

Chapter 5

Entropy

The Second Law of Thermodynamics

5.1 STATEMENTS

Unlike the first law of thermodynamics, the second law does not have just one statement, but several: (1) a cyclic process must transfer heat from a hot to a cold reservoir if it is to convert heat into work; (2) work must be done to transfer heat from a cold to a hot reservoir; (3) no engine can operate more efficiently than a Carnot engine; (4) a perpetual-motion machine of the second kind (one that extracts heat from surroundings at T , does work on surroundings, and returns to its initial state without transferring heat to another system at a temperature lower than T) cannot exist; (5) the entropy, or randomness, of the universe is increasing; etc. Most of these statements can be reduced to the assertion that all real processes are irreversible, i.e., the system and the surroundings cannot both be restored to their original states.

Entropy changes can be used to predict the spontaneity of constant-energy processes. At fixed energy, only those processes will occur spontaneously for which there is an increase in entropy. Predicting the spontaneity of a process under combined changes of energy and entropy will be considered in Section 6.1.

5.2 THE CARNOT CYCLE

The operation of an arbitrary heat engine is represented in Fig. 5-1. A *Carnot engine* is an (idealized) heat engine that follows the cyclic process indicated in Fig. 5-2. This *Carnot cycle* consists of four steps performed on an ideal gas: (1) a reversible isothermal expansion from V_1 to V_2 at T_h , (2) a reversible adiabatic expansion from V_2 to V_3 with a temperature change from T_h to T_c , (3) a reversible isothermal compression from V_3 to V_4 at T_c , and (4) a reversible adiabatic compression from V_4 to V_1 with a temperature change from T_c to T_h .

For a Carnot engine, $q_h = q_1$ and $q_c = q_3$.

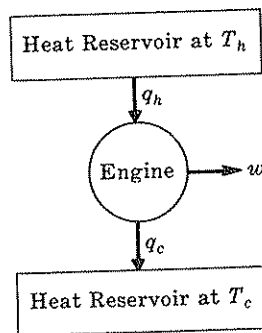


Fig. 5-1

EXAMPLE 5.1. Consider a Carnot engine operating between 500°C and 0°C using 1.00 mol of an ideal monatomic gas. If $V_1 = 0.0100\text{ m}^3$ and $V_2 = 0.1000\text{ m}^3$, calculate V_3 and V_4 ; q , w , and ΔU for each step; and q , w , and ΔU for the overall process. Prepare a sketch similar to Fig. 5-1 for this engine.

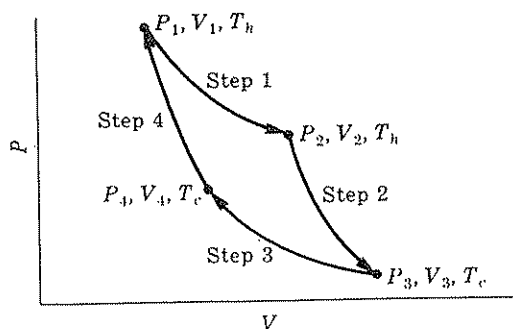


Fig. 5-2

The relationship between the temperatures is given by (3.44) as

$$T_h^{C_v/R} V_2 = T_c^{C_v/R} V_3 \quad T_h^{C_v/R} V_1 = T_c^{C_v/R} V_4$$

Since $C_v = \frac{3}{2}R$ for an ideal monatomic gas,

$$V_3 = V_2 \left(\frac{T_h}{T_c} \right)^{C_v/R} = (0.1000 \text{ m}^3) \left(\frac{773 \text{ K}}{273 \text{ K}} \right)^{3/2} = 0.477 \text{ m}^3$$

Dividing the two volume-temperature equations written above, we obtain

$$V_4 = V_3 \frac{V_1}{V_2} = (0.477 \text{ m}^3) \frac{0.0100 \text{ m}^3}{0.1000 \text{ m}^3} = 0.0477 \text{ m}^3$$

The values of ΔU , q , and w for each step can be determined by using (3.40) and (3.43). For the first step:

$$\Delta U_{(1)} = 0$$

$$-q_1 = w_1 = -nRT_h \ln \frac{V_2}{V_1} = -(1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(773 \text{ K}) \ln \frac{0.1000}{0.0100} = -14.80 \text{ kJ}$$

For the second step:

$$q_2 = 0$$

$$\begin{aligned} \Delta U_{(2)} = w_2 &= n \int_{T_h}^{T_c} C_v dT = n \int_{T_h}^{T_c} \frac{3}{2} R dT \\ &= (1.00 \text{ mol}) \left(\frac{3}{2} \right) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (273 \text{ K} - 773 \text{ K}) \\ &= -6.24 \text{ kJ} \end{aligned}$$

For the third step:

$$\Delta U_{(3)} = 0$$

$$\begin{aligned} -q_3 = w_3 &= -nRT_c \ln \frac{V_4}{V_3} \\ &= -(1.00)(8.314)(273) \ln \frac{0.0477}{0.477} = 5.23 \text{ kJ} \end{aligned}$$

For the fourth step:

$$q_4 = 0$$

$$\Delta U_{(4)} = w_4 = n \int_{T_c}^{T_h} C_v dT = 6.24 \text{ kJ}$$

For the overall cycle it can be shown that

$$\Delta U = 0$$

$$\begin{aligned} -q = w &= -nR(T_h - T_c) \ln \frac{V_2}{V_1} \\ &= -(1.00)(8.314)(733 - 273) \ln \frac{0.1000}{0.0100} = -9.57 \text{ kJ} \end{aligned}$$

The work is equivalent to the area enclosed by the cycle shown in Fig. 5-2. The diagram for this engine is Fig. 5-3.

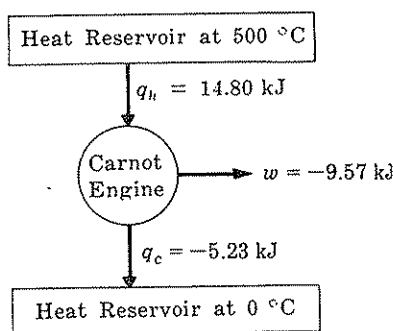


Fig. 5-3

5.3 EFFICIENCY OF A HEAT ENGINE

For an engine that operates between two heat reservoirs, the *efficiency* (expressed in %) is

$$\varepsilon \equiv 100 \frac{-w}{q_h} \quad (5.1)$$

EXAMPLE 5.2. Substitute the expressions for w and q_1 found in Example 5.1 into (5.1) to derive a general expression for the efficiency of a Carnot engine. Calculate the efficiency of the engine described in Example 5.1.

Using the expressions for w and $q_1 = q_h$ gives

$$\varepsilon_{\text{Carnot}} = 100 \frac{T_h - T_c}{T_h} \quad (5.2)$$

Substituting the numerical values into (5.1) gives

$$\varepsilon_{\text{Carnot}} = 100 \frac{-(-9.57 \text{ kJ})}{14.80 \text{ kJ}} = 64.7\%$$

or substituting the temperatures into (5.2) gives

$$\varepsilon_{\text{Carnot}} = 100 \frac{773 \text{ K} - 273 \text{ K}}{773 \text{ K}} = 64.7\%$$

5.4 REFRIGERATORS

An engine can be used as a refrigerator to pump heat from a cold to a hot reservoir, see Fig. 5-4. The *performance factor* of a refrigerator (expressed in %) is

$$\varepsilon_{\text{ref}} \equiv 100 \frac{w}{q_c} \quad (5.3a)$$

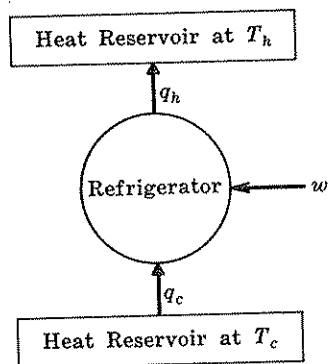


Fig. 5-4

For a Carnot refrigerator,

$$\varepsilon_{\text{ref}} = 100 \frac{T_h - T_c}{T_c} \quad (5.3b)$$

EXAMPLE 5.3. Calculate the maximum performance factor of a commercial refrigerator operating between the temperatures of -10°C (inside temperature) and 25°C (room temperature). What minimum amount of work must be done to remove 100. J of heat from the inside of the refrigerator?

According to one of the statements of the second law, the maximum efficiency occurs in a Carnot engine. Thus (5.3b) gives

$$\varepsilon_{\text{ref}} = 100 \frac{298 \text{ K} - 263 \text{ K}}{263 \text{ K}} = 13.3\%$$

The minimum amount of work required to remove the heat is found using (5.3a) as

$$13.3 = 100 \frac{w}{100. \text{ J}} \quad \text{or} \quad w = 13.3 \text{ J}$$

Entropy Calculations

5.5 DEFINITION OF ENTROPY

For the Carnot cycle, it can be shown that

$$\varepsilon_{\text{Carnot}} = 100 \frac{q_h + q_c}{q_h} = 100 \frac{T_h - T_c}{T_h}$$

which can be rearranged to give

$$\frac{q_c}{T_c} + \frac{q_h}{T_h} = 0$$

Any reversible cyclic process can be considered to be the sum of a large number of smaller Carnot cycles, giving

$$\sum \frac{q_{\text{rev}}}{T} = 0$$

or, as the number of subcycles becomes very large,

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$

The above condition—that the integral over a cycle is zero—is the general definition of a state or point function. Calling this particular function the *entropy* (S), we have

$$dS = \frac{dq_{\text{rev}}}{T} \quad (5.4a)$$

and

$$\Delta S = \int \frac{dq_{\text{rev}}}{T} \quad (5.4b)$$

Equations (5.4) require that *the entropy change for a system be calculated using a reversible process only*. For an irreversible process, a reversible path must be defined that has the same endstates as the actual process, and (5.4) must be applied along this reversible path. For a reversible process,

$$\Delta S(\text{system}) = -\Delta S(\text{surroundings}) \quad (5.5a)$$

and

$$\Delta S(\text{universe}) = \Delta S(\text{system}) + \Delta S(\text{surroundings}) = 0 \quad (5.5b)$$

For an irreversible process,

$$\Delta S(\text{universe}) > 0 \quad (5.6)$$

The units of entropy in the older physical system are cal K^{-1} (or gibbs), which have been represented by eu; in the SI system the units are J K^{-1} .

5.6 $\Delta S(\text{system})$ FOR HEAT TRANSFER

The entropy change for a system to which heat has been transferred reversibly and isothermally is given by (5.4b) as

$$\Delta S(\text{system}) = \frac{q_{\text{rev}}}{T} \quad (5.7)$$

A special case of (5.7) is that for a reversible adiabatic process

$$\Delta S(\text{system}) = 0 \quad (5.8)$$

For a system undergoing a phase transition from I to II (a reversible, isothermal process)

$$\Delta_{\text{I} \rightarrow \text{II}} S(\text{system}) = \frac{\Delta_{\text{I} \rightarrow \text{II}} H}{T} \quad (5.9)$$

EXAMPLE 5.4. What are the entropy changes for 1.00 mol of water undergoing reversible vaporization and fusion at 100°C and 0°C , respectively? Assume $\Delta_{\text{vap}}H = 40.656 \text{ kJ mol}^{-1}$ and $\Delta_{\text{fus}}H = 6.009 \text{ kJ mol}^{-1}$. Qualitatively compare the entropy changes for the two transitions.

For the vaporization, (5.9) gives

$$\begin{aligned} \Delta_{\text{vap}} S(\text{system}) &= \frac{(1.00 \text{ mol})(40.656 \text{ kJ mol}^{-1})[(10^3 \text{ J})/(1 \text{ kJ})]}{373.15 \text{ K}} \\ &= 108.95 \text{ J K}^{-1} \end{aligned}$$

and for the fusion,

$$\Delta_{\text{fus}} S(\text{system}) = \frac{(1.00)(6.009)}{273.15} = 22.00 \text{ J K}^{-1}$$

The values of $\Delta S(\text{system})$ indicate that there is a larger increase in randomness in going from the liquid state to the gaseous state than from the solid state to the liquid state.

5.7 $\Delta S(\text{system})$ FOR VOLUME-PRESSURE-TEMPERATURE CHANGES

For a system undergoing a reversible expansion,

$$\Delta S(\text{system}) = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T} \right)_V dV \quad (5.10a)$$

$$\Delta S(\text{system}) = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T} \right)_P dP \quad (5.10b)$$

For an ideal gas, $(\partial P/\partial T)_V = R/V$ and $(\partial V/\partial T)_P = R/P$, which, upon substitution into (5.10) and integration, gives

$$\Delta S(\text{system, ideal gas}) = \int_{T_1}^{T_2} \frac{C_V}{T} dT + R \ln \frac{V_2}{V_1} \quad (5.11a)$$

$$\Delta S(\text{system, ideal gas}) = \int_{T_1}^{T_2} \frac{C_P}{T} dT - R \ln \frac{P_2}{P_1} \quad (5.11b)$$

For real gases, the derivatives in (5.10) are evaluated from the equations of state and substituted into (5.10) for the integration process. For condensed states, $(\partial P/\partial T)_V = \alpha/\kappa$ and $(\partial V/\partial T)_P = \alpha V$, which, upon substitution into (5.10), gives

$$\Delta S(\text{system, condensed state}) = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{\alpha}{\kappa} dV \quad (5.12a)$$

$$\Delta S(\text{system, condensed state}) = \int_{T_1}^{T_2} \frac{C_P}{T} dT - \int_{P_1}^{P_2} \alpha V dP \quad (5.12b)$$

EXAMPLE 5.5. Consider the reversible isothermal expansion of 1.00 mol of an ideal gas from 0.010 m³ to 0.100 0 m³ at 298 K. Calculate $\Delta S(\text{system})$ for this process.

For the isothermal process, the first term on the right side of (5.11a) is zero, giving

$$\Delta S(\text{system}) = (1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{0.100 \text{ 0}}{0.010 \text{ 0}} = 19.14 \text{ J K}^{-1}$$

EXAMPLE 5.6. Calculate $\Delta S(\text{system})$ for the reversible heating of 1.00 mol of ethane from 298 K to 1 500 K at constant pressure. Assume

$$C_P = 5.351 + 177.669 \times 10^{-3} T - 687.01 \times 10^{-7} T^2 + 8.514 \times 10^{-9} T^3$$

in J K⁻¹ mol⁻¹.

For the isobaric process, the second term on the right side of (5.10b) is zero, giving

$$\begin{aligned} \Delta S(\text{system}) &= (1.00 \text{ mol}) \int_{298 \text{ K}}^{1500 \text{ K}} \frac{C_P}{T} dT \\ &= 5.351 \ln \frac{1500}{298} + (177.669 \times 10^{-3})(1500 - 298) - \left(\frac{687.01 \times 10^{-7}}{2} \right) (1500^2 - 298^2) \\ &\quad + \left(\frac{8.514 \times 10^{-9}}{3} \right) (1500^3 - 298^3) \\ &= 157.47 \text{ J K}^{-1} \end{aligned}$$

EXAMPLE 5.7. Compare the contributions to $\Delta S(\text{system})$ for the reversible cooling of 1.00 mol of an ideal diatomic gas from 25 °C to 0 °C at a constant pressure of 1.00 bar.

Although (5.11b) could be used to calculate the overall $\Delta S(\text{system})$ directly, it does not give the individual contributions from the temperature decrease and from the volume decrease. However, use of (5.11a) gives both

contributions. For the gas, $C_V = \frac{5}{2}R$, and

$$\begin{aligned} V_1 &= \frac{nRT_1}{P} = \frac{(1 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})[(1 \text{ Pa m}^3)/(1 \text{ J})]}{(1.00 \text{ bar})[(10^5 \text{ Pa})/(1 \text{ bar})]} \\ &= 0.0248 \text{ m}^3 \\ V_2 &= \frac{nRT_2}{P} = \frac{(1.00)(8.314)(298)}{(1.00)(10^5)} = 0.0227 \text{ m}^3 \end{aligned}$$

Equation (5.11a) gives the contribution from the cooling as

$$\begin{aligned} \Delta S(\text{system}) &= n \int_{T_1}^{T_2} \frac{C_V}{T} dT = nC_V \ln \frac{T_2}{T_1} \\ &= (1.00 \text{ mol})\left(\frac{5}{2}\right)(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{273 \text{ K}}{298 \text{ K}} \\ &= -1.82 \text{ J K}^{-1} \end{aligned}$$

and the contribution from the volume change as

$$\begin{aligned} \Delta S(\text{system}) &= nR \ln \frac{V_2}{V_1} \\ &= (1.00 \text{ mol})(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \ln \frac{0.0227 \text{ m}^3}{0.0248 \text{ m}^3} \\ &= -0.74 \text{ J K}^{-1} \end{aligned}$$

for a total of

$$\Delta S(\text{system}) = (-1.82 \text{ J K}^{-1}) + (-0.74 \text{ J K}^{-1}) = -2.56 \text{ J K}^{-1}$$

In this case, the temperature change accounts for 71% of the entropy change, and the volume change accounts for 29%.

5.8 $\Delta S(\text{system})$ FOR ISOTHERMAL MIXING

For preparing a mixture under reversible isothermal conditions,

$$\Delta_{\text{mix}} S(\text{system}) = -R \sum_i n_i \ln x_i \quad (5.13a)$$

where n_i is the number of moles and x_i is the mole fraction, of component i in the mixture. For 1 mol of solution, (5.13a) becomes

$$\Delta_{\text{mix}} S(\text{system}) = -R \sum_i x_i \ln x_i \quad (5.13b)$$

EXAMPLE 5.8. What is the entropy change for preparing a mixture containing 1.00 mol of $\text{O}_2(\text{g})$ and 2.00 mol of $\text{H}_2(\text{g})$, assuming no chemical reaction and reversible isothermal mixing?

For the binary mixture, (5.13) gives

$$\begin{aligned} \Delta S(\text{system}) &= -(8.314 \text{ J K}^{-1} \text{ mol}^{-1})[(1.00 \text{ mol}) \ln(0.333) + (2.00 \text{ mol}) \ln(0.667)] \\ &= 15.88 \text{ J K}^{-1} \end{aligned}$$

5.9 $\Delta S(\text{surroundings})$

For the surroundings, it is assumed that the heat can be transferred reversibly and isothermally, so that

$$\Delta S(\text{surroundings}) = \frac{q(\text{surroundings})}{T} \quad (5.14)$$

EXAMPLE 5.9. Compare the values of $\Delta S(\text{surroundings})$ and $\Delta S(\text{universe})$ for the process described in Example 5.5 given that the process is done reversibly and that the process is performed irreversibly against a constant external pressure of 0.100 bar.

For the surroundings, $q(\text{surroundings}) = -nRT \ln(V_2/V_1)$, which upon substitution into (5.14) gives

$$\Delta S(\text{surroundings}) = -nR \ln \frac{V_2}{V_1} = -19.14 \text{ J K}^{-1}$$

For the universe,

$$\Delta S(\text{universe}) = 19.14 + (-19.14) = 0$$

For the irreversible process, $\Delta S(\text{system})$ must be calculated using a reversible path, so

$$\Delta S(\text{system}) = 19.14 \text{ J K}^{-1}$$

as in the reversible case. For the surroundings, (3.41b) gives $q(\text{surroundings}) = P\Delta V$, so (5.14) becomes

$$\begin{aligned} \Delta S(\text{surroundings}) &= \frac{P\Delta V}{T} \\ &= \frac{(0.100 \text{ bar})(-0.0900 \text{ m}^3)[(10^5 \text{ Pa})/(1 \text{ bar})][(1 \text{ J})/(1 \text{ Pa m}^3)]}{298 \text{ K}} \\ &= -3.02 \text{ J K}^{-1} \end{aligned}$$

which is a smaller magnitude than in the reversible case. For the universe,

$$\Delta S(\text{universe}) = 19.14 + (-3.02) = 16.12 \text{ J K}^{-1}$$

which is a positive value, implying that the entropy content of the universe is increasing for a real process.

EXAMPLE 5.10. Calculate $\Delta S(\text{surroundings})$ and $\Delta S(\text{universe})$ for the process described in Example 5.6, assuming that the process is performed irreversibly by placing the gas in an oven at 1 500 K.

For the irreversible process, the heat transferred from the oven is given by

$$\begin{aligned} q(\text{surroundings}) &= -(1.00 \text{ mol}) \int_{298 \text{ K}}^{1500 \text{ K}} C_p dT \\ &= -(5.351)(1500 - 298) - \left(\frac{177.669 \times 10^{-3}}{2} \right) (1500^2 - 298^2) \\ &\quad + \left(\frac{687.01 \times 10^{-7}}{3} \right) (1500^3 - 298^3) - \left(\frac{8.514 \times 10^{-9}}{4} \right) (1500^4 - 298^4) \\ &= -132\,497 \text{ J} \end{aligned}$$

and applying (5.14) gives

$$\Delta S(\text{surroundings}) = \frac{-132\,497}{1500} = -88.33 \text{ J K}^{-1}$$

For the universe,

$$\Delta S(\text{universe}) = 157.47 + (-88.33) = 69.14 \text{ J K}^{-1}$$

The Third Law of Thermodynamics

5.10 STATEMENT

The third law of thermodynamics can be stated as “the entropy content of all perfect crystalline materials is the same at 0 K.” For these materials, the value of S_0° is chosen as zero. For nonperfect crystalline materials, S_0° is greater than zero and must be determined using theoretical considerations.