internally reversible* processes while in Eq. (7.11), T is the temperature at the location on the boundary where heat enters the system. The above equations constitute the mathematical formulation of the second law.

7.1.2 The temperature-entropy diagram

The P - V diagram is a useful graphical aid for representing quasi-static processes because the area under the curve is proportional to the work done during the process. In a similar manner we can use a temperature-entropy diagram (T - S diagram) of a *reversible* process to obtain the heat transfer. This follows from Eq. (7.10), which, for a reversible process, may be written as

$$\delta Q_{rev} = TdS \quad (7.12)$$

Integration of Eq. (7.12) gives

$$Q = \int_i^f TdS \quad (7.13)$$

where i and f represent the initial and final states of the system.

A temperature-entropy diagram for a cyclic process consisting of three *reversible* processes is shown in Fig. 7.2. From Eq. (7.13) it follows that the area under the curve 1-2 is the heat *input* to the system during the *reversible* process 1-2. For the process 2-3 the area is traced in the negative S -direction when the system moves from the initial state 2 to the final state 3. We interpret this as a negative area which corresponds to a heat *output* for the process 2-3. For the process 3-1, $dS = 0$. It follows from Eq. (7.12) that $\delta Q_{rev} = 0$, and therefore the process 3-1 is reversible and adiabatic. Such a process is called an *isentropic* process

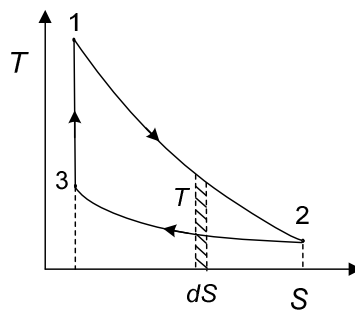


Fig. 7.2 Temperature-entropy (T - S) diagram

because the entropy remains constant during the process and it can be represented by a straight line parallel to the T -axis as seen in Fig. 7.2. For the cyclic process 1-2-3-1 the area enclosed by the three curves is the net heat *input* to the system during the process.

7.1.3 The ' T - ds ' equation

We shall now derive a useful property relation that involves the zeroth law, the first law and the second law for a *simple* thermodynamic system.

Consider an infinitesimal process in a closed system. Applying the first law we have

$$\delta Q = dU + \delta W \quad (7.14)$$

Since the process is reversible

$$\delta W = PdV \quad (7.15)$$

Applying the second law [Eq. (7.10)] to the *reversible* process

$$dS = \left(\frac{\delta Q}{T} \right)_{rev} \quad (7.16)$$

Manipulating Eqs. (7.14), (7.15) and (7.16) we obtain

$$TdS = dU + PdV \quad (7.17)$$

Note that Eq. (7.17) is a relationship between thermodynamic properties of the system and is therefore independent of the process. Moreover, it is independent of the substance constituting the system. This important relation, sometimes called the ' T - dS equation', involves the zeroth law through the concept of temperature, the first law through the internal energy function and the second law through the entropy and thermodynamic temperature.

7.1.4 Entropy of an ideal gas

Since the entropy is a property, it is possible to express the entropy as $S = S(V, T)$, following the two-property rule for a pure substance. We shall now proceed to obtain this property relation for an ideal gas.

Consider a fixed mass m of an ideal gas subjected to a *reversible* process from an initial state (P_o, V_o, T_o) to a final state (P, V, T) .

The equation of state of the ideal gas is

$$PV = mRT \quad (7.18)$$

The internal energy of the ideal gas may be expressed as

$$U = mc_v T + U_{ref} \quad (7.19)$$

where U_{ref} is the internal energy of the reference state.

Differentiating Eq. (7.19)

$$dU = mc_v dT \quad (7.20)$$

Substituting in the T - dS equation [Eq. (7.17)] from Eqs. (7.18) and (7.20) we obtain

$$TdS = mc_v dT + mRTdV/V \quad (7.21)$$

$$dS = mc_v dT/T + mRdV/V \quad (7.22)$$

Integrating Eq. (7.22) from the initial state to the final state we have

$$S = S_o + mc_v \ln(T/T_o) + mR \ln(V/V_o) \quad (7.23)$$

Substituting for V in Eq. (7.23) from Eq. (7.18) we obtain a property relation of the type, $S = S(P, T)$.

$$S = S_o + mc_v \ln(T/T_o) + mR \ln(TP_o/T_o P) \quad (7.24)$$

$$S = S_o + m(c_v + R) \ln(T/T_o) - mR \ln(P/P_o)$$

$$S = S_o + mc_p \ln(T/T_o) - mR \ln(P/P_o) \quad (7.25)$$

We note that Eqs. (7.23) and (7.25) are relationships between properties of an ideal gas and therefore applicable to any *equilibrium* state. Moreover, the initial state denoted by o can be regarded as the reference state in a tabulation of data for the entropy.

The T - S diagram for an ideal gas may be drawn by making use of the analytical expressions in Eqs. (7.23) and (7.25). Since these involve three variables we need to draw families of curves keeping one of the variables fixed. For example, for an ideal gas, the constant-pressure lines on the

T - S diagram are logarithmic curves according to Eq. (7.25). The relevant expressions for these variations are derived in worked example 7.4.

7.1.5 Entropy of a pure thermal system

We shall now obtain a general expression for the entropy change of a pure thermal system which is an idealized model applicable to solids and incompressible fluids. For such systems the specific heat capacity is a constant. Consider an infinitesimal *reversible* heat transfer, δQ to the system. Applying the second law we obtain

$$\delta Q = TdS \quad (7.26)$$

Applying the first law with zero work transfer

$$\delta Q = dU = MCdT \quad (7.27)$$

where M and C are the mass and specific heat capacity of the pure thermal system.

From Eqs. (7.26) and (7.27) we obtain

$$TdS = MCdT \quad (7.28)$$

Integrating Eq. (7.28) from the reference state to the general state

$$S = S_{ref} + MC \ln(T / T_{ref}) \quad (7.29)$$

where the sub-script '*ref*' denotes the properties at the reference state.

7.1.6 Entropy of a pure substance

Shown in Fig. 7.3 is the T - S diagram for a pure substance undergoing a reversible constant pressure heating process. At A, the fluid is a sub-cooled liquid at a pressure P . As heat is supplied to the fluid at constant pressure, the process on the T - S diagram follows the curve A-B up to B where evaporation just begins. The section B-C of the curve corresponds to the evaporation process where S increases while T remains constant because of the constant pressure. At C evaporation is complete and along the section C-D, the vapor becomes superheated.

7.2 Principle of Increase of Entropy

The principal of increase of entropy can be deduced by combining Eqs. (7.10) and (7.11) to the form

$$dS \geq \left(\frac{\delta Q}{T} \right) \quad (7.32)$$

Consider the system A that interacts with a heat reservoir R and a mechanical energy reservoir MR as shown in Fig. 7.4. MR could be a simple pulley-weight arrangement connected to A with a frictionless shaft. During an infinitesimal change in the state of A its entropy increases by dS while the corresponding change in entropy of the reservoir is dS_r . The heat and work interactions between the system and its surroundings, constituted by R and MR, during the process are δQ and δW respectively. Consider an imaginary boundary C, indicated by the broken-lines in Fig. 7.4, enclosing A, R and MR such that nothing outside of it affects the inside significantly. We call the region within C an *isolated* system for which the heat interaction $\delta Q_c = 0$. Applying Eq. (7.32) to the isolated system C we have

$$(dS)_c \geq 0 \quad (7.33)$$

Being an extensive property, we can add the entropy changes of the different sub-regions that constitute C to write Eq. (7.33) in the form

$$(dS)_c = dS + dS_r + dS_{mr} \geq 0 \quad (7.34)$$

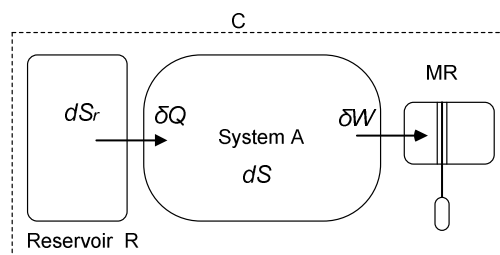


Fig. 7.4 Principle of increase of entropy

Since the entropy change, dS_{mr} of the mechanical energy reservoir MR is zero, Eq. (7.34) becomes

$$dS + dS_r \geq 0 \quad (7.35)$$

We conclude from the above equation that if all the processes occurring within an *isolated* system are *reversible* the entropy of the system remains constant, otherwise the entropy must increase due the *irreversible* processes. This statement, whose mathematical form is Eq. (7.35), is commonly called the *principle of increase of entropy*. Although the principle of increase of entropy stipulates that the entropy of an *isolated* system can only increase or remain constant, the entropy of some of the individual sub-regions that constitute the isolated system may decrease.

Now the heat transfer to the thermal reservoir R is reversible because its temperature is constant. Therefore by applying Eq. (7.32) with the equality sign we obtain the entropy change of R as

$$dS_r = -\delta Q/T_r \quad (7.36)$$

Substituting from Eq. (7.36) in (Eq. 7.35) we have

$$dS - \delta Q/T_r \geq 0 \quad (7.37)$$

Equation (7.37) implies that the entropy of the system A must increase to compensate for the entropy decrease of the reservoir R so that the overall entropy of the isolated system C increases or remains constant. Otherwise the process would violate the second law.

We shall generalize the increase of entropy principle and make it quantitative by introducing a variable called the *entropy production*. Consider any system and its interacting surroundings that are enclosed in an imaginary boundary and therefore *isolated* (Fig 7.4). The entropy production is given by

$$\delta\sigma = dS_{system} + dS_{surroundings} \geq 0 \quad (7.38)$$

The equality sign in Eq. (7.30) applies when all the processes within the *isolated* system are reversible and the entropy production, $\delta\sigma$ is therefore zero. On the other hand positive values of $\delta\sigma$ indicate the occurrence of irreversible processes within the isolated system and its magnitude provides an indirect measure of the impact of the

irreversibilities on the work output. Note that the entropy production σ is not a property of the system like the entropy S . Therefore σ depends on the type of irreversible process experienced by the system.

7.2.1 Storage, production and transfer of entropy

When the principle of increase of entropy, in the form of Eq. (7.38), is applied to real systems we need to distinguish between three different quantities. These are called *stored* entropy, *entropy transfer* and *entropy production*. We shall illustrate the difference between the above terms using a practical situation.

Consider as a system the gas contained in the rigid vessel shown in Fig. 7.5 where a rotating paddle wheel supplies work to the system. The vessel is in thermal communication with a single heat reservoir at temperature T_o . The system undergoes a process where the paddle wheel is rotated for fixed duration of time and then stopped. Denoting the initial and final equilibrium states by 1 and 2 we apply the first law to the process 1-2 executed by the system to obtain

$$U_2 - U_1 = W_{12} - Q_{12} \quad (7.39)$$

where $(U_2 - U_1)$ is the *increase* in internal energy, Q_{12} heat *output* from the system to the reservoir and W_{12} is the work *input* to the system through the paddle wheel during the process.

The application of Eq. (7.32) in the integrated form to the system gives

$$(S_2 - S_1) \geq -\int_1^2 \frac{\delta Q}{T} \quad (7.40)$$

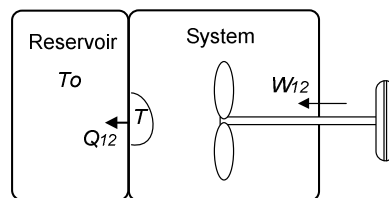


Fig. 7.5 Entropy changes in system and reservoir

The negative sign in Eq. (7.40) signifies a heat *output* from the system as indicated in Fig. 7.5.

We convert Eq. (7.40) to an equality by introducing the entropy production term σ . This gives

$$(S_2 - S_1) = \sigma - \int_1^2 \frac{\delta Q}{T} \quad (7.41)$$

In Eq. (7.41), T is the temperature of the location on the boundary at which heat is transferred from the system to the reservoir.

In order to evaluate the integral in the above equation we need to know how the temperature T varies during the process. Because the irreversible work input by the paddle wheel, shown in Fig 7.5, causes considerable turbulence, it is not possible to determine the variation of T in a straightforward manner. Moreover, T may not be spatially uniform within the system. For the purpose of the present discussion we resolve this difficulty by locating the system boundary in close contact with the reservoir so that T is equal to T_o , the constant reservoir temperature. It is clear that with this arrangement of the system boundary any irreversibility due to heat transfer between the system and the reservoir is now attributed to the system. Hence upon integration, Eq. (7.41) becomes

$$(S_2 - S_1) = \sigma - \frac{Q_{12}}{T_o} \quad (7.42)$$

In some respects Eq. (7.39), which is an energy balance, is analogous to Eq. (7.42) which could be thought of as an *entropy balance equation*. In both equations the left hand side represents an increase in a 'stored' property of the system. The term Q_{12} is the heat transfer which is a boundary interaction. Therefore we interpret the term (Q_{12}/T_o) as the *entropy transfer* out of the system to the reservoir due to heat transfer at the boundary. Although the terms W_{12} and σ in the two equations are not directly related we are aware that the irreversible frictional dissipation of the work input W_{12} contributes to the entropy production in the system.

It is important to note that σ , is either positive or zero but the *entropy change* or *storage*, $(S_2 - S_1)$ in Eq. (7.42) could be positive or

negative depending on the magnitude of the entropy transfer, (Q_{12}/T_o) compared to the entropy production, σ .

The entropy balance equation for the reservoir is given by

$$(S_{r2} - S_{r1}) = \sigma_r + \frac{Q_{12}}{T_o} \quad (7.43)$$

The heat transfer process in the reservoir is reversible because of its uniform temperature, and therefore the entropy production in the reservoir, $\sigma_r = 0$. Consequently, the increase in the stored entropy of the reservoir is entirely due to the entropy transfer associated with heat transfer from the system across the boundary.

The entropy balance equation for the composite system consisting of the gas and the reservoir is obtained by adding Eqs. (7.42) and (7.43). This gives

$$(S_2 - S_1) + (S_{r2} - S_{r1}) = \sigma \quad (7.44)$$

We could have written Eq. (7.44) directly by applying the principle of increase of entropy to the composite system which is an isolated system. In summary, the entropy balance equation for a closed system may be expressed in the general form:

$$Entropy_{storage} = Entropy_{production} + Entropy_{transfer} \quad (7.45)$$

7.2.2 Entropy transfer in a heat engine

Consider the cyclic heat engine operating between two heat reservoirs as shown in Fig. 7.6(a) where the various heat and work interactions and temperatures are indicated. The engine experiences external irreversibilities due heat transfer across finite temperature differences $(T_h - T_{h1})$ and $(T_{c1} - T_c)$ between the cyclic device and the reservoirs. In addition, there are internal mechanical and thermal irreversibilities causing entropy production within the cyclic device.

The T - S diagram for the irreversible heat engine cycle is shown in Fig. 7.6(b). The compression and expansion processes of this cycle are *irreversible adiabatic* processes. However, we assume that during the

heat interactions with the reservoirs the temperature of the working fluid of the cyclic device remains constant.

Applying the equation of entropy balance, expressed by Eq. (7.45), to the cyclic device we obtain

$$S_{cycle} = \sigma + \left(\frac{Q_h}{T_h} - \frac{Q_c}{T_c} \right) \quad (7.46)$$

It should be noted that in the above equation the entropy production due to all irreversibilities, both external and internal, are now included in σ because we use the reservoir temperatures to evaluate the entropy transfers due to heat transfer and not the temperatures at the boundary of the cyclic device. Since the heat engine operates in a cycle its entropy change or storage, $S_{cycle} = 0$. Therefore Eq. (7.46) becomes

$$\sigma = - \left(\frac{Q_h}{T_h} - \frac{Q_c}{T_c} \right) \quad (7.47)$$

Applying the first law to the heat engine, its work output is obtained as

$$W_{act} = Q_h - Q_c \quad (7.48)$$

Substituting for Q_c from Eq. (7.47) in Eq. (7.48)

$$W_{act} = Q_h - T_c \left(\sigma + \frac{Q_h}{T_h} \right) \quad (7.49)$$

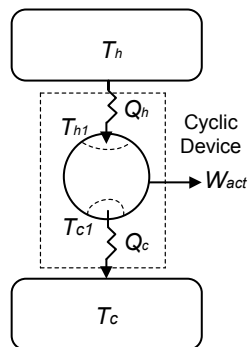


Fig. 7.6(a) Heat engine cycle

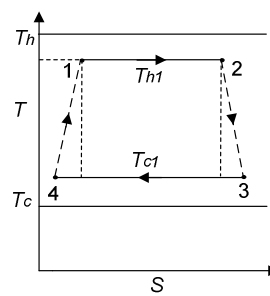


Fig. 7.6(b) T-S diagram

Now the work output of a *reversible* engine operating between the same heat reservoirs and receiving the same heat input Q_h from the hot reservoir is

$$W_{rev} = Q_h \left(1 - \frac{T_c}{T_h} \right) \quad (7.50)$$

Subtracting Eq. (7.49) from Eq. (7.50) we have

$$W_{rev} - W_{act} = T_c \sigma \quad (7.51)$$

We conclude from Eq. (7.51) that the entropy production σ is a measure of the potential loss in work output due to internal and external irreversibilities of the heat engine.

7.2.3 Entropy transfer in steady heat conduction

Consider the *steady* heat conduction in a laterally insulated bar in thermal contact with two heat reservoirs as shown in Fig. 7.7 where the heat interactions and temperatures are indicated. For steady heat conduction the temperature distribution in the bar is linear as indicated in the figure. Applying the entropy balance equation to the bar as the system we have

$$\dot{S}_{bar} = \dot{\sigma} + \left(\frac{\dot{Q}_h}{T_h} - \frac{\dot{Q}_c}{T_c} \right) \quad (7.52)$$

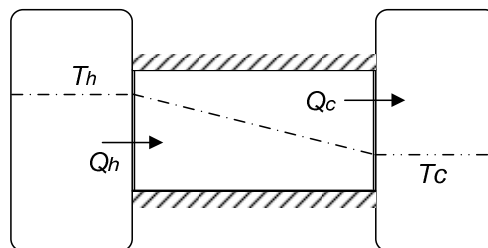


Fig. 7.7 Steady heat conduction in a bar

where the ‘dot’ over a quantity stands for differentiation with respect to time.

Since heat conduction is a steady process the heat flows and the entropy changes are expressed as rates in Eq. (7.52). The entropy storage in the bar is zero because the properties of the bar remain constant under steady conditions. Therefore

$$\dot{S}_{bar} = 0 \quad (7.53)$$

Applying the first law to the bar we have

$$\dot{Q}_h = \dot{Q}_c = \dot{Q} \quad (7.54)$$

where \dot{Q} is the constant heat flow rate through the bar. Substituting from Eqs. (7.53) and (7.54) in Eq. (7.52) we obtain

$$\dot{\sigma} = \left(\frac{\dot{Q}}{T_c} - \frac{\dot{Q}}{T_h} \right) > 0 \quad (7.55)$$

We could have obtained Eq. (7.55) directly by applying the principle of increase of entropy [Eq. (7.38)] to the composite system consisting of the two reservoirs and the bar which is an isolated system. Then the terms (\dot{Q}/T_c) and (\dot{Q}/T_h) are the rate of increase of entropy in the cold reservoir and the rate of decrease of entropy of the hot reservoir respectively. The entropy production given by Eq. (7.55) is due to the *internal thermal irreversibility* in the bar which results from the heat transfer across a finite temperature difference. If the same heat transfer was carried out reversibly by operating a Carnot heat engine between the two reservoirs, then the rate of work output of the engine is

$$\dot{W}_{rev} = \dot{Q} \left(1 - \frac{T_c}{T_h} \right) \quad (7.56)$$

Manipulating Eqs. (7.55) and (7.56) we have

$$\dot{W}_{rev} = T_c \dot{\sigma} \quad (7.57)$$

The above relation is similar to Eq. (7.51) for the work output of an irreversible engine, except that the potential work available is entirely lost in the case of steady heat conduction.

7.3 Limitations Imposed on Work Output by the Second Law

In this section we shall derive expressions for the upper limits of the heat transfer and work done in a given process which are important consequences of the second law. Denoting the initial and final states of the closed system by 1 and 2 we apply the first law to obtain

$$Q_{12} = U_2 - U_1 + W_{12} \quad (7.58)$$

Application of the second law to an infinitesimal change of state gives

$$\delta Q \leq T dS \quad (7.59)$$

Integrating Eq. (7.59) from the initial to the final state we have

$$Q_{12} \leq \int_1^2 T dS \quad (7.60)$$

The heat transfer Q_{12} is a maximum for a reversible process for which the equality sign in Eq. (7.60) applies. In order to evaluate the integral on the right hand side of the Eq. (7.60) we need to know the process path. For a reversible process, the path is usually well-defined and the heat transfer is also the area of the T - S diagram of the process. However, for an irreversible process, for which the inequality sign applies, Eq. (7.60) establishes only the upper limit of the heat transfer. Furthermore, the process path required to carry out the integration on the right hand side of Eq. (7.60) is often difficult to determine for an irreversible process.

Eliminating Q_{12} between Eqs. (7.58) and (7.60) we obtain

$$U_2 - U_1 + W_{12} \leq \int_1^2 T dS \quad (7.61)$$

Hence

$$W_{12} \leq \int_1^2 T dS - (U_2 - U_1) \quad (7.62)$$

The equality sign in Eq. (7.62) applies for *reversible* processes for which the process path is well defined and the equation establishes the maximum work output of the process. However, for *irreversible* processes the evaluation of the integral on the right hand side of

Eq. (7.62) could pose a challenge because the process-path is often not readily available.

7.3.1 Helmholtz and Gibbs free energy

We shall now derive expressions for the maximum work output of several special processes that are of considerable practical significance. First consider the application of Eq. (7.62) to an isothermal process. The integral in the equation is easily evaluated because the temperature is constant. This gives

$$W_{12} \leq T(S_2 - S_1) - (U_2 - U_1) \quad (7.63)$$

$$W_{12} \leq -[(U_2 - TS_2) - (U_1 - TS_1)]$$

Hence
$$W_{iso,max} = -[(U_2 - TS_2) - (U_1 - TS_1)] \quad (7.64)$$

It is seen from Eq. (7.64) that the maximum work output for an *isothermal* process is the change of the function, $(U - TS)$ from state 1 to state 2. This state function is called the *Helmholtz free energy* and usually denoted by F . It is a property of the system because U , T and S are properties. The maximum work output of an isothermal process may be written in terms of the Helmholtz free energy as

$$W_{iso,max} = -(F_2 - F_1) \quad (7.65)$$

The physical interpretation of Eq. (7.65) is that the maximum work output of the system is the decrease in the property F . Although the system possesses internal energy of magnitude U , a fraction TS of this internal energy is not free to be used for the production of useful work. Therefore for an *isothermal* process the fraction of the internal energy that is *free* for work production is the *Helmholtz free energy* F . It is important to note that Eq. (7.64) for the maximum work output is applicable to situations involving different forms of internal energy and work modes. For example, we could envisage an application like a fuel cell where electrical work is produced isothermally at the expense of chemical internal energy of the system.

We shall now obtain the maximum work output of an *isothermal* process that is carried out under *constant pressure*. In other words,

during the isothermal process, the system expands quasi-statically against a *constant* external pressure P . Of the maximum work output of the system a fraction is now used to overcome the external force due to the pressure and therefore not available for *useful* application. Separating the work output into two parts we have

$$W_{iso,max} = W_{useful,max} + P(V_2 - V_1) \quad (7.66)$$

where V_1 and V_2 are the initial and final volumes of the system.

Substituting for $W_{iso,max}$ from Eq. (7.66) in (7.64)

$$W_{useful,max} + P(V_2 - V_1) = -[(U_2 - TS_2) - (U_1 - TS_1)]$$

$$W_{useful,max} = -[(U_2 + PV_2 - TS_2) - (U_1 + PV_1 - TS_1)]$$

$$W_{useful,max} = -[(H_2 - TS_2) - (H_1 - TS_1)] \quad (7.67)$$

From Eq. (7.67) it is clear that the maximum work done by a system under simultaneous *isothermal* and *constant pressure* conditions is the change of a property defined as, $G = H - TS$ where H is the enthalpy. The property G is called the *Gibbs free energy*. Therefore Eq. (7.67) can be written in terms of the Gibbs free energy as

$$W_{useful,max} = -[G_2 - G_1] \quad (7.68)$$

The function G gives the fraction of the enthalpy of the system that could be harnessed to produce *useful non-expansion* work. The fraction TS is once again not free for work production.

7.3.2 Availability

There are numerous engineering applications where a system producing work exchanges heat with a single reservoir like the atmosphere. The arrangement is similar to that shown in Fig. 7.4. In this section we shall derive an expression for the maximum work output of such a system. Let the initial and final states of the closed system and the reservoir be denoted by 1 and 2 respectively. Applying the first law to the system

$$Q_{12} = U_2 - U_1 + W_{12} \quad (7.69)$$

Consider the *isolated* composite system consisting of the given system and the reservoir. We apply the principle of increase of entropy to obtain

$$(S_2 - S_1) - \frac{Q_{12}}{T_r} \geq 0 \quad (7.70)$$

where T_r is the reservoir temperature. In Eq. (7.70) the first term is the increase in entropy of the system while the second term is the decrease in entropy of the reservoir due to heat flow from the reservoir to the system. Eliminating Q_{12} between Eqs. (7.70) and (7.69) we have

$$W_{12} \leq [(U_2 - T_r S_2) - (U_1 - T_r S_1)] \quad (7.71)$$

The maximum work output is therefore the change in the function $(U - T_r S)$ from the initial to the final state.

Now consider a system interacting with a single reservoir as before and undergoing a constant pressure process doing work against the atmosphere in a quasi-static manner. The *useful* work produced is given by

$$W_{\text{useful}} = W_{12} - P_{\text{atm}}(V_2 - V_1) \quad (7.72)$$

where P_{atm} is the constant pressure of the atmosphere.

Eliminating W_{12} between Eqs. (7.72) and (7.71) we obtain

$$W_{\text{useful}} \leq -[(U_2 + P_{\text{atm}} V_2 - T_r S_2) - (U_1 + P_{\text{atm}} V_1 - T_r S_1)] \quad (7.73)$$

It is seen from Eq. (7.73) that the maximum work output is the change of the function, $\Phi = U + P_{\text{atm}} V - T_r S$ from the initial to the final state. If the atmosphere is also the heat reservoir, as it is the case in many engineering systems, then $\Phi = U + P_{\text{atm}} V - T_{\text{atm}} S$. The latter function is clearly a property of the system-atmosphere combination. We can write Eq. (7.73) in terms of Φ as

$$W_{\text{useful}} \leq -[\Phi_2 - \Phi_1] \quad (7.74)$$

The *minimum* value of Φ occurs when the system establishes equilibrium with the atmosphere and its temperature and pressure are therefore T_{atm} and P_{atm} respectively. If this minimum value of the property Φ is Φ_{min} then we define the new property called the *availability* as

$$A = \Phi - \Phi_{\min} \quad (7.75)$$

In terms of the availability, the useful work output given by Eq. (7.74) becomes

$$W_{\text{useful}} \leq -[A_2 - A_1] \quad (7.76)$$

The physical meaning of Eq. (7.76) is that the decrease in the availability of a system-atmosphere combination is the useful work output of a *reversible* process of the system. However, when the system undergoes an *irreversible* process with *same initial and final states* of the system, the work done is less than the change in availability.

7.4 Maximum Work, Irreversibility and Entropy Production

In this section we shall obtain a general relationship between the entropy production and the irreversibility for a *closed* system interacting with a series of thermal reservoirs and producing work as depicted in Fig. 7.8. The atmosphere, shown separately, is chosen as the standard reservoir that undergoes changes of state to accommodate variations of the work output W_o of the system. The system undergoes a process whose initial and final states are denoted by 1 and 2 respectively. The temperatures and the heat interactions between the system and the reservoirs during the process are indicated in the Fig. 7.8.

Applying the first law to the system

$$Q_o + \sum Q_i = U_2 - U_1 + W_o \quad (7.77)$$

where Q_o is the heat flow from the standard reservoir (atmosphere). The second term on the left hand side of Eq. (7.77) is the total heat flow from all the reservoirs *except the standard reservoir*.

Apply the principle of increase of entropy to the isolated composite system consisting of all the thermal reservoirs and the given system. Hence

$$(S_2 - S_1) - \frac{Q_o}{T_o} - \sum \frac{Q_i}{T_i} = \sigma \quad (7.78)$$

where σ is the entropy production in the composite system due to all irreversibilities.

The first term in Eq. (7.78) is the change in entropy of the system while the second and third terms are the changes in the entropy of the atmosphere and the heat reservoirs respectively. Eliminating Q_o between Eqs. (7.77) and (7.78) we have

$$T_o(S_2 - S_1) + \sum Q_i \left(1 - \frac{T_o}{T_i}\right) - (U_2 - U_1) = T_o\sigma + W_o \quad (7.79)$$

$$\sum Q_i \left(1 - \frac{T_o}{T_i}\right) - [(U_2 - T_o S_2) - (U_1 - T_o S_1)] = T_o\sigma + W_o \quad (7.80)$$

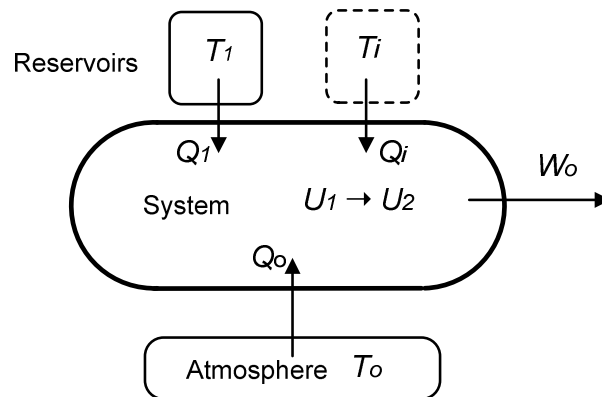


Fig. 7.8 Process in a system interacting with multiple reservoirs

Now consider a *reversible* process that would produce the *same* change of state from 1 to 2 in the system and all the reservoirs *except the atmosphere-reservoir*. The work output for this process, however, would be different from the original process. It is seen from Eq. (7.77) that a change of the work output requires the heat interaction between the system and the atmosphere-reservoir Q_o to adjust to satisfy the latter equation, which is the first law. Now for the *reversible* process the entropy production, $\sigma = 0$. Therefore Eq. (7.80) becomes

$$\sum Q_i \left(1 - \frac{T_o}{T_i} \right) - [(U_2 - T_o S_2) - (U_1 - T_o S_1)] = W_{rev} \quad (7.81)$$

Equation (7.81) gives the maximum work output of the system for the given change of state from 1 to 2. From Eqs. (7.80) and (7.81) it follows that

$$W_{rev} - W_o = T_o \sigma \quad (7.82)$$

The difference between the actual work output of the system W_o and the reversible work output W_{rev} is called the *lost work* or the *irreversibility I*. Substituting in Eq. (7.82) we have

$$I = T_o \sigma \quad (7.83)$$

We obtained equations similar to Eq. (7.82) for the irreversibility of cyclic heat engines [Eq. (7.51)] and steady heat conduction [Eq. (7.57)] in earlier sections of this chapter. Equation (7.83) is a general relationship between the irreversibility and entropy production that is applicable to any process in a *closed* system.

7.5 Entropy, Irreversibility and Natural Processes

The new property called entropy arose as a consequence of the second law and it was defined by Eq. (7.10). This equation enables us to relate entropy to other macroscopic properties like pressure, volume and temperature (see Sec. 7.1.4) of a system and thereby obtain its numerical value which is useful for engineering analysis of systems. However, to appreciate the broader significance of entropy we still need to seek a more satisfying physical interpretation.

From a microscopic view point entropy can be thought of as a measure of the randomness or disorganization of the constituents of a system. For instance, when a gas is compressed the final state confines the molecules of the gas to a smaller volume thereby bringing more organization to the molecules. However, the higher temperature that may result from the compression will make the molecules more agitated and therefore their state more random. This view point is reflected in the expression for the entropy of an ideal gas in Eq. (7.23). The first term on the right hand side gives the level of disorganization due to the

dispersion of energy among the molecules, which may be called the *thermal entropy* and the second term gives the *configurational entropy* which is a measure of the disorganization due to the dispersion of the molecules in the space occupied by the gas. During the compression process of an ideal gas, if the increase in thermal entropy is exactly balanced by the decrease in configurational entropy, then the processes will be isentropic as seen from Eq. (7.23).

In our discussion on natural processes in Chapter 6 we noticed that these processes moved in a preferred direction. For instance, heat always flows unaided from hot to cold regions making the latter region more disorganized. Furthermore, gases expand from regions of high pressure to evacuated spaces increasing the level of disorganization of the molecules of the gas. To reverse these processes we need to expend work which leaves permanent changes in the environment thus making the processes irreversible.

In view of the above observations we can conclude that *natural* processes take systems from more organized states to less organized states thus increasing their entropy. Often we maintain highly organized states of systems by introducing well designed constraints. For example, we need high quality thermal insulation to prevent heat leaks between a hot body and a cold body. Similarly we use walls or membranes to confine high pressure gases from expanding to low pressure regions surrounding them. Once the constraints are removed the states of these systems evolve naturally or unaided to less organized states. Since entropy is a measure of the level of disorganization we are lead to the conclusion that natural processes cause the entropy of systems to increase and they are, therefore, irreversible.

Now consider a pure work interaction with no frictional effects. The sliding of a metal block down a smooth inclined plane is a possible example. The state of organization of the molecules of the block remains unchanged during the sliding because the kinetic energy gained by the block will affect all the molecules of the block equally in an organized fashion. Therefore there is no change in the entropy of the block due to the motion. However, if sliding friction is present some of the work done is converted to a heat interaction at the sliding surface resulting in a rise in temperature of the block which, in turn, increases the disorganization

of its molecules. Therefore the block is at higher entropy in the final state.

An important goal of engineering design is to develop efficient systems to produce work from stored energy sources. Thermal power plants and combustion engines are examples of such systems. A question that follows naturally is how to relate our knowledge on irreversible processes, level of organization of systems, and entropy to processes in energy conversion systems. The answer with regard to friction is straight forward because friction converts some fraction of the work available or produced directly to heat which cannot be reconverted to work completely even using reversible devices. Now consider the presence of components in an energy conversion system where heat is transferred across finite temperature differences. Ideally we could affect the same heat transfer using a reversible heat engine, thus producing some additional work as was seen in Sec. 7.2.3. In other words, heat transfer across a finite temperature difference is a 'lost opportunity' for the production of work. Larger the temperature difference greater would be the potential loss of work. Therefore by allowing the natural process, namely the flow of heat from a higher to a lower temperature in this case, to occur we lost some of the potential work.

The free expansion of a high-pressure fluid stream through a component like a throttle valve is a similar situation. If the expansion is carried out in a fully-resisted manner, perhaps with the aid of an expander, the 'work potential' in the high pressure stream could have been realized. Moreover, in both instances mentioned above the natural process, if allowed to occur, increases the entropy production of the system.

In summary, differences of intensive properties like the temperature and pressure, between systems are usually maintained using appropriate constraints. These property gradients offer us opportunities to produce useful work. If the constraints are simply removed, natural processes will level-off these property gradients resulting in entropy production. However, if appropriate devices are introduced to equalize the property differences in a controlled manner some of the work-potential could be realized. Equations (7.82) and (7.83) are useful relationships that enable

us to evaluate the potential loss of work by computing the entropy production.

7.6 Worked Examples

Example 7.1 (i) An ideal gas undergoes a polytropic process from state 1 to state 2 according to the process law $PV^n = C$. Obtain an expression for the change in entropy of the gas in terms of the initial and final pressures.

(ii) A unit mass of methane is subjected to a quasi-static compression process which follows the relation $PV^{1.2} = C$. The initial temperature and pressure are 28°C and 88 kPa respectively. The final pressure is 400 kPa. For methane is $R = 0.52 \text{ kJkg}^{-1}\text{K}^{-1}$ and the ratio of the specific capacities, $\gamma = 1.3$. Calculate the change in entropy of the methane.

Solution We could derive the required expression for the entropy change for a polytropic process from first principles as was done in Sec. 7.1.4. However, it is more convenient to use the expression already obtained in Sec. 7.1.4 for an ideal gas because the change in entropy depends only on the initial and final states of the ideal gas and not on the process path. The general expression for the change in entropy of an ideal gas is given by Eq. (7.25) as

$$S = S_o + mc_p \ln(T/T_o) - mR \ln(P/P_o) \quad (\text{E7.1.1})$$

Manipulating the ideal gas equation of state, $PV = mRT$ and the polytropic process relation, $PV^n = C$ we obtain

$$P^{(n-1)/n} / T = C_1 \quad (\text{E7.1.2})$$

where C_1 is a constant.

Hence
$$P_o^{(n-1)/n} / T_o = P^{(n-1)/n} / T \quad (\text{E7.1.3})$$

where the sub-script o denotes quantities at the initial state.

Substituting for T/T_o from Eq. (E7.1.3) in Eq. (E7.1.1)

$$S = S_o + mc_p (1 - 1/n) \ln(P/P_o) - mR \ln(P/P_o) \quad (\text{E7.1.4})$$

Using the ideal gas relations,

$$(c_p - c_v) = R \quad \text{and} \quad (c_p / c_v) = \gamma,$$

Equation (E7.1.4) can be expressed in the compact form

$$S = S_o - mR \frac{(\gamma - n)}{n(\gamma - 1)} \ln(P / P_o) \quad (\text{E7.1.5})$$

Note that if we substitute, $n = \gamma$ in Eq. (E7.1.5) the entropy change becomes zero because the process then is *isentropic*.

(ii) The numerical data pertinent to the problem are $m = 1$ kg, $R = 0.52$ kJkg⁻¹K⁻¹, $\gamma = 1.3$ and $n = 1.2$. Substituting in Eq. (E7.1.5)

$$S - S_o = -1 \times 0.52 \times \frac{(1.3 - 1.2)}{1.2(1.3 - 1)} \ln(400/88) = -0.219 \text{ kJK}^{-1}$$

The entropy of the gas has decreased because heat has been transferred out of the gas during the process.

Example 7.2 A fixed quantity of water of mass 1.3 kg at an initial temperature and pressure of 200°C and 30 bar respectively is contained in a piston-cylinder apparatus. The water undergoes a reversible isothermal expansion to a lower pressure while receiving 3500 kJ of heat. Calculate (i) the change in entropy of the water and (ii) the final pressure.

Solution At the initial state 1, the water is a compressed liquid because the pressure is higher than the saturation pressure at 200°C. The path of the isothermal heating process is indicated by the horizontal line 1-2 in Fig. E7.2. The area under the line 1-2 gives the heat supplied during the process because for a reversible process

$$Q_{12} = \int_1^2 T dS \quad (\text{E7.2.1})$$

Since T is constant, Eq. (E7.2.1) can be integrated directly to obtain

$$Q_{12} = Tm(s_2 - s_1) \quad (\text{E7.2.2})$$

where s is the entropy per unit mass.

For compressed water we ignore the effect of pressure and find the saturated liquid entropy at 200°C. From the tabulated data in [6] we obtain by interpolation the liquid entropy as, $s_1 = 2.331 \text{ kJK}^{-1}\text{kg}^{-1}$. Substituting the given numerical data in Eq. (E7.2.2) we have

$$3500 = (200 + 273) \times 1.3 \times (s_2 - s_1) \quad (\text{E7.3.2})$$

From Eq. (7.3.2) the entropy change of water is given by

$$(s_2 - s_1) = 5.69 \text{ kJK}^{-1}\text{kg}^{-1}$$

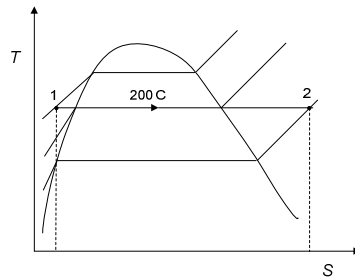


Fig. E7.2 T-S diagram for water

Hence

$$s_2 = 8.02 \text{ kJK}^{-1}\text{kg}^{-1}$$

In order to determine the final state of the steam we need to obtain the pressure of superheated steam at 200°C for which $s_2 = 8.02 \text{ kJK}^{-1}\text{kg}^{-1}$. From the superheated steam data in [6] the pressure is obtained by linear interpolation as 0.68 bar.

Example 7.3 (a) Draw the temperature-entropy diagram for a Carnot refrigeration cycle. Hence obtain an expression for the COP of the cycle. (b) Obtain an expression for thermal efficiency of the reversible heat engine cycle whose T-S diagram is shown in Fig. E7.3(b).

Solution (a) The temperature-entropy diagram for a Carnot refrigeration cycle is shown in Fig. E7.3(a). Heat is extracted from the cold reservoir during the isothermal process 1-2. The process 2-3 is an isentropic compression during which the temperature of the cycle becomes equal to the hot reservoir temperature. Heat is rejected isothermally to the hot reservoir during the process 3-4. Finally, the isentropic expansion

process 4-1 completes the cycle. Since all the processes are reversible, the area under the process path on the T - S diagram is the heat transfer. Using the quantities indicated in the figure we write the following expressions for the heat interactions

$$Q_c = T_c(S_2 - S_1) \quad (\text{E7.3.1})$$

$$Q_h = T_h(S_3 - S_4) \quad (\text{E7.3.2})$$

Applying the first law to the cycle

$$W_{in} = Q_h - Q_c \quad (\text{E7.3.3})$$

The COP of the refrigerator is defined as

$$COP_{ref} = \frac{Q_c}{W_{in}} = \frac{Q_c}{Q_h - Q_c} \quad (\text{E7.3.4})$$

Because of the rectangular shape of the T - S diagram

$$(S_2 - S_1) = (S_3 - S_4) \quad (\text{E7.3.5})$$

Substituting from Eqs. (E7.3.1) and (E7.3.2) in Eq. (E7.3.4) with the condition in Eq. (E7.3.5) we obtain

$$COP_{ref} = \frac{T_c}{T_h - T_c}$$

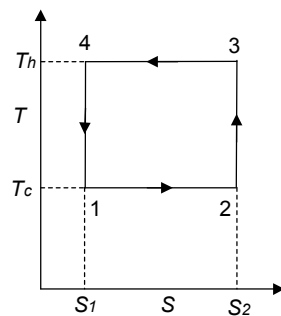


Fig. E7.3(a) T - S diagram

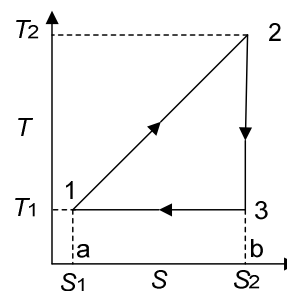


Fig. E7.3(b) T - S diagram

(b) The T - S diagram for the heat engine cycle, shown in Fig. E7.3(b), is a triangle. The engine receives heat during the process 1-2, undergoes an isentropic expansion from 2-3 and rejects heat during the process 3-1 to complete the cycle. The net heat transfer is the area enclosed by the triangle which by the first law is also equal to the net work output.

Therefore

$$W_{net} = Q_{net} = (T_2 - T_1)(S_2 - S_1)/2 \quad (\text{E7.3.6})$$

The total heat input to the cycle is the area of the trapezium 1-2-b-a, which can be written as

$$Q_{in} = (T_1 + T_2)(S_2 - S_1)/2 \quad (\text{E7.3.7})$$

The thermal efficiency of the cycle is

$$\eta = \frac{W_{net}}{Q_{in}} = \frac{(T_2 - T_1)}{(T_2 + T_1)} = 1 - \frac{T_1}{(T_1 + T_2)/2} \quad (\text{E7.3.8})$$

Equation (E7.3.8) shows that the efficiency of the engine is equal to that of a Carnot engine operating with a heat source temperature equal to the mean of the given cycle temperatures.

Example 7.4 (a) Show that for an ideal gas the slope of the constant volume lines on the T - S diagram are larger than the slope of the constant pressure lines.

(b) Sketch the lines of constant pressure and constant volume for an ideal gas on the T - S diagram.

(c) Draw the T - S diagram for a reversible cycle executed by an ideal gas whose P - V diagram is a rectangle.

Solution (a) In Sec. 7.1.4 we obtained the following expressions for the entropy of an ideal gas

$$S = S_o + mc_v \ln(T/T_o) + mR \ln(V/V_o) \quad (\text{E7.4.1})$$

$$S - S_o = mc_p \ln(T/T_o) - mR \ln(P/P_o) \quad (\text{E7.4.2})$$

The above expressions are used to find the required gradients $(\partial T / \partial S)_V$ and $(\partial T / \partial S)_P$ of the constant volume and constant pressure lines respectively on the T - S diagram.

Differentiate Eq. (E7.4.1) with respect to T keeping V constant. Hence

$$(\partial S / \partial T)_V = mc_v / T \quad (\text{E7.4.3})$$

Differentiate Eq. (E7.4.2) with respect to T keeping P constant. Hence

$$(\partial S / \partial T)_P = mc_p / T \quad (\text{E7.4.4})$$

From Eqs. (E7.4.3) and (E7.4.4) we have

$$(\partial T / \partial S)_V = T / mc_v$$

$$(\partial T / \partial S)_P = T / mc_p$$

Now for an ideal gas, $c_p = c_v + R > c_v$. Therefore it follows from the two equations above that

$$(\partial T / \partial S)_V > (\partial T / \partial S)_P$$

(b) In order to sketch the constant volume and constant pressure lines we first obtain functional forms for the variation of S versus T under these conditions. Rearranging Eq. (E7.4.1)

$$(T / T_o) = \exp((S - S_o) / mc_v - R \ln(V / V_o) / c_v)$$

Hence $(T / T_o) = (V_o / V)^{R/c_v} \exp[(S - S_o) / mc_v]$ (E7.4.5)

Similarly, by rearranging Eq. (E7.4.2)

$$(T / T_o) = (P / P_o)^{R/c_p} \exp[(S - S_o) / mc_p] \quad (\text{E7.4.6})$$

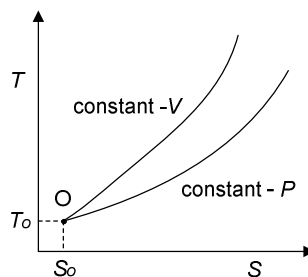


Fig. E7.4(a) T - S diagrams of constant- P and constant- V processes

The exponential curves given by Eqs. (E7.4.5) and (E7.4.6) are sketched in Fig. E7.4(a) where the point O represents the reference state. Notice that the T - V and T - P relations for an isentropic process ($S = S_o$) could be deduced from these equations.

(c) The P - V diagram shown in Fig. 7.4(b) has a rectangular shape with two constant-volume processes 1-2 and 3-4 and two constant-pressure processes 2-3 and 4-1. We use the shapes obtained in part (b) for such processes to sketch the cycle on the T - S diagram shown in Fig. 7.4(c).

The constant pressure and constant volume processes on the T - S diagram are represented by exponential functions according to Eqs. (E7.4.5) and (E7.4.6).

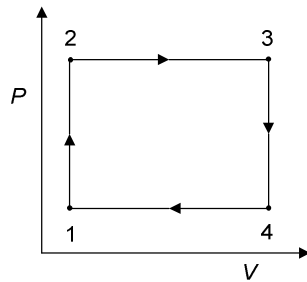


Fig. E7.4(b) P - V diagram

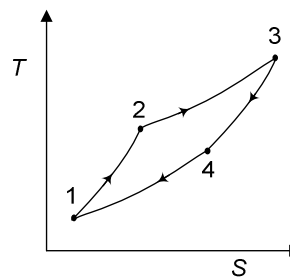
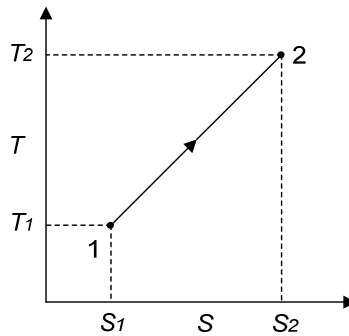


Fig. E7.4(c) T - S diagram

Example 7.5 A fixed quantity of helium gas of mass 0.6 kg undergoes a reversible process that has a linear path on the T - S diagram. The temperature and volume at the initial state are 38°C and 0.3 m^3 respectively. The corresponding values are 260°C and 0.73 m^3 at the final state. Calculate the heat transfer during the process. For helium assume that $c_v = 3.12 \text{ kJkg}^{-1}\text{K}^{-1}$ and $R = 2.08 \text{ kJkg}^{-1}\text{K}^{-1}$.

Solution Let the initial and final states of the process be denoted by 1 and 2 respectively (see Fig. E7.5). Since helium is treated as an ideal gas the change in entropy is obtained from the general ideal gas property relation derived in Sec. 7.1.4. Hence

$$S_2 - S_1 = mc_v \ln(T_2 / T_1) + mR \ln(V_2 / V_1)$$

Fig. E7.5 T - S diagram

Substituting numerical values in the above equation

$$S_2 - S_1 = 0.6 \times 3.12 \times \ln\left(\frac{533}{311}\right) + 0.6 \times 2.08 \times \ln\left(\frac{0.73}{0.3}\right) = 2.1178$$

$$S_2 - S_1 = 2.1178 \text{ kJK}^{-1}$$

Since the process is reversible, the heat transfer is equal to the area of the T - S diagram under the straight line 1-2, which has the trapezoidal shape as seen in Fig. E7.5. Therefore the heat transfer is

$$Q_{12} = 0.5 \times (T_1 + T_2)(S_2 - S_1)$$

$$Q_{12} = 0.5 \times (533 + 311) \times 2.1178 = 893.7 \text{ kJ.}$$

Example 7.6 Two separate quantities of water of masses m_a and m_b of the same constant specific heat capacity c are at temperatures T_a and T_b respectively. The two masses of water are mixed in a well-insulated vessel of heat capacity c_v and mass m_v and left to attain equilibrium.

(a) Obtain expressions for (i) the entropy changes of the water and the vessel after the final equilibrium state is reached and (ii) the entropy production in the composite system.

(b) If the water is first mixed in a well-insulated vessel of negligible thermal capacity and then transferred to the original vessel, obtain expressions for the quantities listed in (a) above.

Solution (a) Applying the first law to the mixing process, considering the water and the vessel as the system we have

$$Q_{12} = U_2 - U_1 + W_{12} \quad (\text{E7.6.1})$$

For the composite system Q_{12} and W_{12} are both zero. Therefore from Eq. (E7.6.1)

$$m_a c_a T_a + m_b c_b T_b + m_v c_v T_v = (m_a c_a + m_b c_b + m_v c_v) T_f$$

where T_f is the final equilibrium temperature of the system.

$$T_f = \frac{m_a c_a T_a + m_b c_b T_b + m_v c_v T_v}{m_a c_a + m_b c_b + m_v c_v} \quad (\text{E7.6.2})$$

The water and the vessel may be treated as pure thermal systems because of their low compressibility. Since entropy is a property we use the general expression, Eq. (7.29), derived earlier in Sec. 7.1.5 for a pure thermal system, to obtain the entropy changes as

$$\Delta S_{\text{water}} = m_a c_a \ln(T_f / T_a) + m_b c_b \ln(T_f / T_b) \quad (\text{E7.6.3})$$

$$\Delta S_{\text{vessel}} = m_v c_v \ln(T_f / T_v) \quad (\text{E7.6.4})$$

The water and the vessel constitute an isolated system that does not exchange heat with the environment. The entropy production of the composite system is therefore equal to the net change in entropy of the water and the vessel.

$$\sigma = \Delta S_{\text{water}} + \Delta S_{\text{vessel}} \quad (\text{E7.6.5})$$

Substituting from Eqs. (E7.6.3) and (E7.6.4) in Eq. (E7.6.5)

$$\sigma = m_a c_a \ln(T_f / T_a) + m_b c_b \ln(T_f / T_b) + m_v c_v \ln(T_f / T_v)$$

(b) Applying the first law to the two-step mixing process it is clear that the final equilibrium temperature of the water and the vessel is same as that given by Eq. (E7.6.2). Since entropy is a property and therefore independent of the process path, the entropy changes and the entropy production for the two-step mixing process are the same as those for part (a) above.

Example 7.7 A rigid tank contains 0.1 kg of air at an initial temperature and pressure of 27°C and 110 kPa respectively. The air receives 8.5 kJ of energy through the following alternative boundary interactions.

(a) A work input of 8.5 kJ by means of a paddle wheel while the tank is well-insulated.

(b) A work input of 8.5 kJ by means of a paddle wheel while the tank loses 1.5 kJ of heat to the surroundings at 30°C.

(c) A heat input of 8.5 kJ from a heat reservoir at 300°C with the tank well-insulated.

(i) Calculate for each of the above processes the change of entropy of the air. (ii) Calculate for the processes (b) and (c) the entropy changes of the reservoirs. (iii) Calculate the entropy production in the universe for each of the three processes.

Solution (a) Applying the first law assuming no heat losses from the tank to the surroundings we obtain

$$0 = mc_v(T_2 - T_1) + W_{12} \quad (\text{E7.7.1})$$

where 1 and 2 denote the initial and final equilibrium states and W_{12} is the work input of the paddle wheel. Substituting numerical values in Eq. (E7.7.1)

$$0 = 0.1 \times 0.718 \times (T_2 - 27) - 8.5$$

Therefore $T_2 = 145.38^\circ\text{C}$

Assuming air to be an ideal gas we apply the following property relation to calculate the entropy change

$$S_2 - S_1 = mc_v \ln(T_2 / T_1) + mR \ln(V_2 / V_1) \quad (\text{E7.7.2})$$

Since the tank is rigid, the volume of air is unchanged. Substituting numerical values in Eq. (E7.7.2) we have

$$S_{a2} - S_{a1} = 0.1 \times 0.718 \times \ln(418.38 / 300) = 0.0239 \text{ kJ K}^{-1}$$

Since the tank is well-insulated there is no entropy transfer due to heat transfer. The entropy production, σ of the system and the surroundings (the universe) is equal to the entropy change of the air. Therefore $\sigma = 0.0239 \text{ kJK}^{-1}$. Note that the work source driving the paddle wheel, which is part of the surroundings, undergoes no entropy change because unlike heat transfer work transfer is not accompanied by any entropy transfer.

(b) Applying the first law to the air we have

$$Q_{12} = mc_v(T_2 - T_1) + W_{12} \quad (\text{E7.7.3})$$

where Q_{12} is the heat loss from the air to the surroundings.

Substituting numerical values in Eq. (E7.7.3)

$$-1.5 = 0.1 \times 0.718 \times (T_2 - 27) - 8.5$$

Hence

$$T_2 = 124.49^\circ\text{C}$$

We substitute numerical values in Eq. (E7.7.2) to find the entropy change of the air. Thus

$$S_{a2} - S_{a1} = 0.1 \times 0.718 \times \ln(397.49/300) = 0.0202 \text{ kJK}^{-1}$$

The entropy change of the surroundings which may be treated as a reservoir at 30°C is given by

$$S_{r2} - S_{r1} = Q_{12}/T_r = 1.5/303 = 0.00495 \text{ kJK}^{-1}$$

The entropy production of the system and the surroundings (the universe) is

$$\sigma = 0.0202 + 0.00495 = 0.02515 \text{ kJK}^{-1}$$

The total entropy production is larger now because in addition to the irreversibility associated with work dissipation by the paddle wheel there is an external irreversibility due to heat transfer between the tank and the surroundings.

(c) The heat input of 8.5 kJ from the reservoir is the same as the work input from the paddle wheel in (a). Therefore the final equilibrium temperature of the air is the same as in (a), that is $T_2 = 145.38^\circ\text{C}$. The entropy change of the air is also the same as in (a), which is given by

$$S_{2a} - S_{1a} = 0.0239 \text{ kJK}^{-1}$$

The entropy change of the high temperature reservoir that supplies the heat input is

$$S_{r2} - S_{r1} = -Q_{12}/T_r = -8.5/573 = -0.0148 \text{ kJK}^{-1}$$

Note that the reservoir experiences a decrease in entropy because of the heat flow out of it. The entropy production of the composite system consisting of the air and the reservoir (the universe) is

$$\sigma = 0.0239 - 0.0148 = 0.009065 \text{ kJK}^{-1}$$

The lowest entropy production occurs with the arrangement in (c) because it involves a heat transfer irreversibility that is not as 'dissipative' as the direct conversion of work to heat as it happens with the paddle wheel in processes (a) and (b).

Example 7.8 An electrical heater with a resistance of 30 ohms is connected to a DC voltage source of 120 V. The mass and specific heat capacity of the heater are 0.015 kg and $0.8 \text{ kJkg}^{-1}\text{K}^{-1}$ respectively. The heater is switched on for 2 s during which time it is maintained at a constant temperature of 30°C by immersing in a heat-sink reservoir. (a) Calculate (i) the change in entropy of the heater, (ii) the change in entropy of the reservoir, (iii) the entropy transfer to the reservoir and (iv) the entropy production in the universe.

(b) If the heater has been well-insulated and initially at a temperature of 30°C , calculate the (i) the change in entropy of the heater and (ii) the entropy production in the universe.

Solution The electrical energy (work) input to the heater during the 2 s is

$$W_{12} = V^2 t / R = 120^2 \times 2 / 30 = 960 \text{ J}$$

Treat the heater as a pure thermal system. Since the heater is maintained at a constant temperature, its change in internal energy is zero. Applying the first law we have

$$Q_{12} = W_{12} = 960 \text{ J}$$

where Q_{12} is the heat transfer from the heater to the heat sink reservoir at 30°C . The change in entropy of the heater is zero because it is a pure thermal system maintained at a constant temperature (see Eq. 7.29). The entropy change in the reservoir is

$$S_{r2} - S_{r1} = Q_{12} / T_r = 0.96 / 303 = 0.003168 \text{ kJK}^{-1}$$

The entropy increase of the reservoir is the same as the entropy transfer to it from the heater because the reservoir does not produce any entropy of its own. The entropy production of the composite system consisting of the heater and the reservoir (the universe) is

$$\sigma = (S_{r2} - S_{r1}) + (S_{h2} - S_{h1}) = 0.003168 \text{ kJK}^{-1}$$

(b) When the heater is insulated the heat transfer $Q_{12} = 0$. Applying the first law we have

$$0 = (U_2 - U_1) + W_{12} = MC(T_2 - T_1) - 960$$

Substituting numerical values

$$0.015 \times 0.8 \times (T_2 - 30) = 0.96$$

The final equilibrium temperature of the heater is, $T_2 = 110^\circ\text{C}$.

Since the heater is a pure thermal system its entropy change is given by

$$S_{h2} - S_{h1} = MC \ln(T_2 / T_1)$$

$$S_{h2} - S_{h1} = 0.015 \times 0.8 \times \ln(383 / 303) = 0.00281 \text{ kJK}^{-1}$$

There is no entropy transfer from the heater because it is thermally insulated. Therefore the entropy production of the universe is equal to the entropy increase of the heater, which is 0.00281 kJK^{-1} .

Example 7.9 A fixed quantity water of mass 1.5 kg and specific heat capacity $4.2 \text{ kJkg}^{-1}\text{K}^{-1}$ is at an initial temperature of 300 K. The following three alternative processes are considered for heating the water to a temperature of 360 K. (a) The water receives heat from a reservoir at 360 K until it attains thermal equilibrium with the reservoir. (b) The water receives heat successively from two reservoirs at 330 K and 360 K attaining equilibrium with each reservoir in turn and (c) The water

receives heat successively from three reservoirs at 320 K, 340 K and 360 K attaining equilibrium with each reservoir in turn. Calculate (i) the entropy change in the water and the reservoirs and (ii) the entropy production in the universe for each of the three scenarios.

Solution We first obtain the general expressions for the change in entropy of the water, treating it as a pure thermal system, and the reservoirs. For the water we have

$$S_{w2} - S_{w1} = m_w c_w \ln(T_{w2} / T_{w1}) \quad (\text{E7.9.1})$$

Applying the first law to the water with no work transfer

$$Q_{12} = m_w c_w (T_{w2} - T_{w1}) \quad (\text{E7.9.2})$$

Applying the first law to the reservoir

$$Q_{12} = -Q_{res} \quad (\text{E7.9.3})$$

The change in entropy of the reservoir is given by

$$S_{r2} - S_{r1} = Q_{res} / T_r \quad (\text{E7.9.4})$$

Substituting in Eq. (E7.9.4) from Eqs. (E7.9.3) and (E7.9.2) we obtain

$$S_{r2} - S_{r1} = -m_w c_w (T_{w2} - T_{w1}) / T_r \quad (\text{E7.9.5})$$

We now apply Eqs. (E7.9.1) and (E7.9.5) to each of the alternative processes to determine the entropy changes.

(a) The change in entropy of the water, from Eq. (E7.9.1) is

$$S_{w2} - S_{w1} = 1.5 \times 4.2 \times \ln(360/300) = 1.148 \text{ kJK}^{-1}$$

The change in entropy of the reservoir from Eq. (E7.9.5) is

$$S_{r2} - S_{r1} = -1.5 \times 4.2 \times (360 - 300) / 360 = -1.05 \text{ kJK}^{-1}$$

The entropy production in the composite system consisting of the water and the reservoir (the universe) is

$$\begin{aligned} \sigma &= (S_{w2} - S_{w1}) + (S_{r2} - S_{r1}) \\ \sigma &= 1.148 - 1.05 = 0.098 \text{ kJK}^{-1} \end{aligned}$$

(b) For the two-step heating process, the initial and final temperatures of the water are the same as for (a). Therefore the change in entropy of the water is also the same as for (a) because the entropy is a function of the temperature. However, the entropy changes in the two reservoirs are different and these are obtained by applying Eq. (E7.9.5) to each reservoir in turn.

$$(S_{r_2} - S_{r_1})_1 = -1.5 \times 4.2 \times (330 - 300) / 330 = -0.5727 \text{ kJK}^{-1}$$

$$(S_{r_2} - S_{r_1})_2 = -1.5 \times 4.2 \times (360 - 330) / 360 = -0.525 \text{ kJK}^{-1}$$

The entropy production in the composite system consisting of the water and the two reservoirs 1 and 2 (the universe) is

$$\sigma = 1.148 - 0.5727 - 0.525 = 0.0503 \text{ kJK}^{-1}$$

(c) We use the same set of equations for the three-step heating process. Again, the entropy change of the water is the same as in (a). The entropy changes of three reservoirs, however, are given by

$$(S_{r_2} - S_{r_1})_1 = -1.5 \times 4.2 \times (320 - 300) / 320 = -0.3937 \text{ kJK}^{-1}$$

$$(S_{r_2} - S_{r_1})_2 = -1.5 \times 4.2 \times (340 - 320) / 340 = -0.3706 \text{ kJK}^{-1}$$

$$(S_{r_2} - S_{r_1})_3 = -1.5 \times 4.2 \times (360 - 340) / 360 = -0.35 \text{ kJK}^{-1}$$

The entropy production of the composite system consisting of the water and the three reservoirs 1, 2 and 3 (the universe) is

$$\sigma = 1.148 - 0.3937 - 0.3706 - 0.35 = 0.034 \text{ kJK}^{-1}$$

From the numerical values for the entropy production for parts (a), (b) and (c) we observe that the entropy production is largest for (a) where, on average, heat is transferred across the largest temperature difference between the reservoir and the water. On the other hand, the three-reservoir heating process, (c) has the smallest entropy production. If the number of reservoirs is further increased, the entropy production would be still lower, and eventually with a series of reservoirs with infinitesimal temperature increments between them, the heating process would approach the reversible limit. Such a process, though ideal, would have zero entropy production. Recall that in worked example 1.4 we discussed a quasi-static heating process based on the same concept.

Example 7.10 A reversible heat engine operating with infinitesimal cycles receives heat from a block of material of mass m_1 and specific heat capacity c_1 and rejects heat to a block of mass m_2 and specific heat capacity c_2 . The initial temperatures of the blocks are T_{1i} and T_{2i} respectively. Finally the two blocks attain equilibrium with their temperatures equal to T_f .

(a) (i) Obtain expressions for the total change of entropy of the two blocks and the reversible engine. (ii) Obtain an expression for final equilibrium temperature T_f . (iii) Obtain an expression for the total work output of the engine.

(b) If an *irreversible* engine is operated between the same blocks with the same initial conditions, (i) obtain an expression for the final equilibrium temperature T_{fi} and (ii) compare the magnitudes of T_f and T_{fi} .

Solution The two blocks may be treated as pure thermal systems whose entropy change is given by Eq. (7.29). We apply this equation to obtain the following expressions for the entropy change of the two blocks

$$S_{1f} - S_{1i} = m_1 c_1 \ln(T_f / T_{1i}) \quad (\text{E7.10.1})$$

$$S_{2f} - S_{2i} = m_2 c_2 \ln(T_f / T_{2i}) \quad (\text{E7.10.2})$$

The reversible engine executes an integral number of cycles during the process. Therefore the entropy change of the cyclic device itself is zero.

$$(S_{ef} - S_{ei}) = 0 \quad (\text{E7.10.3})$$

The entropy production of the composite system consisting of the two blocks and the cyclic engine (the universe) is

$$\sigma = (S_{1f} - S_{1i}) + (S_{2f} - S_{2i}) + (S_{ef} - S_{ei}) \quad (\text{E7.10.4})$$

Substituting in Eq. (E7.10.4) from Eqs. (E7.10.1) to (E7.10.3) we have

$$\sigma = m_1 c_1 \ln(T_f / T_{1i}) + m_2 c_2 \ln(T_f / T_{2i}) + 0 \quad (\text{E7.10.5})$$

For a reversible engine operating between the two blocks the entropy production in the universe is zero. Hence from Eq. (E7.10.5) it follows that

$$m_1 c_1 \ln(T_f / T_{1i}) + m_2 c_2 \ln(T_f / T_{2i}) = 0$$

$$\left(T_f / T_{1i}\right)^{m_1 c_1} \left(T_f / T_{2i}\right)^{m_2 c_2} = 1$$

$$T_f = T_{1i}^{\alpha} T_{2i}^{\beta} \quad (\text{E7.10.6})$$

where the exponents α and β are given by

$$\alpha = m_1 c_1 / (m_1 c_1 + m_2 c_2)$$

and

$$\beta = m_2 c_2 / (m_1 c_1 + m_2 c_2)$$

(iii) Applying the first law to the composite system consisting of the two blocks and the cyclic engine we have

$$Q_{12} = U_f - U_i + W_{out} \quad (\text{E7.10.7})$$

Now the heat transfer between the composite system and the surroundings, Q_{12} is zero. Therefore substituting in Eq. (E7.10.7) we obtain

$$0 = (m_1 c_1 T_f + m_2 c_2 T_f) - (m_1 c_1 T_{1i} + m_2 c_2 T_{2i}) + W_{out}$$

The total work output becomes

$$W_{out} = (m_1 c_1 T_{1i} + m_2 c_2 T_{2i}) - (m_1 c_1 + m_2 c_2) T_f \quad (\text{E7.10.8})$$

where T_f is given by Eq. (E7.10.6).

(b) If an irreversible heat engine is used the entropy production is positive according to the principle of increase of entropy. Therefore using Eq. (7.10.5) we have

$$\sigma = m_1 c_1 \ln(T_{fi} / T_{1i}) + m_2 c_2 \ln(T_{fi} / T_{2i}) \quad (\text{E7.10.9})$$

where T_{fi} is the new final equilibrium temperature of the two blocks. Eq. (E7.10.9) may be expressed in the form

$$\left(T_{fi} / T_{1i}\right)^{m_1 c_1} \left(T_{fi} / T_{2i}\right)^{m_2 c_2} = e^{\sigma}$$

$$T_{fi} = T_{1i}^{\alpha} T_{2i}^{\beta} e^{\lambda} \quad (\text{E 7.10.10})$$

where the exponent λ is given by

$$\lambda = \sigma / (m_1 c_1 + m_2 c_2) > 0 \quad (\text{E7.10.11})$$

Dividing Eq. (E7.10.10) by Eq. (E7.10.6) we have

$$T_{fi}/T_f = e^\lambda > 1$$

because of the condition in Eq. (E7.10.11).

Therefore the final equilibrium temperature of the blocks is larger when the irreversible engine is used. Now the expression in Eq. (E7.10.8) for the work output, which is based on the first law, is applicable both to the reversible engine and the irreversible engine. Due to the higher final equilibrium temperature, ($T_{fi} > T_f$) the work output of the irreversible engine is lower as expected. Compare the present solution with the solution of a similar problem in worked example 6.17 where an alternative approach was used.

Example 7.11 (a) A non-conducting piston of area 10^{-3} m^2 and negligible mass is free to move in a well-insulated cylinder as shown in Fig. E7.11. Initially, the compartment A of the cylinder with a volume of 10^{-4} m^3 contains helium at 315 K and 15 bar while the piston is held in position by a pin. The compartment B is evacuated. The movement of the piston is resisted by a spring with a spring constant of 0.9 kNm^{-1} that is initially uncompressed. The pin is now removed allowing the gas to expand until the piston hits a second pin at a distance of 0.18 m from the first pin.

Calculate (a) (i) the work done by helium, (ii) the change in entropy of helium and (iii) the entropy production of the universe.

(b) If the helium undergoes a free expansion without the spring calculate the quantities listed in (a) for the new arrangement.

(c) If the expansion is carried out in a quasi-static manner, calculate the quantities listed in (a).

(d) Comment on the answers to parts (a), (b) and (c).

For helium $c_v = 3.12 \text{ kJkg}^{-1}\text{K}^{-1}$ and $R = 2.08 \text{ kJkg}^{-1}\text{K}^{-1}$

Solution (a) Applying the equation of state to the initial state

$$P_1 V_1 = mRT_1$$

$$m = 15 \times 100 \times 10^{-4} / (2.08 \times 315) = 2.289 \times 10^{-4} \text{ kg.}$$

The work done by helium is equal to the strain energy stored in the spring because the piston experiences no other external resistance during the expansion.

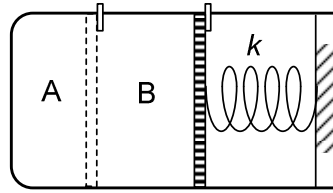


Fig. E7.11 Spring-loaded piston-cylinder set-up

Hence
$$W_{12} = kx_2^2 / 2 - kx_1^2 / 2 \quad (\text{E7.11.1})$$

where x is the compression, k is the spring constant. Sub-scripts 1 and 2 denote the initial and final states of the system.

Substituting numerical values in Eq. (E7.11.1) we obtain the work done as

$$W_{12} = 0.9 \times 0.18^2 / 2 = 0.01458 \text{ kJ} \quad (\text{E7.11.2})$$

Applying the first law to the helium gas with, $Q_{12} = 0$ we have

$$0 = U_2 - U_1 + W_{12} \quad (\text{E7.11.3})$$

Substituting in Eq. (E7.11.3) from Eq. (E7.11.2)

$$0 = mc_v(T_2 - T_1) + 0.01458 \quad (\text{E7.11.4})$$

Substituting numerical values in Eq. (E7.11.4)

$$0 = 2.289 \times 10^{-4} \times 3.12 \times (T_2 - 315) + 0.01458$$

Therefore
$$T_2 = 294.58 \text{ K}$$

Assuming that helium is an ideal gas we use the following property relation [Eq. (7.23)] to find the entropy change.

$$S_2 - S_1 = mc_v \ln(T_2 / T_1) + mR \ln(V_2 / V_1) \quad (\text{E7.11.5})$$

Substituting numerical values in Eq. (E7.11.5)

$$S_2 - S_1 = 2.289 \times 10^{-4} \times [3.12 \ln(294.58 / 315) + 2.08 \ln(0.28 / 0.1)]$$

$$S_2 - S_1 = 4.42 \times 10^{-4} \text{ kJK}^{-1}$$

The entropy production is also equal to the entropy change of the helium because there is no entropy transfer to the surroundings.

Hence
$$\sigma = 4.42 \times 10^{-4} \text{ kJK}^{-1}$$

(b) When helium undergoes a free expansion the work done is zero because of the vacuum on the outside of the piston offers no resistance. The heat interaction is also zero because of the thermal insulation. Therefore from the first law it follows that the internal energy is constant. Since helium is an ideal gas, $T_2 = T_1$.

Applying Eq. (7.11.5), the entropy change is

$$S_2 - S_1 = 2.289 \times 10^{-4} [3.12 \ln(315/315) + 2.08 \ln(0.28/0.1)]$$

$$S_2 - S_1 = 4.902 \times 10^{-4} \text{ kJK}^{-1}$$

The entropy production is the same as the entropy change of the helium.

Therefore
$$\sigma = 4.902 \times 10^{-4} \text{ kJK}^{-1}$$

(c) If the helium is expanded to the same final volume in a quasi-static process, with the cylinder insulated, the entropy change is zero according to Eq. (7.10). Applying Eq. (E7.11.5) we have

$$mc_v \ln(T_2 / T_1) + mR \ln(V_2 / V_1) = 0$$

Substituting numerical values in the above equation

$$3.12 \ln(T_2 / 315) + 2.08 \ln(0.28 / 0.1) = 0$$

Hence
$$T_2 = 158.5 \text{ K}$$

Applying the first law

$$0 = mc_v(T_2 - T_1) + W_{12}$$

Substituting numerical values

$$0 = 2.289 \times 10^{-4} \times 3.12 \times (158.5 - 315) + W_{12}$$

Therefore
$$W_{12} = 0.112 \text{ kJ}$$

(d) From the numerical results for the three different expansion processes we observe that the maximum work output is obtained with the reversible adiabatic process which produces zero entropy. The free expansion which has no work output produces the largest entropy. The *partially-resisted* expansion using a spring delivers some work output and produces less entropy than the free expansion. We note that entropy production is a measure of the irreversibility of the process.

Example 7.12 A slab of thermal insulation of thickness 0.08 m, area 1.2 m² and thermal conductivity 0.05 Wm⁻¹K⁻¹ is placed between a heat source at 80°C and a heat sink at 25°C, both of which can be treated as reservoirs. There is steady one-dimensional heat flow through the insulation slab.

(a) Calculate (i) the rate of change of entropy of the insulation, (ii) the net rate of entropy transfer from the insulation slab and (iii) the entropy production rate in the insulation.

(b) If the insulation slab is replaced with one having a thermal conductivity of 0.035 Wm⁻¹K⁻¹, what would be the entropy production in the insulation?

Solution (a) Applying Fouriers' law of heat conduction we obtain the steady heat flow rate through the slab as

$$\dot{Q} = kA(T_h - T_c) / \Delta L = 0.05 \times 1.2 \times (80 - 25) / 0.08 = 41.25 \text{ W}$$

Since the slab is in a steady state all its properties are constant with time. Therefore the *change* in entropy of the slab is zero. However, the rate of entropy *production* in steady heat conduction is given by Eq. (7.55). Applying this equation we have

$$\dot{\sigma} = \left(\dot{Q} / T_c - \dot{Q} / T_h \right)$$

$$\dot{\sigma} = (41.25 / 298 - 41.25 / 353) = 0.0216 \text{ WK}^{-1}.$$

We recall that there is entropy transfer at the interfaces between the insulation slab and the two reservoirs. The rate of entropy transfer out of the slab exceeds the entropy transfer into the slab because of the entropy

production within the slab. The net entropy transfer rate is equal to the entropy production rate.

(b) With the new insulation slab the heat flow rate is

$$\dot{Q} = kA(T_h - T_c) / \Delta L = 0.035 \times 1.2 \times (80 - 25) / 0.08 = 28.88 \text{ W}$$

The entropy production rate becomes

$$\sigma = (28.88 / 298 - 28.88 / 353) = 0.0151 \text{ WK}^{-1}$$

We note that the use of an insulation slab with a lower thermal conductivity, that is a superior insulation, reduces the entropy production and therefore the irreversibility.

Example 7.13 Experimental data have been recorded on the work done by a fixed mass of helium gas executing an adiabatic process. Due to an oversight the initial and final states of the gas have not been reliably identified. The available data for two states 1 and 2 are as follows:

State	P bar	V m ³
1	6.9	0.085
2	1.01	0.28

(a) Identify correctly the initial and final states of the process.

(b) Calculate the work done by the process.

Assume that helium is an ideal gas for which $c_v = 3.12 \text{ kJkg}^{-1}\text{K}^{-1}$ and $R = 2.08 \text{ kJkg}^{-1}\text{K}^{-1}$

Solution Let us assume that the initial and final states are 1 and 2 respectively. Since the process is adiabatic, the entropy can only increase or remain constant according to the principle of increase of entropy. Assuming helium to be an ideal gas the entropy change is given by the property relation

$$S_2 - S_1 = mc_v \ln(T_2 / T_1) + mR \ln(V_2 / V_1)$$

Substituting for T from the ideal gas equation we have

$$S_2 - S_1 = mc_v \ln(P_2 V_2 / P_1 V_1) + mR \ln(V_2 / V_1)$$

$$S_2 - S_1 = mc_v \ln(P_2 / P_1) + m(c_v + R) \ln(V_2 / V_1)$$

$$S_2 - S_1 = mc_v \ln(P_2 / P_1) + mc_p \ln(V_2 / V_1)$$

Substituting the given experimental data

$$(S_2 - S_1) / m = 3.12 \times \ln(101 / 690) + (3.12 + 2.08) \ln(0.28 / 0.085)$$

$$(S_2 - S_1) / m = 0.204 > 0$$

Therefore we conclude that 1 and 2, respectively are the initial and final states of the helium.

Applying the first law to the adiabatic process

$$0 = U_2 - U_1 + W_{12}$$

Substituting the ideal gas relations in the above equation

$$W_{12} = mc_v (T_1 - T_2) = c_v (P_1 V_1 - P_2 V_2) / R$$

Substituting numerical values in the above equation

$$W_{12} = 3.12 \times (690 \times 0.085 - 101 \times 0.28) / 2.08 = 45.55 \text{ kJ.}$$

Example 7.14 An experimental heat engine operates between a heat source reservoir at 1000 K and a heat sink reservoir at 300 K as shown schematically in Fig. E7.14(a). The measured work output and thermal efficiency of the engine are 200 kW and 35 percent respectively. The temperature differences between the working fluid and the heat reservoir are 60°C and 20°C for the hot and cold reservoirs respectively. Assume that the temperature of the working fluid is constant during the heat interactions.

Calculate (i) the rates of entropy transfer, the entropy change and the entropy production for the cycle and the heat reservoirs, (ii) the entropy production due to heat transfer at the two reservoirs and (iii) the entropy production in the universe.

Solution The heat flow rates from the reservoirs, the work output and the relevant temperatures are indicated in the energy-flow diagram in Fig. E7.14(a). The T - S diagram is shown in Fig. E7.14(b). The pertinent numerical data are:

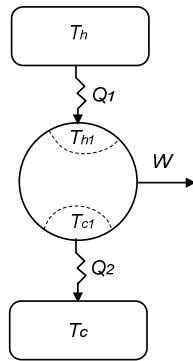
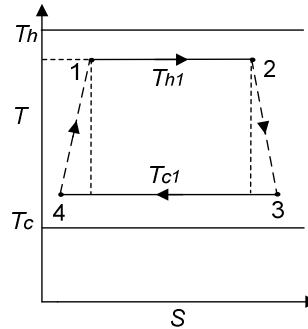


Fig. E7.14(a) Heat engine cycle

Fig. E7.14(b) T - S diagram

$$T_c = 300 \text{ K}, \quad T_{c1} = 300 + 20 = 320 \text{ K}, \quad T_h = 1000 \text{ K},$$

$$T_{h1} = 1000 - 60 = 940 \text{ K}, \quad W = 200 \text{ kW}, \quad \eta = 35\% .$$

From the given data the efficiency is

$$\eta = W / Q_1 = 200 / Q_1 = 0.35$$

Hence the heat input rate is, $Q_1 = 571.4 \text{ kW}$

Applying the first law to the cycle, the heat rejection rate is

$$Q_2 = Q_1 - W = 571.4 - 200 = 371.4 \text{ kW}$$

The rates of entropy change in the hot and cold reservoirs are:

$$S_{rh} = -Q_1 / T_h = -571.4 / 1000 = -0.5714 \text{ kWK}^{-1}$$

$$S_{rc} = Q_2 / T_c = 371.4 / 300 = 1.238 \text{ kWK}^{-1}$$

For the cyclic engine the entropy *transfer* rates are:

$$S_{e1} = Q_1 / T_{h1} = 571.4 / (1000 - 60) = 0.608 \text{ kWK}^{-1}$$

$$S_{e2} = Q_2 / T_{c1} = 371.4 / (300 + 20) = 1.16 \text{ kWK}^{-1}$$

Since the engine operates in a cycle, its entropy *change* is zero. Applying the entropy balance equation to the engine we have

$$S_{eng} = S_{e1} - S_{e2} + \sigma_e$$

Hence
$$\sigma_e = 1.16 - 0.608 = 0.552 \text{ kWK}^{-1}$$

which is the entropy production rate in the engine due to *internal* irreversibilities.

The entropy production rates due to heat transfer across the finite temperature differences between the hot and cold reservoirs and the working fluid of the engine are given by Eq. (7.55) as

$$\sigma_{hot} = Q_1(1/T_{h1} - 1/T_h) = 571.4 \times (1/940 - 1/1000) = 0.0365$$

$$\sigma_{hot} = 0.0365 \text{ kWK}^{-1}$$

$$\sigma_{cold} = Q_2(1/T_c - 1/T_{c1}) = 371.4 \times (1/300 - 1/320)$$

$$\sigma_{cold} = 0.0774 \text{ kWK}^{-1}$$

The above entropy productions are caused by the *external* heat transfer irreversibilities of the engine. The total entropy production rate in the composite system consisting of the two heat reservoirs and the cyclic engine (the universe) is

$$\sigma_{tot} = \sigma_e + \sigma_{hot} + \sigma_{cold}$$

$$\sigma_{tot} = 0.552 + 0.0365 + 0.0774 = 0.666 \text{ kWK}^{-1}$$

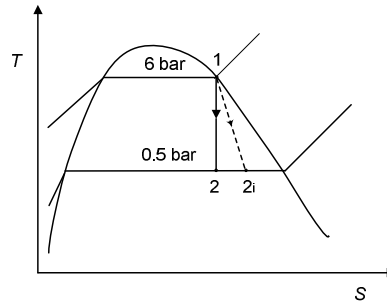
Note that by applying the entropy balance for composite system we can verify that

$$S_{rh} + S_{rc} = -0.5714 + 1.238 = 0.666 = \sigma_{tot}$$

Example 7.15 (a) A fixed quantity of dry saturated steam of mass 0.1 kg undergoes a reversible adiabatic expansion from an initial pressure of 600 kPa to a final pressure of 50 kPa. Calculate the work done by the steam.

(b) If an irreversible adiabatic expansion to the same final pressure produces 80% of the work produced by the reversible process, calculate the final equilibrium state of the steam for the irreversible process.

(c) Indicate these processes on a T - S diagram for water.

Fig. E7.15 T - S diagram for water

Solution During the reversible adiabatic expansion the entropy of the steam remains constant. From the data for saturated steam at 600 kPa, we obtain [6] for the initial state

$$s_{g1} = 6.761 \text{ kJK}^{-1}\text{kg}^{-1}$$

Assume that at the final pressure of 50 kPa the steam is wet. From the saturated steam table [6] at 0.5 bar

$$s_{g2} = 7.593 \text{ kJK}^{-1}\text{kg}^{-1} \quad \text{and} \quad s_{f2} = 1.0991 \text{ kJK}^{-1}\text{kg}^{-1}$$

Equating the entropies for final and initial states we have

$$ms_1 = ms_2$$

where m is the mass of steam.

$$\text{Now} \quad s_2 = x_2 s_{g2} + (1 - x_2) s_{f2}$$

where x_2 is the steam quality at state 2.

Substituting numerical values in the above equation

$$6.761 = 7.593x_2 + 1.091(1 - x_2)$$

$$\text{Therefore} \quad x_2 = 0.872$$

Since the final quality of steam is less than one the original assumption that the steam is wet is valid.

Applying the first law to the adiabatic expansion we obtain

$$0 = U_2 - U_1 + W_{12}$$

The internal energies are obtained from the saturated steam table [6]. On substitution in the above equation

$$0 = m[x_2 u_{g2} + (1 - x_2) u_{f2}] - m u_{g1} + W_{12}$$

$$W_{12} = -0.1 \times [0.872 \times 2483 + (1 - 0.872) \times 340] + 0.1 \times 2568$$

Hence $W_{12} = 35.93 \text{ kJ}$

(b) Applying the first law to the irreversible process we have

$$0 = U_2 - U_1 + 0.8W_{12}$$

Substituting numerical values

$$0 = U_2 - 2568 \times 0.1 + 0.8 \times 35.93$$

Therefore $U_2 = 228.056 \text{ kJ}$

Assume that the steam is wet in the final state. Hence

$$U_2 = 228.056 = 0.1 \times [2483 x_{2i} + 340(1 - x_{2i})]$$

where x_{2i} is the quality of the steam in the final state of the irreversible expansion. From the above equation, $x_{2i} = 0.905$. Note that the steam is in a drier state at the end of the irreversible expansion compared to the reversible expansion.

Example 7.16 An absorption refrigeration system can be represented by a simplified model in which a cyclic device exchanges heat with three reservoirs with no work interaction with the surroundings. The device receives 15kW of heat from a high temperature reservoir at 100°C while absorbing 10 kW from a cold space at 5°C. It rejects heat to a heat sink at a temperature of 30°C. (a) Calculate (i) the rate of change of entropy in the three reservoirs and (ii) the rate of entropy production in the universe. (b) If the device is operated reversibly, what would be the required heat input from the high temperature reservoir to absorb 10 kW from the cold space?

Solution Denote the quantities associated with the high temperature source by 1, the cold space by 2 and the heat sink by 3. We obtain the entropy changes of the hot and cold reservoirs as follows

$$\Delta S_1 = Q_1 / T_1 = -15 / 373 = -0.04021 \text{ kWK}^{-1}$$

$$\Delta S_2 = Q_2 / T_2 = -10 / 278 = -0.03597 \text{ kWK}^{-1}$$

The entropy *change* of the cyclic device is zero because it operates in a cycle.

Applying the first law to the cyclic device with zero work transfer

$$Q_3 = Q_1 + Q_2 = 15 + 10 = 25 \text{ kW}$$

For the heat-sink reservoir

$$\Delta S_3 = Q_3 / T_3 = 25 / 303 = 0.08251 \text{ kWK}^{-1}$$

The entropy production in the composite system consisting of the three reservoirs and the cyclic device is

$$\sigma = \Delta S_1 + \Delta S_2 + \Delta S_3$$

$$\sigma = -0.04021 - 0.03597 + 0.08251 = 0.6328 \times 10^{-2} \text{ kWK}^{-1}$$

Since the entropy production is positive the composite system operates under irreversible conditions. However, the present computation does not reveal the exact source of the irreversibility that causes the entropy production.

(b) If the system is operated reversibly the total entropy production is zero. Applying the same equations as in part (a) for the change of entropy of the reservoirs we obtain the total entropy production as

$$-Q_1 / T_1 - Q_2 / T_2 + (Q_1 + Q_2) / T_3 = 0$$

Substituting numerical values in the above equation we obtain

$$-Q_1 / 373 - 10 / 278 + (Q_1 + 10) / 303 = 0$$

Hence

$$Q_1 = 4.79 \text{ kW}$$

Note that the heat input required to operate the absorption refrigerator increases from a minimum of 4.79 kW to 15 kW due to the irreversibilities of the first system.

Example 7.17 A real refrigeration system extracts heat from a cold space at 10°C and rejects heat to the surroundings at 27°C . Both the cold space and the surroundings may be treated as heat reservoirs as shown schematically in Fig. E7.17. The measured COP and the work input to the refrigerator are 2.1 and 80 kW respectively. The temperature differences between the working fluid and the heat reservoirs are 6°C and 10°C for the cold and hot reservoirs respectively. Assume that the temperature of the working fluid is constant during the heat interactions.

Calculate (i) the rates of entropy transfer, the entropy change and the entropy production for the cycle and the heat reservoirs and (ii) the entropy production due to heat transfer at the two reservoirs.

Solution The heat flow rates, the work input and the temperatures of the refrigeration cycle are indicated in the energy flow diagram in Fig. E7.17(a). The T - S diagram of the irreversible refrigeration cycle is shown in Fig. E7.17(b). We assume that during the heat interactions the working fluid of the cyclic device remains at constant temperature. The numerical data pertinent to the problem are as follows:

$$T_c = 273 + 10 = 283 \text{ K}, \quad T_{c1} = 283 - 6 = 277 \text{ K},$$

$$T_h = 273 + 27 = 300 \text{ K}, \quad T_{h1} = 300 + 10 = 310 \text{ K}.$$

$$W = 80 \text{ kW}, \quad COP = 2.1$$

For the refrigeration cycle,

$$COP_{ref} = Q_c / W = Q_c / 80 = 2.1$$

Hence $Q_c = 168 \text{ kW}$

Applying the first law to the cycle

$$Q_h = Q_c + W = 80 + 168 = 248 \text{ kW}.$$

The entropy *change* of the cyclic device is zero because it operates in a cycle manner.

The net entropy transfer rate *out* of the cyclic device is

$$\Delta S_{tr,c} = -Q_c / T_{c1} + Q_h / T_{h1}$$

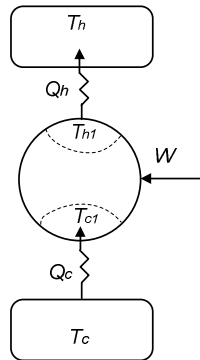
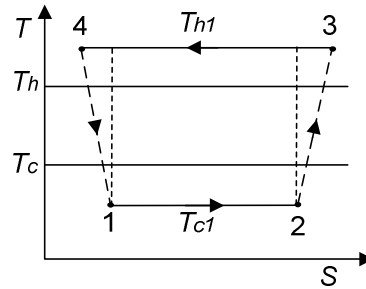


Fig. E7.17(a) Refrigeration cycle

Fig. E7.17(b) T - S diagram

$$\Delta S_{tr,c} = -168/277 + 248/310 = 0.1935 \text{ kWK}^{-1}$$

Applying the entropy balance equation to the cyclic device

$$\Delta S_{change} = \sigma + \Delta S_{trans}$$

$$0 = \sigma - 0.1935$$

Therefore the entropy production rate in the cyclic device is

$$\sigma = 0.1935 \text{ kWK}^{-1}$$

The entropy change of the cold reservoir is

$$\Delta S_{r,cold} = -Q_c / T_c = -168/283 = -0.5936 \text{ kWK}^{-1}$$

The entropy change of the hot reservoir is

$$\Delta S_{r,hot} = Q_h / T_h = 248/300 = 0.8267 \text{ kWK}^{-1}$$

The entropy production of the heat reservoirs are zero because the heat transfer processes in the reservoirs are reversible. Therefore the entropy *transfers* to the two reservoirs are equal to their respective entropy *changes* which were calculated above.

The heat transfer between the cyclic device and the two reservoirs occur across finite temperature differences as indicated in Fig. E7.15(a). These are *external* irreversibilities of the cyclic device. The entropy

production due to heat transfer at the two reservoirs is obtained by applying Eq. (7.55).

$$\sigma_{cold} = Q_c (1/T_{c1} - 1/T_c) = 168 \times (1/277 - 1/283)$$

$$\sigma_{cold} = 0.01286 \text{ kWK}^{-1}$$

$$\sigma_{hot} = Q_h (1/T_h - 1/T_{h1}) = 248 \times (1/300 - 1/310)$$

$$\sigma_{hot} = 0.02667 \text{ kWK}^{-1}$$

Note that it could be easily verified that the sum of the entropy production of the cyclic device and the entropy production due to the two heat transfer irreversibilities is equal to the net entropy change of the two reservoirs.

Example 7.18 A cyclic heat engine is operated between a system and a single thermal reservoir at a temperature T_r as shown in Fig. E7.18. The system does expansion work against an atmosphere at P_o while it undergoes a process from an initial state 1 to a final state 2. The engine executes an integral number of cycles during the process. Obtain an expression for maximum work output of the engine.

Solution Consider an infinitesimal cycle of the engine whose heat and work interactions are indicated in Fig. E7.18. Apply the first law to the system to obtain

$$-\delta Q = dU + P_o dV \quad (\text{E7.18.1})$$

Apply the first law to the cyclic engine. Hence

$$\delta Q = \delta W + \delta Q_r \quad (\text{E7.18.2})$$

Applying the second law to the composite system

$$dS + \delta Q_r / T_r \geq 0 \quad (\text{E7.18.3})$$

Adding Eqs. (E7.18.1) and (E7.18.2) we have

$$dU + P_o dV + \delta W + \delta Q_r = 0 \quad (\text{E7.18.4})$$

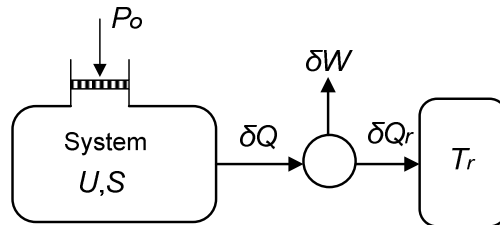


Fig. E7.18 Maximum work output of a closed system

Substituting from Eq. (E7.18.4) in Eq. (E7.18.3)

$$-(dU + P_o dV + \delta W) + T_r dS \geq 0$$

$$\delta W \leq T_r dS - dU - P_o dV \quad (\text{E7.18.5})$$

Integrating Eq. (E7.18.5) from the initial to the final state of the system

$$W_{12} \leq T_r (S_2 - S_1) - (U_2 - U_1) - P_o (V_2 - V_1)$$

$$W_{12} \leq (U_1 + P_o V_1 - T_r S_1) - (U_2 + P_o V_2 - T_r S_2)$$

Therefore the maximum work output is

$$W_{12, \max} = (U_1 + P_o V_1 - T_r S_1) - (U_2 + P_o V_2 - T_r S_2)$$

Example 7.19 A waste-heat recovery device is to be designed to produce a work output from a fixed mass of hot exhaust air at a temperature and pressure of 1100°C and 4 bar respectively. The air finally attains equilibrium with the atmosphere at 1 bar pressure and 30°C temperature. Calculate the maximum work that could be extracted from the hot air under the given conditions. Assume that air is an ideal gas.

Solution We derived an expression (see Sec. 7.3.2 and worked example 7.18) for the maximum useful work that could be produced by a *closed* system exchanging heat with a single reservoir at T_o , P_o as

$$W_{12, \max} = (U_1 + P_o V_1 - T_o S_1) - (U_2 + P_o V_2 - T_o S_2) \quad (\text{E7.19.1})$$

where 1 and 2 denote the initial and final states of the system.

The final temperature and pressure of the air are equal to the corresponding values of the atmosphere because the air attains equilibrium with the latter. Hence

$$T_2 = T_o \quad \text{and} \quad P_2 = P_o \quad (\text{E7.19.2})$$

Assume that air is an ideal gas with the equation state

$$PV = mRT \quad (\text{E7.19.3})$$

The entropy change of an ideal gas is obtained from the property relation

$$S - S_o = mc_p \ln(T/T_o) - mR \ln(P/P_o) \quad (\text{E7.19.4})$$

Substituting from Eqs. (E7.19.2), (E7.19.3) and (E7.19.4) in Eq. (E7.19.1)

$$\frac{W_{12,\max}}{m} = c_v (T_1 - T_o) + P_o \left(\frac{RT_1}{P_1} - \frac{RT_o}{P_o} \right) - T_o \left[c_p \ln \left(\frac{T_1}{T_o} \right) - R \ln \left(\frac{P_1}{P_o} \right) \right]$$

Substituting the given numerical values and the properties of air in the above equation we have

$$\begin{aligned} W_{12,\max} / m &= 0.718 \times (1373 - 303) + 0.287 \times (1373/4 - 303/1) \\ &\quad - 303 \times [1.005 \times \ln(1373/303) - 0.287 \times \ln(4/1)] \\ W_{12,\max} &= 440.2 \text{ kJ per kg of air.} \end{aligned}$$

Example 7.20 A process plant has excess steam at 1.5 bar pressure and 200°C temperature. The steam is brought to equilibrium with the atmosphere at 1 bar and 20°C. Calculate the maximum work that could be produced using this change of state of the steam.

Solution We apply the general relation derived earlier for the maximum work available from a process interacting with a single reservoir. Thus

$$W_{12,\max} = (U_1 + P_o V_1 - T_o S_1) - (U_2 + P_o V_o - T_o S_2) \quad (\text{E7.20.1})$$

where 1 and 2 represent the initial and final states of the steam.

For superheated steam at 1.5 bar and 200°C we obtain from the steam tables [6]:

$$u_1 = 2656 \text{ kJkg}^{-1}, \quad v_1 = 1.445 \text{ m}^3\text{kg}^{-1}, \quad s_1 = 7.643 \text{ kJkg}^{-1}\text{K}^{-1}$$

In the final equilibrium state, the liquid water is sub-cooled. We ignore the effect of pressure and use the saturated liquid data at 20°C. Hence

$$u_2 = 83.9 \text{ kJkg}^{-1}, \quad v_2 = 1.0018 \times 10^{-2} \text{ m}^3\text{kg}^{-1}, \quad s_2 = 0.296 \text{ kJkg}^{-1}\text{K}^{-1}$$

The ambient conditions are:

$$T_o = 20 + 273 = 293 \text{ K} \quad \text{and} \quad P_o = 100 \text{ kPa.}$$

Substituting the above numerical values in Eq. (E7.20.1) we obtain the maximum work output per unit mass of steam as

$$\begin{aligned} W_{12,\max} &= (2656 + 100 \times 1.445 - 293 \times 7.643) \\ &\quad - (83.9 + 100 \times 1.0018 \times 10^{-2} - 293 \times 0.296) = 562.9 \text{ kJkg}^{-1} \end{aligned}$$

Problems

P7.1 Show that any reversible process executed by a system could be replaced with a combination of two reversible adiabatic processes and a reversible isothermal process for which the magnitudes of the work and heat interactions are the same as those of the original process. Hence show that for a reversible cycle, $\oint_{\text{cycle}} \delta Q/T = 0$.

P7.2 A fixed quantity of steam of mass 0.12 kg is compressed in a reversible and adiabatic process from an initial pressure of 0.8 bar and quality 0.9 until the steam is just dry saturated. Calculate (i) the pressure in the final state, and (ii) the work done. [Answers: (i) 5.126 bar, (ii) 33.04 kJ]

P7.3 A block of copper of mass 1.5 kg at a temperature of 80°C is placed in thermal contact with a block of iron of mass 2 kg at a temperature of 20°C. The two blocks are well insulated from the surroundings. Calculate

(i) the final equilibrium temperature of the blocks, (ii) the change in entropy of the blocks, and (iii) the entropy production in the universe. The specific heat capacities of copper and iron are $0.38 \text{ kJkg}^{-1}\text{K}^{-1}$ and $0.5 \text{ kJkg}^{-1}\text{K}^{-1}$ respectively.

[Answers: (i) 41.8°C , (ii) -0.0653 kJK^{-1} , 0.0717 kJK^{-1} , (iii) 0.0064 kJK^{-1}]

P7.4 A fixed quantity of air of mass 0.12 kg is trapped in a well-insulated cylinder behind a piston. The initial equilibrium pressure and temperature are 1.1 bar and 283 K respectively. A large mass is now placed on the piston and released. After a few oscillations the system attains an equilibrium state with an air pressure of 1.6 bar . (a) Calculate (i) the final temperature of the air and (ii) the entropy change of the air. (b) Suggest a series of reversible processes to take the air back to its original state. [Answers: (a) (i) 46.7°C , (ii) 0.00182 kJK^{-1} , (b) Reversible adiabatic expansion to 1.0436 bar and 283 K , reversible isothermal compression to 1.1 bar]

P7.5 In an experiment a fixed quantity of steam at 4 bar and 150°C undergoes an adiabatic expansion to a pressure of 1 bar . The final equilibrium quality of the steam has been measured as 0.94 . (i) Check whether the process is feasible. (ii) If the expansion was reversible what should be the final quality of the steam? [Answers: feasible, $s_f - s_i = 0.066 > 0$, $x_2 = 0.929$]

P7.6 A closed system consisting of 0.15 kg of air, initially at 100 kPa and 303 K , undergoes a process to a final state of 360 kPa and 500 K , while in thermal contact with a reservoir at 500 K from which it receives 8 kJ of heat.

Calculate (i) the change in entropy of the air, (ii) the change in entropy of the reservoir, (iii) the entropy production in the universe and (iv) the minimum reversible work input for the same change of state of the system and the reservoir with a standard ambient reservoir at 293 K . [Answers: (i) 0.02036 kJK^{-1} , (ii) -0.016 kJK^{-1} , (iii) 0.00436 kJK^{-1} , (iv) 11.8 kJ]

P7.7 A fixed mass of air is trapped in a cylinder behind a frictionless piston of diameter 0.035 m. The mass of the piston and the weights placed on it is 12 kg and the external pressure on the piston is zero.

Initially, the conditions of the gas are: $P_1 = 1.5$ bar, $V_1 = 10^{-4}$ m³ and $T_1 = 30^\circ\text{C}$. The piston is held in position by a pin. The air, the piston and cylinder are in thermal equilibrium with the surroundings which may be regarded as a thermal reservoir at 30°C . The pin is now removed and the piston moves up until a final equilibrium state is reached. (a) Calculate (i) change in entropy of the air, (ii) the change in entropy of the surroundings and (iii) the entropy production in the universe. (b) Suggest a reversible process to return the air to the original state. [Answers: (a) (i) 1.0×10^{-5} kJK⁻¹, (ii) -0.912×10^{-5} kJK⁻¹, (iii) 0.88×10^{-6} kJK⁻¹, (b) reversible isothermal compression with a work input of 3.055×10^{-3} kJ]

P7.8 A piston-cylinder apparatus contains 0.12 m³ of nitrogen at pressure of 1.0 bar and temperature 28°C , initially. The nitrogen undergoes a compression process with a work input of 48 kJ until its pressure and temperature become 12 bar and 220°C respectively. During the process the nitrogen exchanges heat with the surroundings at 28°C . Calculate (i) the heat transfer from the nitrogen, (ii) the entropy change of the nitrogen, (iii) the entropy change of the surroundings treating it as a reservoir, and (iv) the entropy production in the universe. For nitrogen, $c_p = 1.04$ kJkg⁻¹K⁻¹, $c_v = 0.743$ kJkg⁻¹K⁻¹. [Answers: (i) -28.88 kJ, (ii) -0.0301 kJK⁻¹, (iii) 0.0959 kJK⁻¹, (iv) 0.0658 kJK⁻¹]

P7.9 The water in a tank is maintained at a steady uniform temperature of 80°C by an electrical immersion heater. The tank is thermally insulated with a material of thickness 0.05 m and thermal conductivity 0.045 Wm⁻¹K⁻¹. The temperature of outer surface of the insulation is equal to the ambient temperature of 20°C . The tank is in a steady state with a constant mass of water.

Calculate per unit area of insulation (i) the rate of change of entropy of the water, (ii) the rate of change of entropy of the ambient which can

be regarded as a reservoir at 20°C, and (iii) the rate of entropy production in the tank, the insulation and the universe. [Answers: (i) 0 WK⁻¹m⁻², (ii) 0.184 WK⁻¹m⁻², (iii) 0.153, 0.031, 0.184 WK⁻¹m⁻²]

P7.10 A poorly-insulated vessel contains a block of ice of mass 600 kg at a temperature of -20°C and pressure of 1 bar. The ice exchanges heat with the surroundings at 30°C and eventually attains thermal equilibrium with the latter. The pressure remains constant during the process. Calculate (i) the total heat flow between the surroundings and the ice, (ii) the change in entropy of the ice, (iii) the change in entropy of the surroundings and (iv) the entropy production in the universe. Neglect the heat capacity of the vessel. The specific heat capacity and latent heat of fusion of ice are 2.1 kJkg⁻¹K⁻¹ and 334 kJkg⁻¹ respectively. [Answer: (i) 301.2×10³ kJ, (ii) 1092.6 kJK⁻¹, (iii) 994.0 kJK⁻¹, (iv) 98.6 kJK⁻¹]

P7.11 A real heat engine operates between two reservoirs at 800 K and 290K. The cyclic device of the engine experiences a temperature difference of 15 K and 10 K at the hot and cold reservoirs respectively due to heat transfer. The efficiency of the engine is 28% and the power output is 600 kW. Calculate (i) entropy change in the two reservoirs, (ii) the entropy production due to heat transfer at the two reservoirs and (iii) the internal entropy production of the cyclic device. [Answers: (i) -2.68 kWK⁻¹, 5.32 kWK⁻¹, (ii) 0.0512 kWK⁻¹, 0.1773 kWK⁻¹, (iii) 2.411 kWK⁻¹]

P7.12 A fixed quantity of air of mass 0.2 kg is at a pressure of 10 bar and temperature 80°C. The air is to undergo a process exchanging heat with a standard-ambient reservoir at 20°C and 1 bar until the final pressure and temperature are 2 bar and 30°C. Calculate the maximum useful work that could be produced for this change of state of the air. [Answer: 18.58 kJ]

P7.13 The specific heat capacity of an ideal gas varies with temperature according to the relationship, $c_v = a + bT$. The equation of state of the ideal gas is $PV = mRT$. Obtain (i) an expression for the change in entropy from state 1 to state 2, (ii) the T - V relationship for an isentropic

expansion of the gas from state 1 to state 2, and (iii) an expression for the efficiency of a Carnot cycle using the ideal gas as the working fluid.

[Answers: (i) $S_2 - S_1 = ma \ln(T_2/T_1) + mb(T_2 - T_1) + mR(V_2/V_1)$,
(ii) $V_2/V_1 = (T_1/T_2)^{(a/R)} \exp[b(T_1 - T_2)/R]$, (iii) $\eta = 1 - T_c/T_h$]

P7.14 An internally irreversible heat engine operating with an ideal gas receives a quantity of heat Q_h per cycle isothermally from a reservoir at T_h and rejects heat isothermally to a reservoir at T_c . The entropy production during the adiabatic compression and expansion process of the cycle are σ_c and σ_e respectively. Sketch the T - S diagram of the cycle. Obtain an expression for the difference in efficiency between this cycle and a Carnot cycle operating between the same reservoirs.

[Answer: $\eta_{Carnot} - \eta = T_c (\sigma_c + \sigma_e) / Q_h$]

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