

5.5 ENTROPY CHANGES OF AN IDEAL GAS

For one mole or a unit mass of fluid undergoing a mechanically reversible process in a closed system, the first law, Eq. (2.8), becomes:

$$dU = dQ_{\text{rev}} - P dV$$

Differentiation of the defining equation for enthalpy, $H = U + PV$, yields:

$$dH = dU + P dV + V dP$$

Eliminating dU gives:

$$dH = dQ_{\text{rev}} - P dV + P dV + V dP$$

$$dQ_{\text{rev}} = dH - V dP$$

For an ideal gas, $dH = C_p^{ig} dT$ and $V = RT/P$. With these substitutions and then division by T ,

As a result of Eq. (5.11), this becomes:

$$\frac{dQ_{\text{rev}}}{T} = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P}$$

$$dS = C_p^{ig} \frac{dT}{T} - R \frac{dP}{P} \quad \text{or} \quad \frac{dS}{R} = \frac{C_p^{ig}}{R} \frac{dT}{T} - d \ln P$$

where S is the molar entropy of an ideal gas. Integration from an initial state at conditions T_0 and P_0 to a final state at conditions T and P gives:

$$\boxed{\frac{\Delta S}{R} = \int_{T_0}^T \frac{C_p^{ig}}{R} \frac{dT}{T} - \ln \frac{P}{P_0}} \quad (5.14)$$

Although derived for a mechanically reversible process, this equation relates properties only, and is independent of the process causing the change of state. It is therefore a general equation for the calculation of entropy changes of an ideal gas.

Example 5.2

For an ideal gas with constant heat capacities undergoing a reversible adiabatic (and therefore isentropic) process, Eq. (3.30b) can be written:

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{(\gamma-1)/\gamma}$$

Show that this same equation results from application of Eq. (5.14) with $\Delta S = 0$.

Solution 5.2

Because C_p^{ig} is constant, Eq. (5.14) can be written:

$$0 = \ln \frac{T_2}{T_1} - \frac{R}{C_p^{ig}} \ln \frac{P_2}{P_1}$$

By Eq. (3.19) for an ideal gas, with $\gamma = C_p^{ig}/C_v^{ig}$:

$$C_p^{ig} = C_v^{ig} + R \quad \text{or} \quad \frac{R}{C_p^{ig}} = \frac{\gamma - 1}{\gamma}$$

Whence,
$$\ln \frac{T_2}{T_1} = \frac{\gamma - 1}{\gamma} \ln \frac{P_2}{P_1}$$

This result is readily rearranged into the given equation.

5.6 MATHEMATICAL STATEMENT OF THE SECOND LAW

Consider two heat reservoirs, one at temperature T_H and a second at the lower temperature T_C . Let a quantity of heat $|Q|$ be transferred from the hotter to the cooler reservoir. The entropy changes of the reservoirs at T_H and at T_C are:

$$\Delta S_H^t = \frac{-|Q|}{T_H} \quad \text{and} \quad \Delta S_C^t = \frac{|Q|}{T_C}$$

These two entropy changes are added to give:

$$\Delta S_{\text{total}} = \Delta S_H^t + \Delta S_C^t = \frac{-|Q|}{T_H} + \frac{|Q|}{T_C} = |Q| \left(\frac{T_H - T_C}{T_H T_C} \right)$$

Since $T_H > T_C$, the total entropy change as a result of this irreversible process is positive. Also, ΔS_{total} becomes smaller as the difference $T_H - T_C$ gets smaller. When T_H is only infinitesimally higher than T_C , the heat transfer is reversible, and ΔS_{total} approaches zero. Thus for the process of irreversible heat transfer, ΔS_{total} is always positive, approaching zero as the process becomes reversible.

Consider now an irreversible process in a closed system wherein no heat transfer occurs. Fig. 5.6, shows an irreversible, adiabatic expansion of 1 mol of fluid from an initial equilibrium state at point A to a final equilibrium state at point B.

Now suppose the fluid is restored to its initial state by a reversible process consisting of two steps: first, the reversible, adiabatic (constant-entropy) compression of the fluid to the initial pressure, and second, a reversible, constant-pressure step that restores the initial volume. If the initial process results in an entropy change of the fluid, then there must be heat transfer during the reversible, constant-P second step such that:

$$\Delta S^t = S_A^t - S_B^t = \int_B^A \frac{dQ_{\text{rev}}}{T}$$

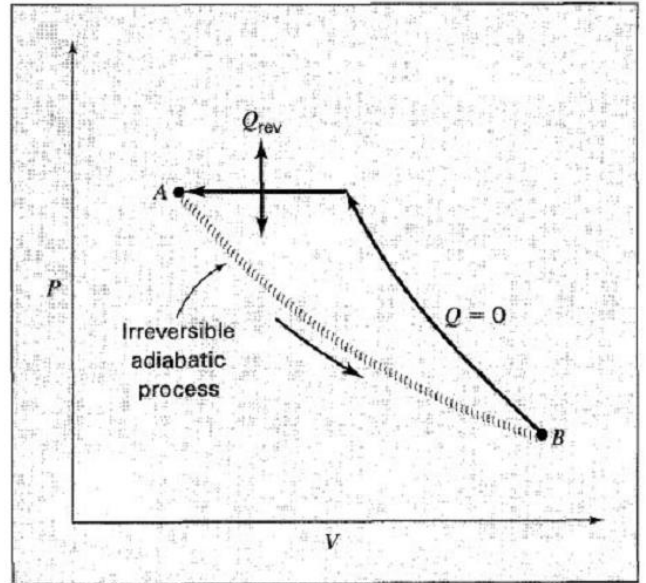


Figure 5.6 Cycle containing an irreversible adiabatic process A to B

The original irreversible process and the reversible restoration process constitute a cycle for which $\Delta U = 0$ and for which the work is therefore:

$$-W = Q_{\text{rev}} = \int_B^A dQ_{\text{rev}}$$

However, according to statement 1a of the second law, Q_{rev} cannot be directed into the system.

Statement 1a: It is impossible by a cyclic process to convert the heat absorbed by a system completely into work done by the system.

Thus, $\int dQ_{\text{rev}}$ is negative, and it follows that $S_A^t - S_B^t$ is also negative; whence $S_B^t > S_A^t$. Because the original irreversible process is adiabatic ($\Delta S_{\text{surr.}}=0$), the total entropy change of the system and surroundings as a result of the process is $\Delta S_{\text{total}} = S_B^t - S_A^t > 0$.

Thus the same result is found for adiabatic processes as for direct heat transfer: ΔS_{total} is always positive, approaching zero as a limit when the process becomes reversible. This same conclusion can be demonstrated for any process whatever, leading to the general equation:

$$\boxed{\Delta S_{\text{total}} \geq 0} \quad (5.19)$$

This mathematical statement of the second law affirms that every process proceeds in such a direction that the total entropy change associated with it is positive, the limiting value of zero being attained only by a reversible process. No process is possible for which the total entropy decreases.

The total entropy change of the heat engine is the sum of the entropy changes of the heat reservoirs:

$$\Delta S_{\text{total}} = \frac{-|Q_H|}{T_H} + \frac{|Q_C|}{T_C}$$

The work produced by the engine is

$$|W| = |Q_H| - |Q_C| \quad (5.1)$$

Elimination of $|Q_C|$ between these two equations and solution for $|W|$ gives:

$$|W| = -T_C \Delta S_{\text{total}} + |Q_H| \left(1 - \frac{T_C}{T_H}\right)$$

This is the general equation for work of a heat engine for temperature levels T_C and T_H

The maximum work is obtained when the engine is reversible, in which case $\Delta S_{\text{total}} = 0$, and the equation reduces to the second term on the right, the work of a Carnot engine.

Example 5.4

A 40-kg steel casting ($C_p = 0.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at a temperature of 450°C is quenched in 150 kg of oil ($C_p = 2.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$) at 25°C . If there are no heat losses, what is the change in entropy of (a) the casting, (b) the oil, and (c) both considered together?

Solution 5.4

The final temperature t of the oil and the steel casting is found by an energy balance. Because the change in energy of the oil and steel together must be zero,

$$(40)(0.5)(t - 450) + (150)(2.5)(t - 25) = 0$$

Solution yields $t = 46.52^\circ\text{C}$.

(a) Change in entropy of the casting:

$$\begin{aligned}\Delta S^t &= m \int \frac{C_P dT}{T} = m C_P \ln \frac{T_2}{T_1} \\ &= (40)(0.5) \ln \frac{273.15 + 46.52}{273.15 + 450} = -16.33 \text{ kJ K}^{-1}\end{aligned}$$

(b) Change in entropy of the oil:

$$\Delta S^t = (150)(2.5) \ln \frac{273.15 + 46.52}{273.15 + 25} = 26.13 \text{ kJ K}^{-1}$$

(c) Total entropy change:

$$\Delta S_{\text{total}} = -16.33 + 26.13 = 9.80 \text{ kJ K}^{-1}$$

Note that although the total entropy change is positive, the entropy of the casting has decreased.

5.10 THE THIRD LAW OF THERMODYNAMICS

The absolute entropy is zero for all perfect crystalline substances at absolute zero temperature.