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Thermodynamics

الديناميكا الحرارية

اعداد الدكتور
علي شاكر باقر الجابري

Thermodynamics الديناميكا الحرارية

CHAPTER FIVE The Second Law of Thermodynamics

5.1 Heat Engines, Heat Pumps, and Refrigerators

5.2 Statements of the Second Law

5.3 Reversibility

5.4 The Carnot Engine

5.5 Carnot Efficiency

5.6 Entropy

5.7 The Inequality of Clausius

5.8 Entropy Change for an Irreversible Process

5.9 The Second Law Applied to a Control Volume

Quiz No. 1

Quiz No. 2

The classical presentation of the second law of thermodynamics starts with the concept of heat engines and refrigerators. A heat engine produces work from a heat transfer obtained from a thermal reservoir, and its operation is limited by the Kelvin–Planck statement. Refrigerators are functionally the same as heat pumps, and they drive energy by heat transfer from a colder environment to a hotter environment, something that will not happen by itself. The Clausius statement says in effect that the refrigerator or heat pump does need work input to accomplish the task. To approach the limit of these cyclic devices, the idea of reversible processes is discussed and further explained by the opposite, namely, irreversible processes and impossible machines. A perpetual motion machine of the first kind violates the first law (energy equation), and a perpetual machine of the second kind violates the second law of thermodynamics.

The limitations for the performance of heat engines (thermal efficiency) and heat pumps or refrigerators (coefficient of performance or COP) are expressed by the corresponding Carnot-cycle device. Two propositions about the Carnot cycle device are another way of expressing the second law of thermodynamics instead of the statements of Kelvin–Planck or Clausius. These propositions lead to the establishment of the thermodynamic absolute temperature, done by Lord Kelvin, and the Carnot-cycle efficiency. We show this temperature to be the same as the ideal-gas temperature introduced in Chapter 3.

You should have learned a number of skills and acquired abilities from studying this chapter that will allow you to

- Understand the concepts of heat engines, heat pumps, and refrigerators.
- Have an idea about reversible processes.
- Know a number of irreversible processes and recognize them.
- Know what a Carnot-cycle is.
- Understand the definition of thermal efficiency of a heat engine.
- Understand the definition of coefficient of performance of a heat pump.
- Know the difference between the absolute and relative temperature.
- Know the limits of thermal efficiency as dictated by the thermal reservoirs and the Carnot-cycle device.
- Have an idea about the thermal efficiency of real heat engines.
- Know the limits of coefficient of performance as dictated by the thermal reservoirs and the Carnot-cycle device.
- Have an idea about the coefficient of performance of real refrigerators.

The inequality of Clausius and the property entropy (s) are modern statements of the second law. The final statement of the second law is the entropy balance equation that includes generation of entropy. All the results that were derived from the classical formulation of the second law in Chapter 7 can be re-derived with the entropy balance equation applied to the cyclic devices. For all reversible processes, entropy generation is zero and all real (irreversible) processes have a positive entropy generation. How large the entropy generation is depends on the actual process.

Thermodynamic property relations for s are derived from consideration of a reversible process and leads to Gibbs relations. Changes in the property s are covered through general tables, approximations for liquids and solids, as well as ideal gases. Changes of entropy in various processes are examined in general together with special cases of polytropic processes. Just as a reversible specific boundary work is the area below the process curve in a P - v diagram, the reversible heat transfer is the area below the process curve in a T - s diagram.

You should have learned a number of skills and acquired abilities from studying this chapter that will allow you to

- Know that Clausius inequality is an alternative statement of the second law.
- Know the relation between the entropy and the reversible heat transfer.
- Locate states in the tables involving entropy.
- Understand how a Carnot cycle looks in a T - s diagram.
- Know how different simple process curves look in a T - s diagram.
- Understand how to apply the entropy balance equation for a control mass.
- Recognize processes that generate entropy and where the entropy is made.
- Evaluate changes in s for liquids, solids, and ideal gases.
- Know the various property relations for a polytropic process in an ideal gas.
- Know the application of the unsteady entropy equation and what a flux of s is.

The Second Law of Thermodynamics

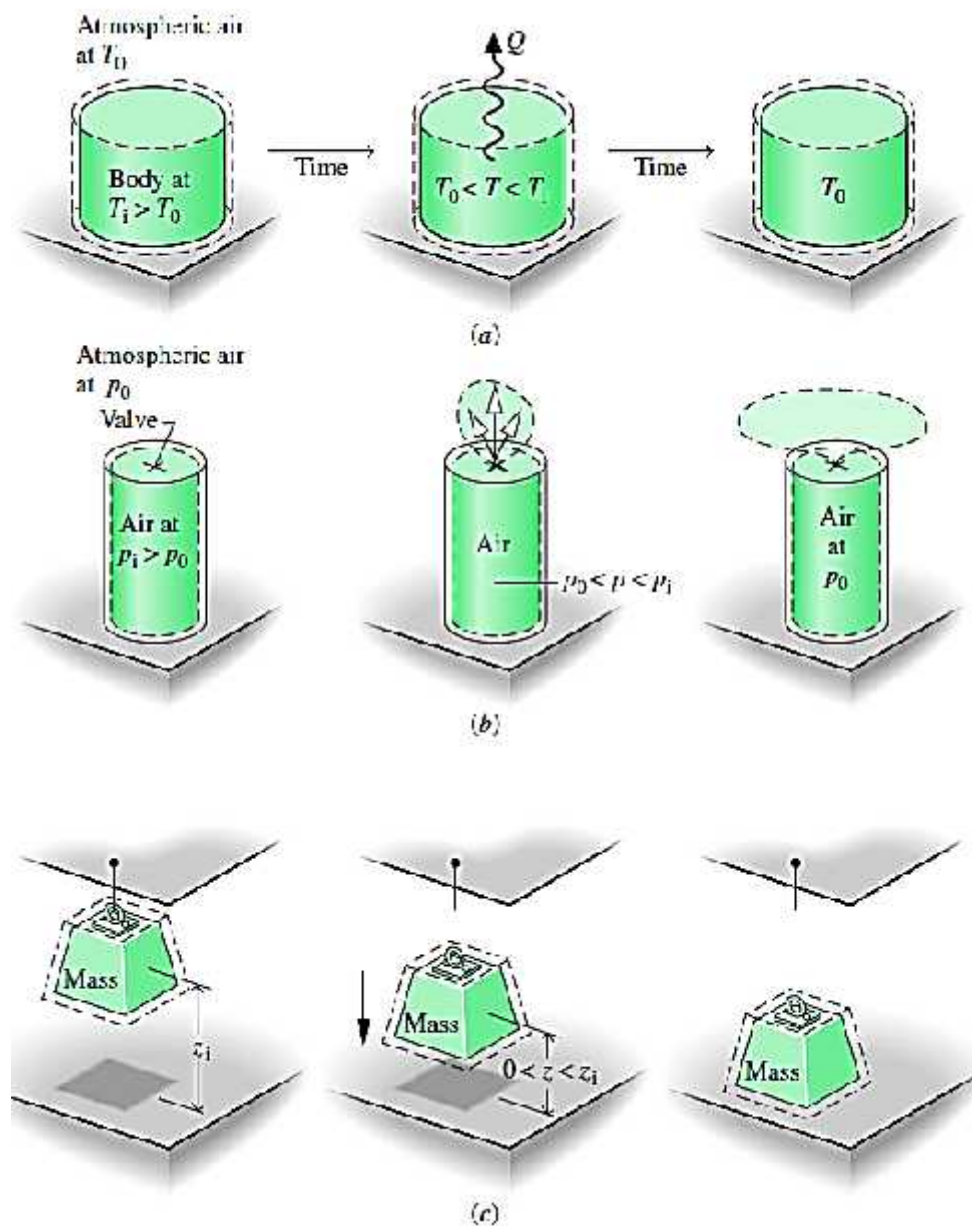
Water flows down a hill, heat flows from a hot body to a cold one, rubber bands unwind, fluid flows from a high-pressure region to a low-pressure region, and we all get old! Our experiences in life suggest that processes have a definite direction. The first law of thermodynamics relates the several variables involved in a physical process, but does not give any information as to the direction of the process. It is the second law of thermodynamics that helps us establish the direction of a particular process.

Consider, for example, the work done by a falling weight as it turns a paddle wheel thereby increasing the internal energy of air contained in a fixed volume. It would not be a violation of the first law if we postulated that an internal energy decrease of the air can turn the paddle and raise the weight. This, however, would be a violation of the second law and would thus be impossible.

In the first part of this chapter, we will state the second law as it applies to a cycle. It will then be applied to a process and finally a control volume; we will treat the second law in the same way we treated the first law.

Motivating the Second Law

تحفيز القانون الثاني



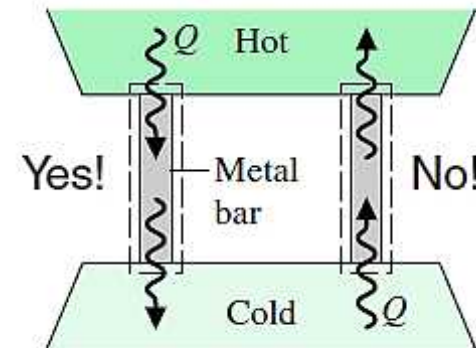
▲ **Figure 5.1** Illustrations of spontaneous processes and the eventual attainment of equilibrium with the surroundings. (a) Spontaneous heat transfer. (b) Spontaneous expansion. (c) Falling mass.

Statements of the Second Law

CLAUSIUS STATEMENT OF THE SECOND LAW

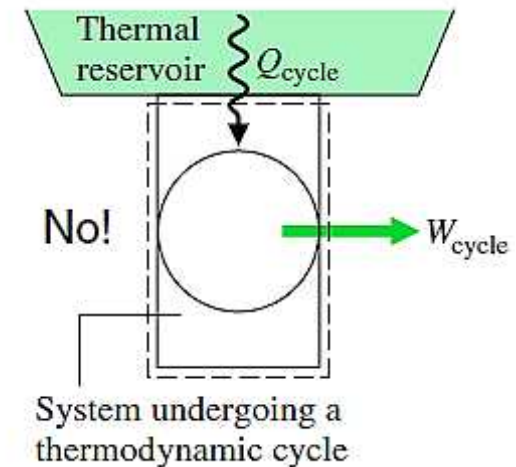
The Clausius statement of the second law asserts that: It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.

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KELVIN-PLANCK STATEMENT OF THE SECOND LAW

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir



5.1 Heat Engines, Heat Pumps, and Refrigerators

We refer to a device operating on a cycle as a heat engine, a heat pump, or a refrigerator, depending on the objective of the particular device. If the objective of the device is to perform work it is a *heat engine*; if its objective is to transfer heat to a body it is a *heat pump*; if its objective is to transfer heat from a body, it is a *refrigerator*.

Generically, a heat pump and a refrigerator are collectively referred to as a refrigerator. A schematic diagram of a simple heat engine is shown in Fig. 5.1. An engine or a refrigerator operates between two *thermal energy reservoirs*, entities that are capable of providing or accepting heat without changing temperatures. The atmosphere and lakes serve as *heat sinks*; furnaces, solar collectors, and burners serve as *heat sources*. Temperatures T_H and T_L identify the respective temperatures of a source and a sink. The net work W produced by the engine of Fig. 5.1 in one cycle would be equal to the net heat transfer, a consequence of the first law :

$$W = Q_H - Q_L$$

where Q_H is the heat transfer to or from the high-temperature reservoir, and Q_L is the heat transfer to or from the low-temperature reservoir.

If the cycle of Fig. 5.1 were reversed, a net work input would be required, as shown in Fig. 5.2. A heat pump would provide energy as heat Q_H to the warmer body (e.g., a house), and a refrigerator would extract energy as heat Q_L from the cooler body (e.g., a freezer). The work would also be given by above equation , where we use magnitudes only.

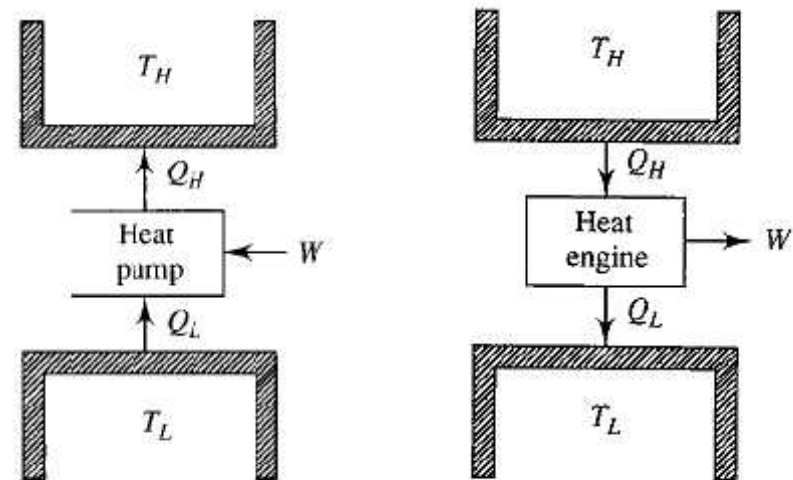


Figure 5.2 A refrigerator. Figure 5.1 A heat engine.

The *thermal efficiency* of the heat engine and the *coefficients of performance* (abbreviated COP) of the refrigerator and the heat pump are defined as follows:

$$\eta = \frac{W}{Q_H} \quad \text{COP}_{\text{ref}} = \frac{Q_L}{W} \quad \text{COP}_{\text{hp}} = \frac{Q_H}{W} \quad \text{COP} = \frac{Q_L}{W} = \frac{T_H}{T_H - T_L}$$

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_L}{T_H} \quad \eta_{\text{thermal}} = \frac{W(\text{energy sought})}{Q_H(\text{energy that costs})} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

where W is the net work output of the engine or the work input to the refrigerator.

Each of the performance measures represents the desired output divided by the input (energy that is purchased).

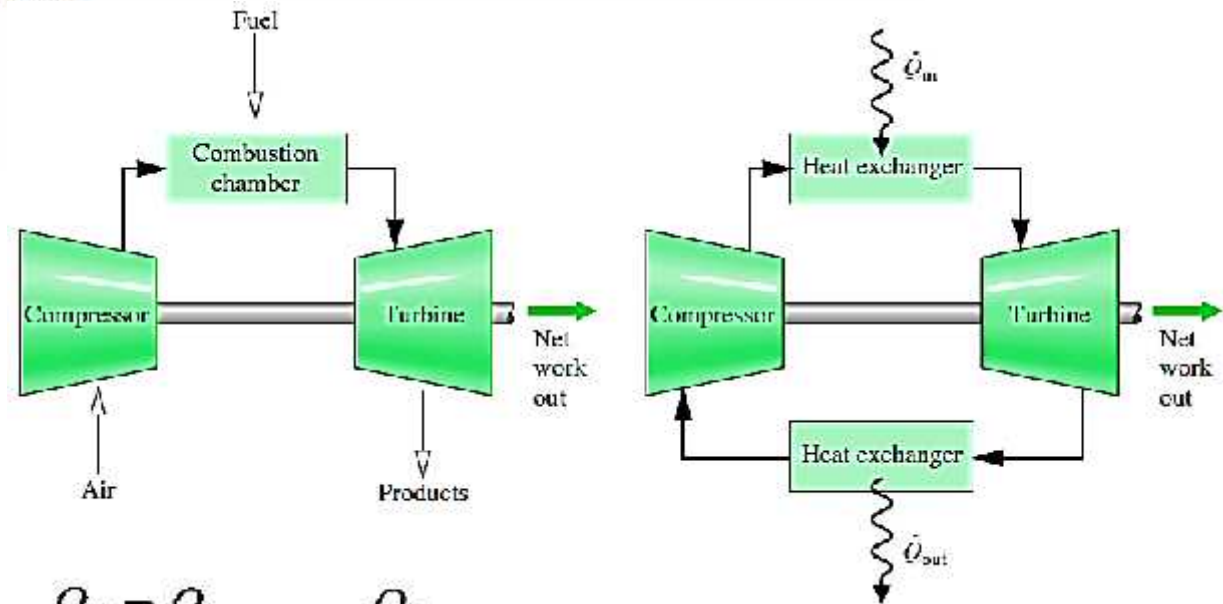
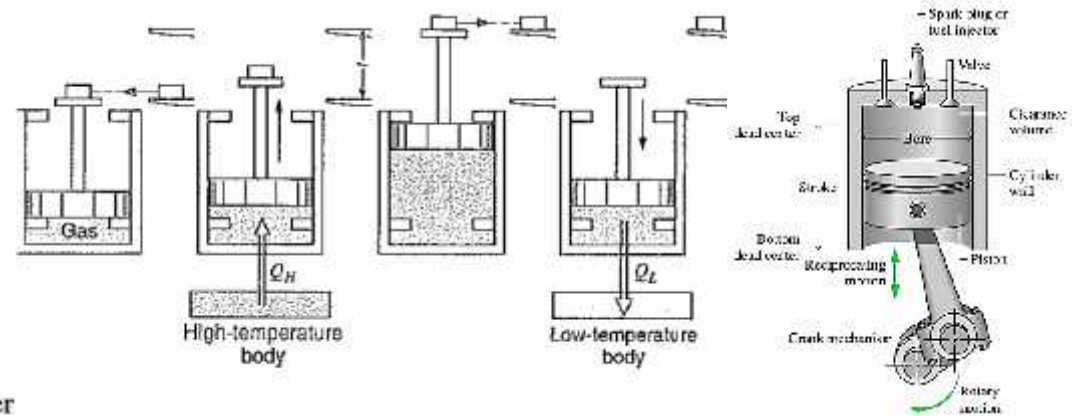
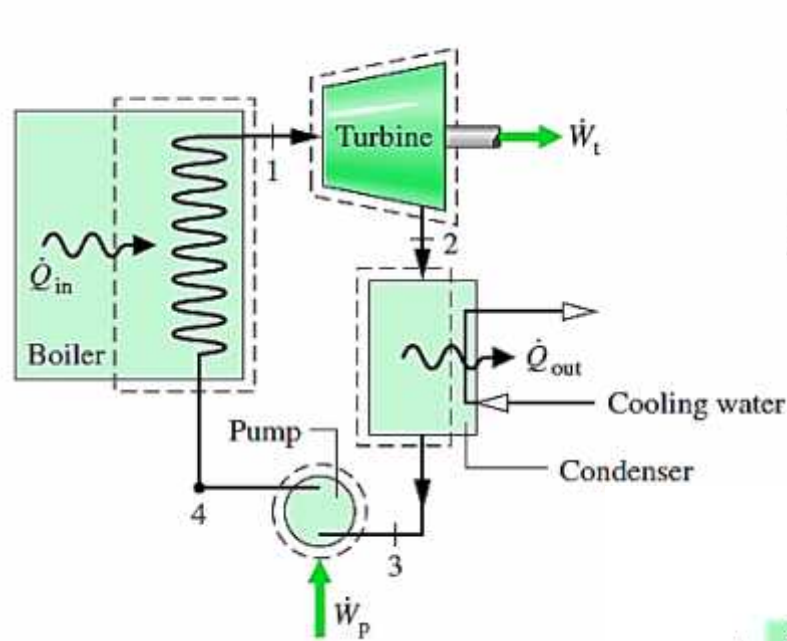
The second law of thermodynamics will place limits on the above measures of performance. The first law would allow a maximum of unity for the thermal efficiency and an infinite coefficient of performance. The second law, however, establishes limits that are surprisingly low, limits that cannot be exceeded regardless of the cleverness of proposed designs.

One additional note: There are devices that we will refer to as heat engines that do not strictly meet our definition; they do not operate on a thermodynamic cycle but instead exhaust the working fluid and then intake new fluid. The internal combustion engine is an example. Thermal efficiency, as defined above, remains a quantity of interest for such engines.

Heat engines vary greatly in size and shape, from large steam engines, gas turbines, or jet engines, to gasoline engines for cars and diesel engines for trucks or cars, to much smaller engines for lawn mowers or hand-held devices such as chain saws or trimmers. Typical values for the thermal efficiency of real engines are about 35–50% for large power plants, 30–35% for gasoline engines, and 35–40% for diesel engines. Smaller utility-type engines may have only about 20% efficiency, owing to their simple carburetion and controls and to the fact that some losses scale differently with size and therefore represent a larger fraction for smaller machines.

Heat Engine

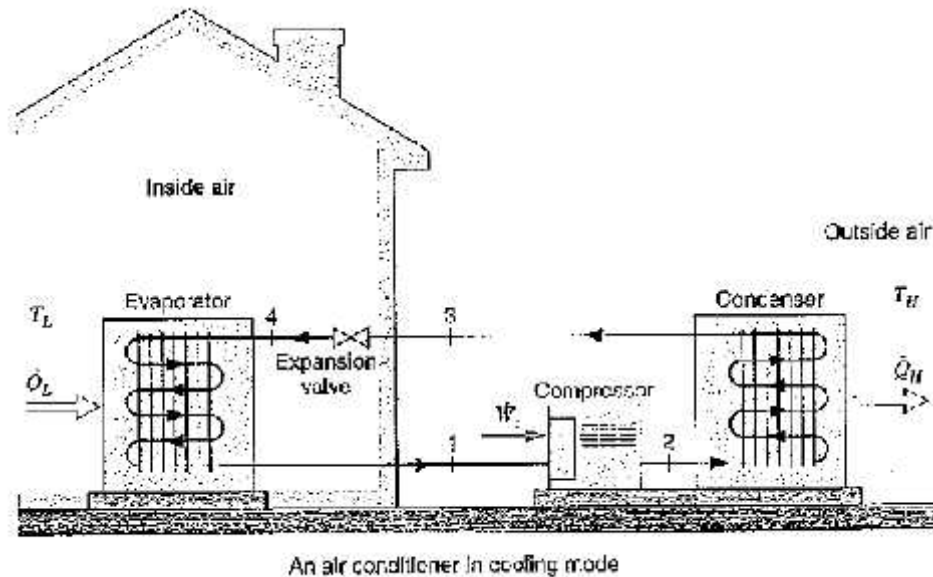
Steam turbine



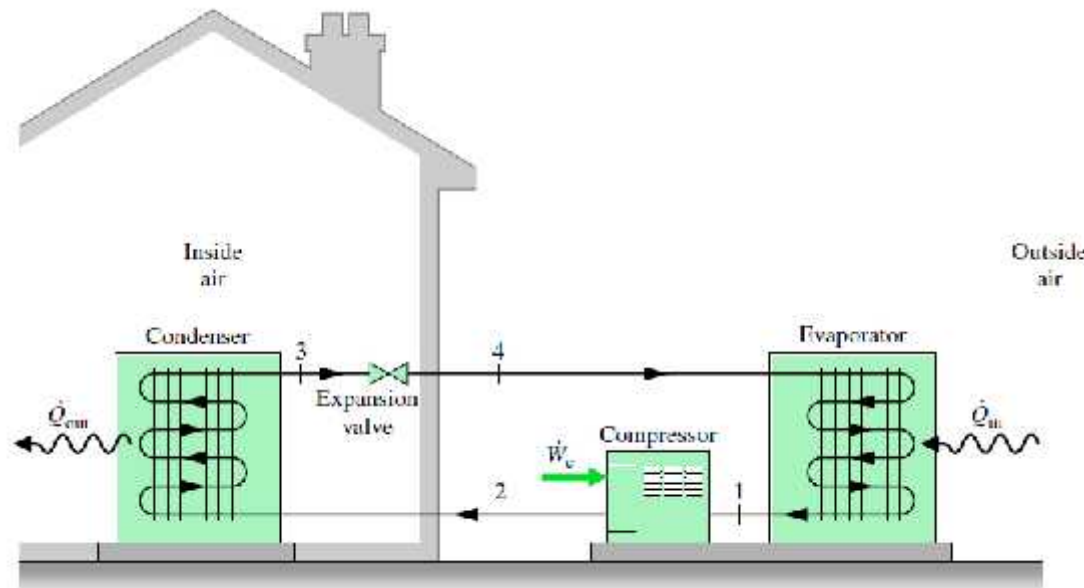
$$\eta_{\text{thermal}} = \frac{W(\text{energy sought})}{Q_H(\text{energy that costs})} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

gas turbine

Heat Pump and Refrigerator



Refrigerator



Heat Pump

Example An automobile engine produces 136 hp on the output shaft with a thermal efficiency of 30%. The fuel it burns gives 35 000 kJ/kg as energy release. Find the total rate of energy rejected to the ambient and the rate of fuel consumption in kg/s.

Solution

From the definition of a heat engine efficiency, Eq. 7.1, and the conversion of hp from Table A.1 we have:

$$\dot{W} = \eta_{\text{eag}} \dot{Q}_H = 136 \text{ hp} \times 0.7355 \text{ kW/hp} = 100 \text{ kW}$$

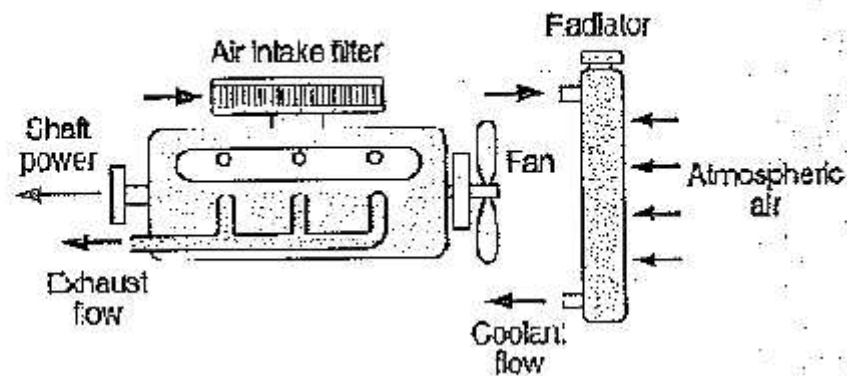
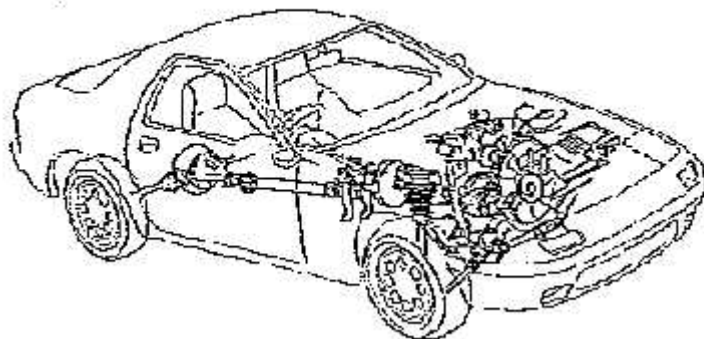
$$\dot{Q}_H = \dot{W} / \eta_{\text{eag}} = 100 / 0.3 = 333 \text{ kW}$$

The energy equation for the overall engine gives:

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = (1 - 0.3) \dot{Q}_H = 233 \text{ kW}$$

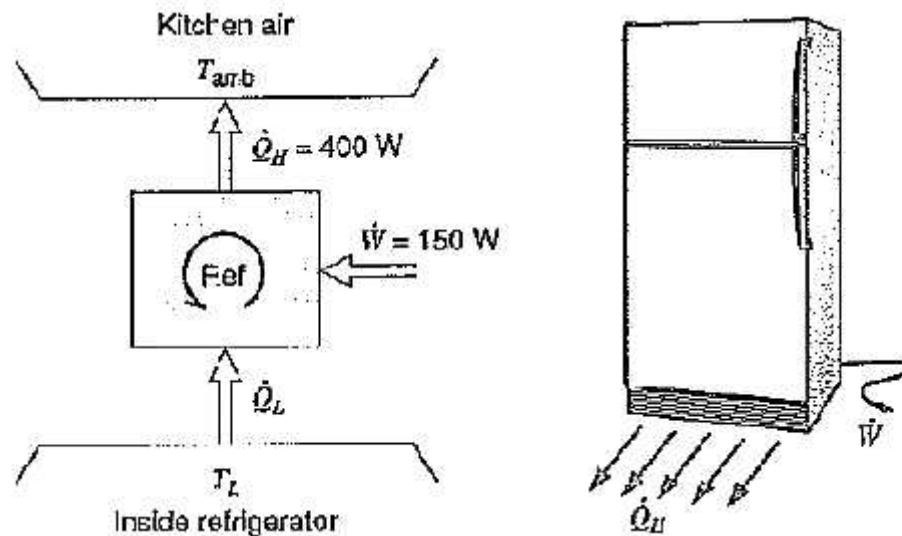
From the energy release in the burning we have: $\dot{Q}_H = \dot{m} q_H$, so

$$\dot{m} = \dot{Q}_H / q_H = \frac{333 \text{ kW}}{35\,000 \text{ kJ/kg}} = 0.0095 \text{ kg/s}$$



Example

The refrigerator in a kitchen shown in Fig. 7.7 receives an electrical input power of 150 W to drive the system, and it rejects 400 W to the kitchen air. Find the rate of energy taken out of the cold space and the coefficient of performance of the refrigerator.



Solution

C.V. refrigerator. Assume steady state so there is no storage of energy. The information provided is $\dot{W} = 150 \text{ W}$, and the heat rejected is $\dot{Q}_H = 400 \text{ W}$.

The energy equation gives:

$$\dot{Q}_L = \dot{Q}_H - \dot{W} = 400 - 150 = 250 \text{ W}$$

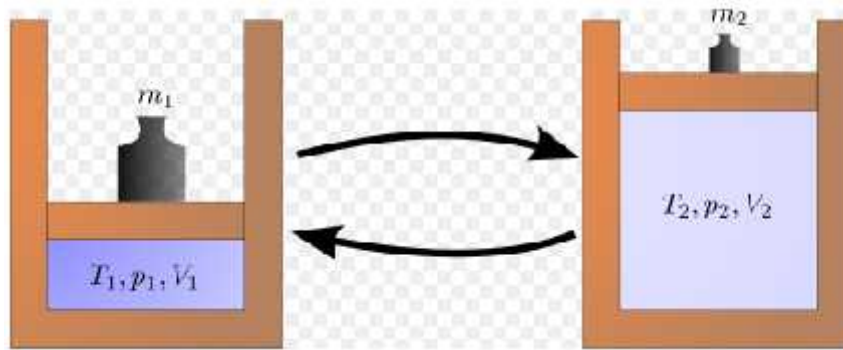
This is also the rate of energy transfer into the cold space from the warmer kitchen due to heat transfer and exchange of cold air inside with warm air when you open the door.

From the definition of the coefficient of performance, Eq. 7.2

$$\text{COP}_{\text{refrig}} = \frac{\dot{Q}_L}{\dot{W}} = \frac{250}{150} = 1.67$$

5.3 Reversibility

عملية عكوسية الكيمياء الفيزياء (بالإنجليزية : reversible process) عملية بأنها
 عكوسية يمكن عكسها تغير طفيف التغيرات
 طفيفة يكون هذا التغير عملية عكوسية مثالياً .
 عكوسية عملية عكوسية .
 زمنية حوله حوله هي نفسها
 تغير نهايتها . يمكن تعريف العملية العكوسية بأنها العملية يمكن عكسها انتهاءها غير
 فيها المحيط . وبصيغة الحرارية thermodynamic العملية بأنها عملية
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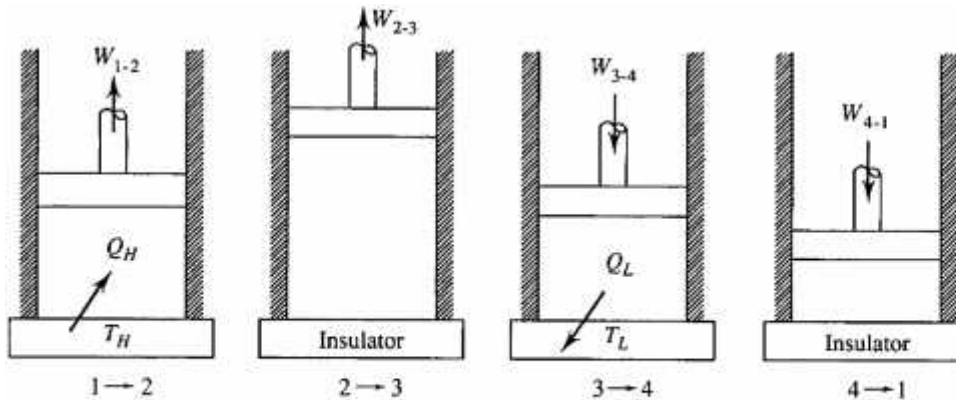


irreversibility

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 عكوسية بأنها عملية سريان العملية
 عملية غير عكوسية يتغير يكون
 المحيط به يكون تغير
 غير عكوسية نذكرها حيث
 (.
 غازين (حيث يتغير)
 عملية تنفيذ حرارية و

5.5 The Carnot Engine

The heat engine that operates the most efficiently between a high-temperature reservoir and a low-temperature reservoir is the *Carnot engine*. It is an ideal engine that uses reversible processes to form its cycle of operation; thus it is also called a *reversible engine*. We will determine the efficiency of the Carnot engine and also evaluate its reverse operation.



1 → 2: Isothermal expansion. Heat is transferred reversibly from the high-temperature reservoir at the constant temperature T_H . The piston in the cylinder is withdrawn and the volume increases.

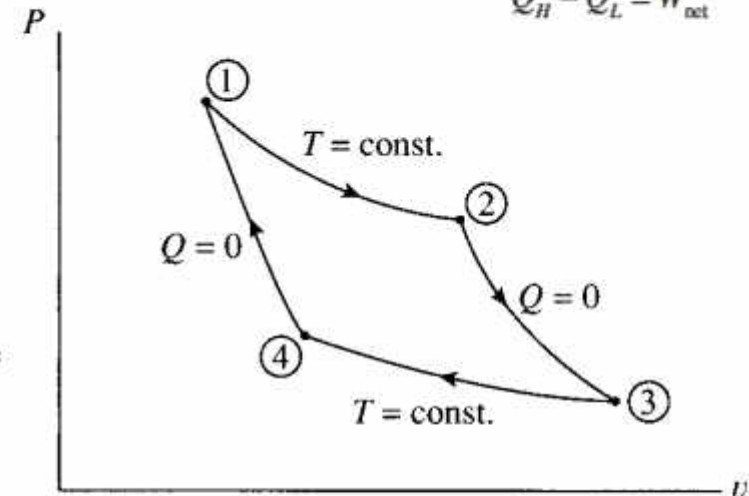
2 → 3: Adiabatic reversible expansion. The cylinder is completely insulated so that no heat transfer occurs during this reversible process. The piston continues to be withdrawn, with the volume increasing.

3 → 4: Isothermal compression. Heat is transferred reversibly to the low-temperature reservoir at the constant temperature T_L . The piston compresses the working substance, with the volume decreasing.

4 → 1: Adiabatic reversible compression. The completely insulated cylinder allows no heat transfer during this reversible process. The piston continues to compress the working substance until the original volume, temperature, and pressure are reached, thereby completing the cycle.

Applying the first law to the cycle, we note that

$$Q_H - Q_L = W_{\text{net}}$$



Applying the first law to the cycle, we note that

$$Q_H - Q_L = W_{\text{net}}$$

where Q_L is assumed to be a positive value for the heat transfer to the low-temperature reservoir. This allows us to write the thermal efficiency [see Eq. (5.2)] for the Carnot cycle as

$$\eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

The following examples will be used to prove the following three postulates:

Postulate 1 *It is impossible to construct an engine, operating between two given temperature reservoirs, that is more efficient than the Carnot engine.*

Postulate 2 *The efficiency of a Carnot engine is not dependent on the working substance used or any particular design feature of the engine.*

Postulate 3 *All reversible engines, operating between two given temperature reservoirs, have the same efficiency as a Carnot engine operating between the same two temperature reservoirs.*

5.6 Entropy

الإنتروبيا أساسيا الفيزياء والكيمياء قوانين التحريك اليونانية ومعناها " . "

للثرموديناميك يتعامل العمليات الفيزيائية الكبيرة جزيئات ويبحث سلوكها كعملية تلقائيا . ينص للديناميكا الحرارية يقول : فيزيائي تغير يحدث تلقائيا يصحبه ازدياد "إنتروبيته" .

التغير تلقائيا بزيادة أنتروبيته يصل توزيع جميع أجزائه، يميل غير يحتاج هذا رويدا رويدا يصبح فيه ترايدت إنتروبية النقية + إنتروبية النقية إنتروبية " للإنتروبية الطبيعية أهمية هاما تحديد الحرارية الديزل وغيرها فنجدها ميكانيكي إنتروبيا سهل ويتم طبيعيا، وهو ثانيا ليصبح لدينا عملية له إنتروبيا كبيرة، بينما يكون أنتروبيتها العملية عمليات يومية بتسخين فهي طريق تبخير

الإنتروبيا

ولكنها تستهلك ! يمكن
ديناميكي (هذا ينص عليه للديناميكا الحرارية ينص عليه _____
_____ يعمل بالبنزين فإنه يستخدم _____
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الإنتروبيا وتبين له أنه يمكن تحويل كمية _____
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5.6 Entropy

To allow us to apply the second law of thermodynamics to a process we will identify a property called entropy. This will parallel our discussion of the first law; first we stated the first law for a cycle and then derived a relationship for a process.

Consider the reversible Carnot engine operating on a cycle consisting of the processes described in Sec. 5.5. The quantity $\oint \frac{\delta Q}{T}$ is the cyclic integral of the heat transfer divided by the absolute temperature at which the heat transfer occurs. Since the temperature T_H is constant during the heat transfer Q_H and T_L is constant during heat transfer Q_L , the integral is given by

$$\oint \frac{\delta Q}{T} = \frac{Q_H}{T_H} - \frac{Q_L}{T_L} \quad *$$

where the heat Q_L leaving the Carnot engine is considered to be positive. Using Eqs.

$$\eta = 1 - \frac{T_L}{T_H} \quad \eta = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

we see that, for the Carnot cycle,

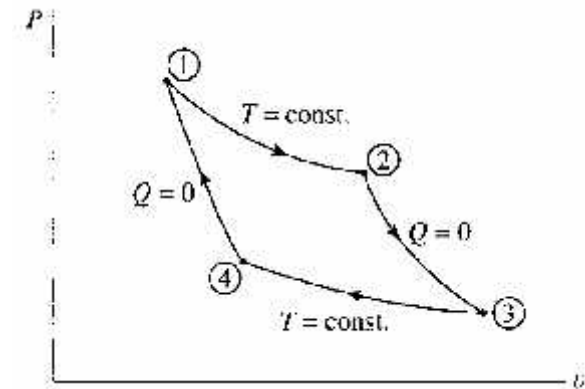
$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad \text{or} \quad \frac{Q_H}{T_H} = \frac{Q_L}{T_L}$$

Substituting this into Eq. *, we find the interesting result

$$\oint \frac{\delta Q}{T} = 0$$

Thus, the quantity $\delta Q/T$ is a perfect differential, since its cyclic integral is zero. We let this differential be denoted by dS , where S depends only on the state of the system. This, in fact, was our definition of a property of a system. We shall call this extensive property *entropy*; its differential is given by

$$dS = \left. \frac{\delta Q}{T} \right|_{\text{rev}}$$



where the subscript “rev” emphasizes the reversibility of the process. This can be integrated for a process to give

$$\Delta S = \int_1^2 \frac{\delta Q}{T}_{\text{rev}}$$

From the above equation we see that the entropy change for a reversible process can be either positive or negative depending on whether energy is added to or extracted from the system during the heat transfer process. For a reversible adiabatic process ($Q = 0$) the entropy change is zero. If the process is adiabatic but irreversible, it is not generally true that $\Delta S = 0$.

We often sketch a temperature-entropy diagram for cycles or processes of interest. The Carnot cycle provides a simple display when plotting temperature vs. entropy; it is shown in Fig. 5.7. The change in entropy for the first isothermal process from state 1 to state 2 is

$$S_2 - S_1 = \int_1^2 \frac{\delta Q}{T} = \frac{Q_H}{T_H}$$

The entropy change for the reversible adiabatic process from state 2 to state 3 is zero. For the isothermal process from state 3 to state 4 the entropy change is negative that of the first process from state 1 to state 2; the process from state 4 to state 1 is also a reversible adiabatic process and is accompanied with a zero entropy change. The heat transfer during a reversible process can be expressed in differential form as

$$dS = \frac{\delta Q}{T}_{\text{rev}} \quad \delta Q = TdS \quad \text{or} \quad Q = \int_1^2 TdS$$

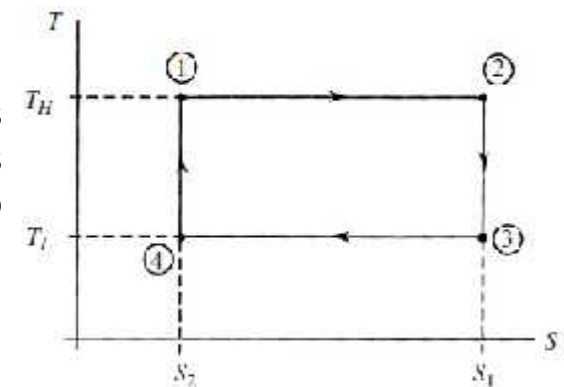


Figure 5.7 The Carnot cycle.

Hence, the area under the curve in the T - S diagram represents the heat transfer during any reversible process. The rectangular area in Fig. 5.6 thus represents the net heat transfer during the Carnot cycle. Since the heat transfer is equal to the work done for a cycle, the area also represents the net work accomplished by the system during the cycle. For this Carnot cycle $Q_{\text{net}} = W_{\text{net}} = \Delta T \Delta S$.

The first law of thermodynamics, for a reversible infinitesimal change, becomes, using the last equation ,

$$TdS - PdV = dU$$

This is an important relationship in our study of simple systems. We arrived at it assuming a reversible process. However, since it involves only properties of the system, it holds for any process including any irreversible process. If we have an irreversible process, in general, $\delta W \neq PdV$ and $\delta Q \neq TdS$ but previous equation still holds as a relationship between the properties since changes in properties do not depend on the process. Dividing by the mass, we have

$$Tds - Pdv = du \quad **$$

where the specific entropy is $s = S/m$.

To relate the entropy change to the enthalpy change we differentiate the definition of enthalpy and obtain

$$dh = du + Pdv + v dP$$

Substituting into Eq. ** for du , we have

$$Tds = dh - v dP \quad ***$$

Equations ** and *** will be used in subsequent sections of our study of thermodynamics for various reversible and irreversible processes.

A rigid tank of volume 0.5m^3 contains saturated water mixture with quality of 50% at 120°C is heated until its temperature becomes 200°C . Find (a) final state of the water and pressure, (b) heat transfer (c) change of entropy.

Solution: The given rigid tank $V=0.5\text{m}^3$ sat water $T_1=120^\circ\text{C}$, $x_1=0.5$
The final temperature is $T_2=200^\circ\text{C}$

At $T_1=120^\circ\text{C}$ and from sat. Water table it is found that

$$v_{f1} = 0.001060\text{m}^3/\text{kg} \quad v_{g1} = 0.8919\text{m}^3/\text{kg}$$

$$u_{f1} = 503.5\text{kJ}/\text{kg} \quad u_{fg1} = 2025.8\text{kJ}/\text{kg}$$

$$s_{f1} = 1.5276\text{kJ}/\text{kg}\cdot\text{K} \quad s_{fg1} = 5.602\text{kJ}/\text{kg}\cdot\text{K}$$

$$v_1 = v_{f1} + x_1(v_{g1} - v_{f1}) = 0.00106 + 0.5 \times (0.8919 - 0.00106) = 0.44648\text{m}^3/\text{kg}$$

$$m = \frac{V}{v_1} = \frac{0.5}{0.44648} = 1.12\text{kg}$$

$$u_1 = u_{f1} + x_1 u_{fg1} = 503.5 + 0.5 \times 2025.8 = 1516.4\text{kJ}/\text{kg}$$

$$s_1 = s_{f1} + x_1 s_{fg1} = 1.5276 + 0.5 \times 5.602 = 4.3286\text{kJ}/\text{kg}\cdot\text{K}$$

Because the tank is rigid $v_1 = v_2$

$$v_2 = 0.44648\text{m}^3/\text{kg} \text{ at } T_2 = 200^\circ\text{C}$$

It is found that the second state is super-heated steam because $v_2 > v_g$ at the temperature 200°C . The pressure is between 0.4MPa and 0.5MPa

And by using the interpolation as follows

P MPa	v m ³ /kg	u kJ/kg	s kJ/kg.K
0.4	0.5342	2646.8	7.1706
.48	0.44648	2643.67	7.0812
0.5	0.4249	2642.9	7.0592

(a) the final pressure is $P_2=480\text{kPa}$

(b) because the tank is rigid

$$Q = \Delta U = m\Delta u = 1.12(2646.67 - 1516.4) = 1265.9\text{kJ}$$

$$\Delta S = m\Delta s = m(s_2 - s_1) = 1.12(7.0812 - 4.3286) = 3.083$$

Piston cylinder contains 2kg of steam at a pressure of 200kPa and quality of 75% is heated with constant pressure until it becomes dry saturated vapor. Find (a) the work done (b) the heat transfer and (c) the change in entropy.

Solution: the given sat. water mixture at $P_1=200\text{kPa}$ and $x_1=0.75$ $m=2\text{kg}$, the final state is sat. vapor at the same pressure of 200kPa.

(a) $v_1 = v_f + x_1 v_{fg}$ and $v_2 = v_g$ at $P = 200\text{kPa}$

$$W = P(V_2 - V_1) = Pm(v_2 - v_1) = Pm(v_g - (v_f + x_1 v_{fg}))$$

$$W = Pm(v_{fg} - x_1 v_{fg}) Pm(1 - x_1)(v_g - v_f) = 200 \times 2 \times (1 - 0.75)(0.8857 - 0.001061)$$

$$W = 88.464\text{kJ}$$

(b) $h_1 = h_f + x_1 h_{fg}$ and $h_2 = h_g$

$$Q = m\Delta h = m(h_2 - h_1) = m(1 - x_1)h_{fg} = 2 \times (1 - 0.75) \times 2209.1 = 1104.55\text{kJ}$$

(c) $s_1 = s_f + x_1 s_{fg}$ and $s_2 = s_g$

$$\Delta S = m(s_2 - s_1) = m(1 - x_1)s_{fg} = 2 \times (1 - 0.75) \times 5.597 = 2.7985\text{kJ/K}$$

Piston cylinder device contains 0.5kg of refrigerant-12 at 20°C and quality of 40%. The refrigerant is expanded isothermally until its final pressure becomes 240kPa. Find (1) the change in entropy (2) heat transfer (3) the work done.

Solution: the given R-12 $T_1=T_2=20^\circ\text{C}$, $x_1=0.4$, $P_2=240\text{kPa}$

At the initial state

$$u_1 = u_f + x_1 u_{fg} = 54.44 + 0.4 \times (178.32 - 54.44) = 103.992 \text{ kJ / kg}$$

$$s_1 = s_f + x_1 s_{fg} = 0.2078 + .4 \times (0.6884 - 0.2078) = 0.4 \text{ kJ / kg.K}$$

At the final state

$$u_2 = 182.53 \text{ kJ / kg} \quad s_2 = 0.7624 \text{ kJ / kg.K}$$

$$(1) \Delta S = m(s_2 - s_1) = 0.5 \times (0.7624 - 0.4) = 0.1812 \text{ kJ / K}$$

(2) The process is isothermal so $T=\text{constant}$

$$Q = \int TdS = T \int dS = T\Delta S = (20 + 273) \times 0.1812 = 53.092 \text{ kJ}$$

$$(3) W = Q - \Delta U = 53.092 - 0.5 \times (182.53 - 103.992) = 13.787 \text{ kJ}$$

One kg of steam at a pressure of 700kPa and quality of 80% is expanded hyperbolically to a pressure of 150kPa. Determine (a) the final state of the vapor and (b) change in entropy

Solution: the given $m=1\text{kg}$, $P_1=700\text{kPa}$, $x_1=0.8$, $P_2=150\text{kPa}$

The Process is hyperbolically $P_1V_1=P_2V_2$

At $P_1=700\text{kPa}$, $x_1=0.8$

$$v_1 = v_f + x_1(v_g - v_f) = 0.001108 + 0.8 \times (0.02729 - 0.001108) = 0.21854 \text{ m}^3 / \text{kg}$$

$$s_1 = s_f + x_1 s_{fg} = 1.9922 + 0.8 \times 4.7158 = 5.7648 \text{ kJ} / \text{kg} \cdot \text{K}$$

$$v_2 = \frac{P_1 v_1}{P_2} = \frac{700 \times 0.21854}{150} = 1.01985 \text{ m}^3 / \text{kg}$$

$$v_2 < v_g \text{ at } P_2 = 150 \text{ kPa}$$

$$x_2 = \frac{v_2 - v_f}{v_g - v_f} = \frac{1.0198 - 0.001053}{1.1593 - 0.001053} = 0.8796 = 87.96\%$$

$$s_2 = s_f + x_2 s_{fg} = 1.4336 + 0.8796 \times 5.7897 = 6.526 \text{ kJ} / \text{kg} \cdot \text{K}$$

$$\Delta S = m(s_2 - s_1) = 1 \times (6.526 - 5.7648) = 0.7612 \text{ kJ} / \text{K}$$

ENTROPY FOR AN IDEAL GAS WITH CONSTANT SPECIFIC HEATS

Assuming an ideal gas

$$Tds - Pd v - du \quad \text{becomes} \quad ds = \frac{du}{T} + \frac{Pd v}{T} = C_v \frac{dT}{T} + R \frac{d v}{v} \quad \text{where we have used } du = C_v dT \text{ and } Pv = RT.$$

Last equation is integrated, assuming constant specific heat, to yield

$$s_2 - s_1 = C_v \ln \frac{T_2}{T_1} + R \ln \frac{v_2}{v_1} \quad \dots 1$$

$$Tds - dh - v dP \quad \text{Similarly, this equation is rearranged and integrated to give } s_2 - s_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1} \quad \dots 2$$

Note again that the above equations were developed assuming a reversible process; however, they relate the change in entropy to other thermodynamic properties at the two end states. Since the change of a property is independent of the process used in going from one state to another, the above relationships hold for any process, reversible or irreversible, providing the working substance can be approximated by an ideal gas with constant specific heats.

If the entropy change is zero, as in a reversible adiabatic process, Eqs. 1 and 2 can be used to obtain

$$\frac{T_2}{T_1} = \left(\frac{v_1}{v_2} \right)^{k-1} \quad \frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \quad \frac{P_2}{P_1} = \left(\frac{v_1}{v_2} \right)^k$$

These are, of course, identical to the equations obtained in Chap. 4 for an ideal gas with constant specific heats undergoing a quasiequilibrium adiabatic process. We now refer to such a process as an **isentropic process**.

EXAMPLE 5.6

Air is contained in an insulated, rigid volume at 20°C and 200 kPa. A paddle wheel, inserted in the volume, does 720 kJ of work on the air. If the volume is 2m³, calculate the entropy increase assuming constant specific heats

Solution

To determine the final state of the process we use the energy equation, assuming zero heat transfer. We have $-W = \Delta U = m C_v \Delta T$. The mass m is found from the ideal-gas equation to be

$$m = \frac{PV}{RT} = \frac{200 \times 2}{0.287 \times 293} = 4.76 \text{ kg}$$

The first law, taking the paddle-wheel work as negative, is then

$$\begin{aligned} -W - mC_v \Delta T \\ -(-720) = 4.76 \times 0.717 \times (T_2 - 293) \quad \therefore T_2 = 504.0 \text{ K} \end{aligned}$$

Using Eq. (1) for this constant-volume process there results $\Delta S = mC_v \ln \frac{T_2}{T_1} = 4.76 \times 0.717 \times \ln \frac{504}{293} = 1.851 \text{ kJ/K}$

EXAMPLE 5.7

After a combustion process in a cylinder the pressure is 1200 kPa and the temperature is 350°C. The gases are expanded to 140 kPa with a reversible adiabatic process. Calculate the work done by the gases, assuming they can be approximated by air with constant specific heats.

Solution

The first law can be used, with zero heat transfer, to give $-w = \Delta u = C_v(T_2 - T_1)$. The temperature T_2 is found from Eq. (2) to be

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{(k-1)/k} = 623 \left(\frac{140}{1200} \right)^{0.4/1.4} = 337 \text{ K}$$

This allows the work to be calculated:

$$w = C_v(T_2 - T_1) = 0.717 \times (623 - 337) = 205 \text{ kJ/kg}$$

0.05m³ of air at a pressure of 800kPa and temperature 20°C expands to eight times its original volume and the final temperature after expansion is 25°C. Calculate the change of entropy of air during this process.

Solution: the givens air $V_1=0.05\text{m}^3$, $P_1=800\text{kPa}$, $T_1=20^\circ\text{C}=293\text{K}$

$V_2 = 8 \times V_1 = 8 \times 0.05 = 0.4\text{m}^3$, $T_2=25^\circ\text{C}=298\text{K}$

$$m = \frac{P_1 V_1}{R T_1} = \frac{800 \times 0.05}{0.287 \times 293} = 0.476 \text{ kg}$$

$$\Delta S = m \left(C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \right) = 0.476 \left(0.718 \ln \frac{298}{293} + 0.287 \ln \frac{8}{1} \right) = 0.29 \text{ kJ / K}$$

Calculate the change of entropy of 2kg of air, when it is heated at constant volume from 100kPa to 400kPa. Also calculate the heat transfer during the process.

Solution: the given Air $m=2\text{kg}$, $P_1=100\text{kPa}$, $P_2=400\text{kPa}$, and the volume is constant then

$$\Delta S = m C_v \ln \frac{P_2}{P_1} = 2 \times 0.718 \ln \frac{400}{100} = 1.991 \text{ kJ / K}$$

Air occupies 0.084m^3 at 1.25MPa and 537°C . It is expanded at a constant temperature to a final volume of 0.336m^3 . Calculate:

- (i) the pressure at the end of expansion, (ii) work done during expansion (iii) heat transfer to the air, and (iv) the entropy

Solution: the givens air $V_1=0.084\text{m}^3$, $P_1=1250\text{kPa}$,
 $T_1=T_2=537^\circ\text{C}=810\text{K}$, $V_2=0.336\text{m}^3$

$$(i) P_2 = P_1 \frac{V_1}{V_2} = 1250 \times \frac{0.084}{0.336} = 312.5 \text{ kPa}$$

$$(ii) W = P_1 V_1 \ln \frac{V_2}{V_1} = 1250 \times 0.084 \times \ln \frac{0.336}{0.084} = 145.561 \text{ kJ}$$

$$(iii) Q = W = 145.56 \text{ kJ}$$

$$(iv) \Delta S = \frac{Q}{T} = \frac{145.561}{810} = 0.18 \text{ kJ / K}$$

A volume of 0.14m^3 of air at 100kPa and 90°C is compressed to 0.014m^3 according to $PV^{1.3}=\text{const}$. Heat is then added at a constant volume until the pressure is 6600kPa . Determine:

(1) heat exchange with the cylinder walls during compression, and

(2) Change of entropy during each portion of the process.

Solution: given Air $V_1=0.14\text{m}^3$, $P_1=100\text{kPa}$, $T_1=90^\circ\text{C}$, $V_2=0.014\text{m}^3$, $P_3=6600\text{kPa}$, $P_1V_1^{1.3} = P_2V_2^{1.3}$, $V_2 = V_3$

$$m = \frac{P_1V_1}{RT_1} = \frac{100 \times 0.14}{0.287 \times (90 + 273)} = 0.1855 \text{ kg}$$

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{n-1} = 363 \left(\frac{0.14}{0.014} \right)^{1.3-1} = 724.28 \text{ K}$$

$$P_2 = P_1 \left(\frac{V_1}{V_2} \right)^n = 100 \left(\frac{0.14}{0.014} \right)^{1.3} = 1995 \text{ kPa}$$

$$W_{12} = \frac{mR(T_2 - T_1)}{1 - n} = \frac{0.1855 \times 0.287 \times (724.28 - 363)}{1 - 1.3} = -64.11 \text{ kJ}$$

$$\Delta U_{12} = mCv(T_2 - T_1) = 0.1855 \times 0.718 \times (724.28 - 363) = 48.12 \text{ kJ}$$

$$Q_{12} = W_{12} + \Delta U_{12} = -64.11 + 48.12 = 15.99 \text{ kJ}$$

$$\Delta S_{12} = \frac{mCv(k-1)}{(n-1)} \text{Ln} \frac{T_2}{T_1} = \frac{0.1855 \times 0.718(1.4-1)}{1.3-1} \text{Ln} \frac{724.28}{363} = 0.12267 \text{ kJ / K}$$

The second process is constant volume process so

$$\Delta S_{23} = mCv \text{Ln} \frac{P_3}{P_2} = 0.1855 \times 0.718 \times \text{Ln} \frac{6600}{1995} = 0.159 \text{ kJ / K}$$

ENTROPY FOR STEAM, SOLIDS, AND LIQUIDS

The entropy change has been found for an ideal gas with constant specific heats and for an ideal gas with variable specific heats. For pure substances, such as steam, entropy is included as an entry in the steam tables (given in App. C). In the quality region, it is found using the relation

$$s = s_f + x s_{fg}$$

Note that the entropy of saturated liquid water at 0°C is arbitrarily set equal to zero. It is only the change in entropy that is of interest.

For a compressed liquid it is included as an entry in Table C.4, the compressed liquid table, or it can be approximated by the saturated liquid values s_f at the given temperature (ignoring the pressure). From the compressed liquid table at 10 Mpa and 100°C, $s = 1.30$ kJ/kg · K, and from the saturated steam table C.1 at 100°C, $s_f = 1.31$ kJ/kg · K; this is an insignificant difference.

The temperature-entropy diagram is of particular interest and is often sketched during the problem solution. A T - s diagram is shown in Fig. 5.8; for steam it is essentially symmetric about the critical point. Note that the high-pressure lines in the compressed liquid region are indistinguishable from the saturated liquid line. It is often helpful to visualize a process on a T - s diagram, since such a diagram illustrates assumptions regarding irreversibilities.

For a solid or a liquid, the entropy change can be found quite easily if we can assume the specific heat to be constant. Returning to Eq. (1), we can write, assuming the solid or liquid to be incompressible so that $dv = 0$,

$$Tds = du = CdT$$

where we have dropped the subscript on the specific heat since for solids and liquids $C_p \cong C_v$, such as Table B.4, usually list values for C_p ; these are assumed to be equal to C . Assuming a constant specific heat, we find that

$$\Delta s = \int_{T_1}^{T_2} C \frac{dT}{T} = C \ln \frac{T_2}{T_1}$$

If the specific heat is a known function of temperature, the integration can be performed. Specific heats for solids and liquids are listed in Table B.4.

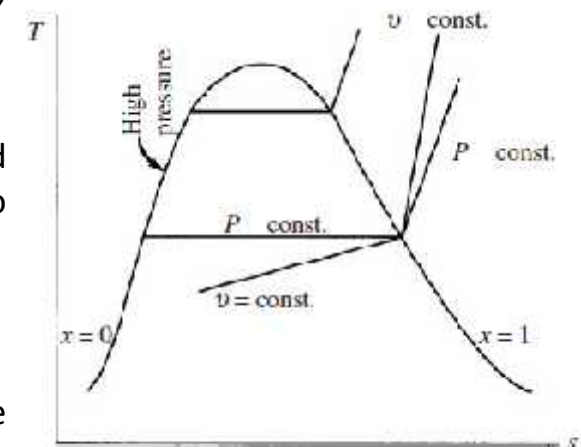


Figure 5.8 The T - s diagram for steam.

EXAMPLE 5.10

Steam is contained in a rigid container at an initial pressure of 600 kPa and 300°C. The pressure is reduced to 40 kPa by removing energy via heat transfer. Calculate the entropy change and the heat transfer.

Solution

From the steam tables, $v_1 = v_2 = 0.4344 \text{ m}^3/\text{kg}$. State 2 is in the quality region. Using the above value for v_2 the quality is found as follows:

$$0.4344 = 0.0011 + x(0.4625 - 0.0011) \quad \therefore x = 0.939$$

The entropy at state 2 is $s_2 = 1.777 + 0.939 \times 5.1197 = 6.584 \text{ kJ/kg} \cdot \text{K}$.

The entropy change is then

$$\Delta s = s_2 - s_1 = 6.584 - 7.372 = -0.788 \text{ kJ/kg} \cdot \text{K}$$

The heat transfer is found from the first law using $w = 0$ and $u_1 = 2801 \text{ kJ/kg}$:

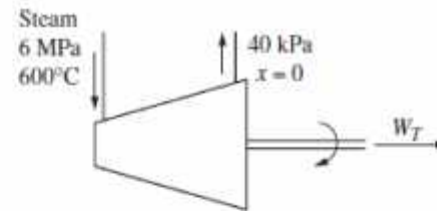
$$q = u_2 - u_1 = (604.3 + 0.939 \times 1949.3) - 2801 = -366 \text{ kJ/kg}$$

Quiz No. 1

- An inventor claims a thermal engine operates between ocean layers at 27 and 10°C. It produces 10 kW and discharges 9900 kJ/min. Such an engine is
 - Impossible
 - Reversible
 - Possible
 - Probable
- A heat pump is to provide 2000 kJ/h to a house maintained at 20°C. If it is -20°C outside, what is the minimum power requirement?
 - 385 kJ/h
 - 316 kJ/h
 - 273 kJ/h
 - 184 kJ/h
- Select an acceptable paraphrase of the Kelvin-Planck statement of the second law.
 - No process can produce more work than the heat that it accepts.
 - No engine can produce more work than the heat that it intakes.
 - An engine cannot produce work without accepting heat.
 - An engine has to reject heat.
- A power plant burns 1000 kg of coal each hour and produces 500 kW of power. Calculate the overall thermal efficiency if each kg of coal produces 6 MJ of energy.
 - 0.35
 - 0.30
 - 0.25
 - 0.20
- Two Carnot engines operate in series between two reservoirs maintained at 327 and 27°C, respectively. The energy rejected by the first engine is input into the second engine. If the first engine's efficiency is 20 percent greater than the second engine's efficiency, calculate the intermediate temperature.
 - 106°C
 - 136°C
 - 243°C
 - 408°C
- A heat pump is to maintain a house at 20°C when the outside air is at -25°C. It is determined that 1800 kJ is required each minute to accomplish this. Calculate the minimum power required.
 - 3.87 kW
 - 4.23 kW
 - 4.61 kW
 - 3.99 kW
- Which of the following entropy relationships is incorrect?
 - Air, $V = \text{const}$: $\Delta s = C_p \ln T_2/T_1$
 - Water: $\Delta s = C_p \ln T_2/T_1$
 - Reservoir: $\Delta s = C_p \ln T_2/T_1$
 - Copper: $\Delta s = C_p \ln T_2/T_1$
- Two kilograms of air are heated at constant pressure of 200 kPa to 500°C. Calculate the entropy change if the initial volume is 0.8 m³.
 - 2.04 kJ/K
 - 2.65 kJ/K
 - 3.12 kJ/K
 - 4.04 kJ/K
- Two kilograms of air are compressed from 120 kPa and 27°C to 600 kPa in a rigid container. Calculate the entropy change.
 - 5.04 kJ/K
 - 4.65 kJ/K
 - 3.12 kJ/K
 - 2.31 kJ/K

10. A paddle wheel provides 200 kJ of work to the air contained in a 0.2-m³ rigid volume, initially at 400 kPa and 40°C. Determine the entropy change if the volume is insulated.
- (A) 0.504 kJ/K
 (B) 0.443 kJ/K
 (C) 0.312 kJ/K
 (D) 0.231 kJ/K
11. 0.2 kg of air is compressed slowly from 150 kPa and 40°C to 600 kPa, in an adiabatic process. Determine the final volume.
- (A) 0.0445 m³
 (B) 0.0662 m³
 (C) 0.0845 m³
 (D) 0.0943 m³
12. A rigid, insulated 4-m³ volume is divided in half by a membrane. One chamber is pressurized with air to 100 kPa and the other is completely evacuated. The membrane is ruptured and after a period of time equilibrium is restored. The entropy change of the air is nearest
- (A) 0.624 kJ/K
 (B) 0.573 kJ/K
 (C) 0.473 kJ/K
 (D) 0.351 kJ/K
13. Ten kilograms of air are expanded isentropically from 500°C and 6 MPa to 400 kPa. The work accomplished is nearest
- (A) 7400 kJ
 (B) 6200 kJ
 (C) 4300 kJ
 (D) 2990 kJ
14. Find the work needed to isentropically compress 2 kg of air in a cylinder at 400 kPa and 400°C to 2 MPa.
- (A) 1020 kJ
 (B) 941 kJ
 (C) 787 kJ
 (D) 563 kJ

15. Calculate the total entropy change if 10 kg of ice at 0°C are mixed in an insulated container with 20 kg of water at 20°C. Heat of melting for ice is 340 kJ/kg.
- (A) 6.19 kJ/K
 (B) 3.95 kJ/K
 (C) 1.26 kJ/K
 (D) 0.214 kJ/K
16. A 5-kg block of copper at 100°C is submerged in 10 kg of water at 10°C, and after a period of time, equilibrium is established. If the container is insulated, calculate the entropy change of the universe.
- (A) 0.082 kJ/K
 (B) 0.095 kJ/K
 (C) 0.108 kJ/K
 (D) 0.116 kJ/K
17. Find w_T of the insulated turbine shown.



- (A) 910 kJ/kg
 (B) 1020 kJ/kg
 (C) 1200 kJ/kg
 (D) 1430 kJ/kg
18. The efficiency of the turbine of Prob. 17 is nearest
- (A) 92%
 (B) 89%
 (C) 85%
 (D) 81%

19. A nozzle accelerates steam at 120 kPa and 200°C from 20 m/s to the atmosphere. If it is 85 percent efficient, the exiting velocity is nearest
- (A) 290 m/s
 - (B) 230 m/s
 - (C) 200 m/s
 - (D) 185 m/s
20. A turbine produces 4 MW by extracting energy from 4 kg of steam which flows through the turbine every second. The steam enters at 600°C and 1600 kPa and exits at 10 kPa. The turbine efficiency is nearest
- (A) 82%
 - (B) 85%
 - (C) 87%
 - (D) 91%
4. An automobile that has a gas mileage of 13 km/L is traveling at 100 km/h. At this speed essentially all the power produced by the engine is used to overcome air drag. If the air drag force is given by $\frac{1}{2}\rho V^2 AC_D$ determine the thermal efficiency of the engine at this speed using projected area $A = 3 \text{ m}^2$, drag coefficient $C_D = 0.28$, and heating value of gasoline 9000 kJ/kg. Gasoline has a density of 740 kg/m³.
- (A) 0.431
 - (B) 0.519
 - (C) 0.587
 - (D) 0.652
5. A proposed power cycle is designed to operate between temperature reservoirs of 900 and 20°C. It is supposed to produce 43 hp from the 2500 kJ of energy extracted each minute. Is the proposal feasible?
- (A) No
 - (B) Yes
 - (C) Maybe
 - (D) Insufficient information

Quiz No. 2

1. An engine operates on 100°C geothermal water. It exhausts to a 20°C stream. Its maximum efficiency is nearest
- (A) 21%
 - (B) 32%
 - (C) 58%
 - (D) 80%
2. Which of the following can be assumed to be reversible?
- (A) A paddle wheel
 - (B) A burst membrane
 - (C) A resistance heater
 - (D) A piston compressing gas in a race engine
3. A Carnot engine operates between reservoirs at 20 and 200°C. If 10 kW of power is produced, find the rejected heat rate.
- (A) 26.3 kJ/s
 - (B) 20.2 kJ/s
 - (C) 16.3 kJ/s
 - (D) 12.0 kJ/s
6. A Carnot refrigeration cycle is used to estimate the energy requirement in an attempt to reduce the temperature of a specimen to absolute zero. Suppose that we wish to remove 0.01 J of energy from the specimen when it is at $2 \times 10^{-6} \text{ K}$. How much work is necessary if the high-temperature reservoir is at 20°C?
- (A) 622 kJ
 - (B) 864 kJ
 - (C) 1170 kJ
 - (D) 1465 kJ
7. One kilogram of air is heated in a rigid container from 20 to 300°C. The entropy change is nearest
- (A) 0.64 kJ/K
 - (B) 0.54 kJ/K
 - (C) 0.48 kJ/K
 - (D) 0.34 kJ/K

8. Which of the following second law statements is incorrect?
- The entropy of an isolated system must remain constant or increase.
 - The entropy of a hot copper block decreases as it cools.
 - If ice is melted in water in an insulated container, the net entropy decreases.
 - Work must be input if energy is transferred from a cold body to a hot body.
9. A piston allows air to expand from 6 MPa to 200 kPa. The initial volume and temperature are 500 cm³ and 800°C. If the temperature is held constant calculate the entropy change.
- 11.9 kJ/K
 - 9.51 kJ/K
 - 8.57 kJ/K
 - 7.41 kJ/K
10. The entropy change in a certain expansion process is 5.2 kJ/K. The nitrogen, initially at 80 kPa, 27°C, and 4 m³, achieves a final temperature of 127°C. Calculate the final volume.
- 255 m³
 - 223 m³
 - 158 m³
 - 126 m³
11. A piston is inserted into a cylinder causing the pressure in the air to change from 50 to 4000 kPa while the temperature remains constant at 27°C. To accomplish this, heat transfer must occur. Determine the entropy change.
- 0.92 kJ/kg · K
 - 0.98 kJ/kg · K
 - 1.08 kJ/kg · K
 - 1.26 kJ/kg · K
12. A torque of 40 N · m is needed to rotate a shaft at 40 rad/s. It is attached to a paddle wheel located in a rigid 2-m³ volume. Initially the temperature is 47°C and the pressure is 200 kPa; if the paddle wheel rotates for 10 min and 500 kJ of heat is transferred to the air in the volume, determine the entropy increase assuming constant specific heats.
- 3.21 kJ/K
 - 2.81 kJ/K
 - 2.59 kJ/K
 - 2.04 kJ/K
13. Four kilograms of air expand in an insulated cylinder from 500 kPa and 227°C to 20 kPa. What is the work output?
- 863 kJ
 - 892 kJ
 - 964 kJ
 - 1250 kJ
14. Steam, at a quality of 85 percent, is expanded in a cylinder at a constant pressure of 800 kPa by adding 2000 kJ/kg of heat. Compute the entropy increase.
- 3.99 kJ/kg · K
 - 3.74 kJ/kg · K
 - 3.22 kJ/kg · K
 - 2.91 kJ/kg · K
15. Two kilograms of saturated steam at 100°C are contained in a cylinder. If the steam undergoes an isentropic expansion to 20 kPa, determine the work output.
- 376 kJ
 - 447 kJ
 - 564 kJ
 - 666 kJ
16. Ten kilograms of iron at 300°C are chilled in a large volume of ice and water. Find the total entropy change.
- 0.88 kJ/K
 - 1.01 kJ/K
 - 1.26 kJ/K
 - 1.61 kJ/K

17. Five kilograms of ice at -20°C are mixed with 10 kg of water initially at 20°C . If there is no significant heat transfer from the container, determine the net entropy change. It takes 330 kJ to melt a kg of ice.
- (A) 0.064 kJ/K
 - (B) 0.084 kJ/K
 - (C) 1.04 kJ/K
 - (D) 1.24 kJ/K
18. Two kilograms of air are stored in a rigid volume of 2 m^3 with the temperature initially at 300°C . Heat is transferred from the air until the pressure reaches 120 kPa. Calculate the entropy change of the air.
- (A) -0.292 kJ/K
 - (B) -0.357 kJ/K
 - (C) -0.452 kJ/K
 - (D) -0.498 kJ/K
19. Calculate the entropy change of the universe for Prob. 18 if the surroundings are at 27°C .
- (A) 0.252 kJ/K
 - (B) 0.289 kJ/K
 - (C) 0.328 kJ/K
 - (D) 0.371 kJ/K
20. Two hundred kilowatts are to be produced by a steam turbine. The outlet steam is to be saturated at 80 kPa and the steam entering will be at 600°C . For an isentropic process, determine the mass flow rate of steam.
- (A) 0.342 kg/s
 - (B) 0.287 kg/s
 - (C) 0.198 kg/s
 - (D) 0.116 kg/s