

Example 6.2

Consider a Carnot heat engine with $T_H = 1000$ K, $T_L = 300$ K, $Q_H = 1000$ kJ. What is the entropy of the HTR and the LTR? Answer: Recall that a Carnot heat engine is based on reversible processes.

Then calculate HTR entropy change from reversible heat transfer $\Delta S_H = \frac{Q_H}{T_H} = \frac{1000 \text{ kJ}}{1000 \text{ K}} = 1 \text{ kJ/K}$.

Next since Equation 6.1 holds, solve for Q_L from this equation $Q_L = Q_H \frac{T_L}{T_H} = 1000 \frac{300}{1000} = 300$ kJ.

Calculate LTR entropy change $\Delta S_L = \frac{Q_L}{T_L} = \frac{300 \text{ kJ}}{300 \text{ K}} = 1 \text{ kJ/K}$. We see the entropy changes are the same. They have opposite signs and there is no net entropy change.

6.1.3 ENTROPY CHANGE OF ISOTHERMAL EXPANSION

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To further illustrate entropy and the second law, consider isothermal reversible expansion of a gas from state 1 (P_1, V_1) to state 2 (P_2, V_2). Recall from Chapter 4 that this reversible expansion performs mechanical work W that must equal heat transfer Q into the gas to keep the temperature constant at T :

$$Q_{rev} = W_{rev} = nRT \ln \left(\frac{V_2}{V_1} \right) = -nRT \ln \left(\frac{P_2}{P_1} \right) \quad (6.7)$$

We use subscript *rev* to emphasize this is reversible. The change of entropy is $\Delta S = Q_{rev}/T$ and therefore

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) = -nR \ln \left(\frac{P_2}{P_1} \right) \quad (6.8)$$

This represents the entropy change and it is the same amount of entropy change in the surroundings.

Now, consider irreversible isothermal expansion between the same states (P_1, V_1) and (P_2, V_2) against the pressure P_{ext} of the surroundings. The heat Q_{irr} exchanged is not the same as in the reversible path. To see this, assuming $P_2 = P_{ext}$ we can calculate the PV work involved to get $W_{irr} = P_2(V_2 - V_1)$, which is less than the work done reversibly. A heat flow Q_{irr} equal to this work is transferred from the surroundings to keep the temperature constant at T . Now using the ideal gas law

$$Q_{irr} = W_{irr} = nRT \left(1 - \frac{P_2}{P_1} \right) = nRT \frac{V_2 - V_1}{V_2}. \text{ Therefore, the ratio } \frac{Q_{irr}}{T} \text{ due to this heat flow is } \frac{Q_{irr}}{T} = nR \left(1 - \frac{P_2}{P_1} \right) = nR \frac{V_2 - V_1}{V_2}.$$

Comparing to Equation 6.8 we see that $\Delta S > \frac{Q_{irr}}{T}$ as predicted by the Clausius inequality. The difference $\Delta S - \frac{Q_{irr}}{T}$ is entropy generated in the surroundings.

Example 6.3

Compare reversible and irreversible isothermal expansion of 40 moles of a gas previously compressed 10 times respect to atmospheric pressure and held at standard room temperature (25°C or 298 K). What is the change of entropy of the reversible expansion? What is the ratio of heat transfer to temperature of the irreversible expansion? Answer: We will use Equation 6.7 to calculate work performed by reversible expansion,

$$Q_{rev} = W_{rev} = -nRT \ln\left(\frac{P_2}{P_1}\right) = -40 \times 8.314 \times 298 \times \ln\left(\frac{1}{10}\right) \text{ J}$$

$$= 40 \times 8.314 \times 298 \times 2.303 \text{ J} = 228.235 \text{ kJ}$$

and then the change of entropy is $\Delta S = \frac{Q_{rev}}{T} = \frac{228.235 \text{ kJ}}{298 \text{ K}} = 765.89 \text{ J/K}$. Now we calculate irreversible work done against the atmospheric pressure $Q_{irr} = W_{irr} = nRT \left(1 - \frac{P_2}{P_1}\right) = nRT(1 - 1/10)$ and substituting values $Q_{irr} = 40 \times 8.314 \times 298 \times \left(\frac{9}{10}\right) \text{ J} = 89.192 \text{ kJ}$. Then, $\frac{Q_{irr}}{T} = \frac{89.192 \text{ kJ}}{298 \text{ K}} = 299.3 \text{ J/K}$. Compare to $\Delta S = 765.89 \text{ J/K} > 299.3 \text{ J/K} = \frac{Q_{irr}}{T}$.

6.1.4 CARNOT LIMIT AND ENTROPY

We will now examine the Carnot limit using the concept of entropy and the second law. Since entropy increases, the entropy change at the LTR heat engine should be larger than that at the HTR, $\Delta S_L \geq \Delta S_H$. Using the definition of entropy on both sides we get $\frac{Q_L}{T_L} \geq \frac{Q_H}{T_H}$, which can be rewritten as $\frac{Q_L}{Q_H} \geq \frac{T_L}{T_H}$ and recalling that thermal efficiency is $\eta = 1 - \frac{Q_L}{Q_H}$, we can change the sign of the inequality and add 1 to both sides to obtain $1 - \frac{Q_L}{Q_H} \leq 1 - \frac{T_L}{T_H}$ or $\eta \leq 1 - \frac{T_L}{T_H}$. We can see that the Carnot limit $\eta_{max} = 1 - \frac{T_L}{T_H}$ is the right-hand side of the inequality and this means that efficiency is always less or equal to the Carnot limit $\eta \leq 1 - \frac{T_L}{T_H} = \eta_{max}$. In other words, ideal efficiency corresponds to the case of equal entropy change $\Delta S_L = \Delta S_H$. It should be noted that a reversible process is an idealized model, which is not achieved in practice due to other losses such as friction or wasted power.

We can divide both sides of Equation 6.5 by dt to obtain the rate of change of entropy $\frac{dS}{dt} = \frac{\delta Q_{rev}/dt}{T}$ as a function of the rate of change of heat or heat flow for a reversible process. Using dot notation for derivative, we can write for brevity $\dot{S} = \frac{\dot{Q}}{T}$, but note that this is not rigorous because δQ is not an exact differential.

Example 6.4

Consider a heat engine with $T_H = 1000 \text{ K}$, $T_L = 300 \text{ K}$, $\dot{Q}_H = 10^6 \text{ J/s}$, $\eta = 40\%$. What is the difference in entropy rates? Answer: First calculate change of entropy of the HTR $\dot{S}_H = \frac{\dot{Q}_H}{T_H} = \frac{10^6 \text{ J/s}}{10^3 \text{ K}} = 10^3 \text{ J/s K}^{-1}$. Then, the LTR $\dot{S}_L = \frac{\dot{Q}_L}{T_L} = \frac{0.6 \times 10^6 \text{ J/s}}{300 \text{ K}} = 2 \times 10^3 \text{ J/s K}^{-1}$. Subtract to obtain $\Delta \dot{S} = -\dot{S}_H + \dot{S}_L = -1000 + 2000 = 1000 \text{ J/s K}^{-1}$.

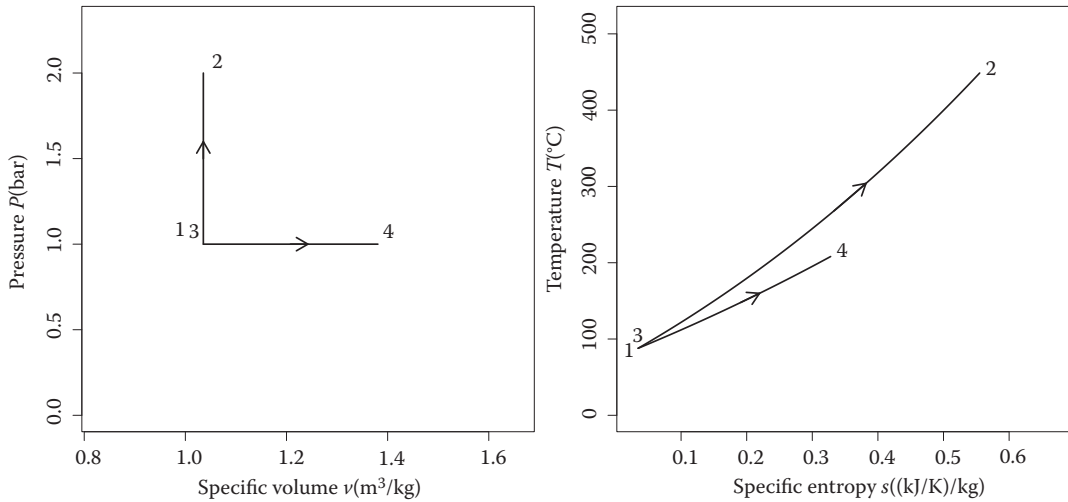


FIGURE 6.2 Reversible isochoric and isobaric paths in the P - V and T - s plane. Left: 1–2: isochor, $87.8^\circ\text{C} \rightarrow 448.7^\circ\text{C}$, $W = 0 \text{ kJ/kg}$, $Q = 272.5 \text{ kJ/kg}$; 3–4: isobar, expansion $87.8^\circ\text{C} \rightarrow 208.1^\circ\text{C}$, $W = -34.5 \text{ kJ/kg}$, $Q = 122.7 \text{ kJ/kg}$. Right: 1–2: isochor, $87.8^\circ\text{C} \rightarrow 448.7^\circ\text{C}$, $W = 0 \text{ kJ/kg}$, $Q = 272.5 \text{ kJ/kg}$; 3–4: isobar, expansion $87.8^\circ\text{C} \rightarrow 208.1^\circ\text{C}$, $W = -34.5 \text{ kJ/kg}$, $Q = 122.7 \text{ kJ/kg}$.

an isobaric process, will be represented by an exponential on the T - s plane. A similar equation applies for an isochoric process when replacing c_p for c_v . As we know from Chapter 4, specific heat capacity varies with temperature, and therefore these equations will change for a broader temperature range.

To plot paths in the T - s plane we can use the same function `path.lines` of the `renpow` package, which we introduced in Chapter 4. But we use argument `plane='Ts'` when making the call, that is to say, `path.lines(x, plane='Ts')`. The following code produces Figure 6.1. We use `plane='Pv'` just to be explicit but it is not needed because argument `plane` defaults to `'Pv'`.

```
x1 <- list(V=c(20,30),T=c(100,NA),S=c(1,NA),path='isotherm',lab=c("1","2"))
x2 <- list(V=c(20,30),T=c(100,NA),S=c(1,NA),path='adiabat',lab=c("3","4"))
x <- list(x1,x2)
path.lines(x,plane='Pv')
path.lines(x,plane='Ts')
```

Note that we have used an additional argument `value` to specify the initial value of entropy. The function calculates entropy starting from this value.

Example 6.5

Use `path.lines` to produce Figure 6.2. Answer:

```
x1 <- list(V=c(30,NA),P=c(1,2),S=c(1,NA),path='isochor',lab=c("1","2"))
x2 <- list(V=c(30,40),P=c(1,NA),S=c(1,NA),path='isobar',lab=c("3","4"))
x <- list(x1,x2)
path.lines(x,plane='Pv')
path.lines(x,plane='Ts')
```

which indeed produces Figure 6.2.