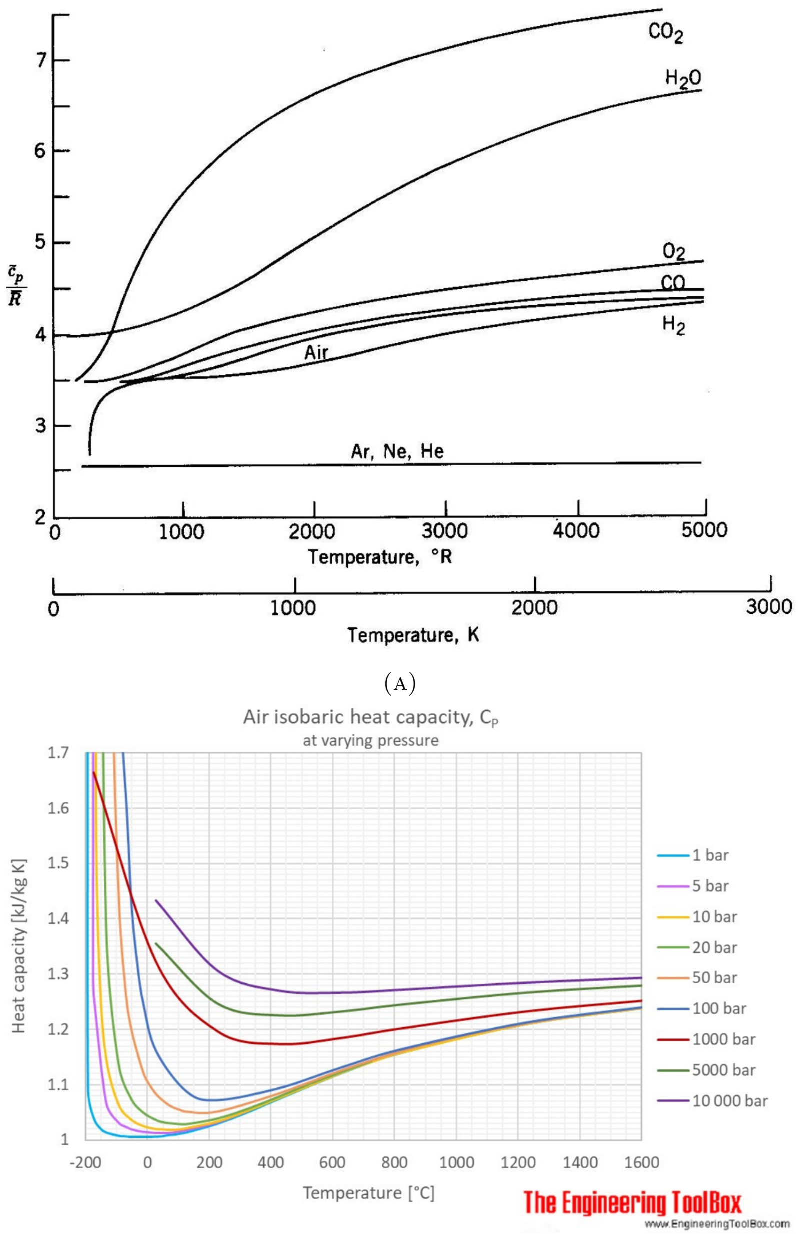
Not part of this reading.



(A)

(B)

Figure 3.29. Plots of (A) $\bar{c}_p/\bar{R}_U$ as a function of temperature for various gases. (Figure from ???.) (B) c_p as a function of temperature for air at various pressures. (Figure from *The Engineering ToolBox*.)

3.6. The Second Law of Thermodynamics

The First Law must be satisfied for a process to occur, but it doesn't indicate if the process will occur. For example, consider a system consisting of a block sliding down an inclined surface under the action of gravity. The block is initially at rest and is at rest at the final state so the change in kinetic energy is zero. Assume there are also no heat or work interactions with the surroundings. In this scenario,

$$\Delta U + mg\Delta z = 0 \implies \Delta U = -mg\Delta z. \tag{3.101}$$

Hence, if the block moves down the inclined plane ($\Delta z < 0$), the block's internal energy increases ($\Delta U > 0$). This scenario is reasonable based on our experience with blocks on planes. However, the First Law also states that if the block moves up the plane ($\Delta z > 0$), then the internal energy of the block would decrease ($\Delta U < 0$). We never see this process occurring spontaneously in practice, but the First Law doesn't preclude it from happening.

The Second Law of Thermodynamics is frequently used to predict the direction or possibility of a process, such as in the case of the block on an inclined plane described previously. In addition, the Second Law is used for other purposes, including,

- establishing conditions for equilibrium,
- establishing theoretical limits of a process, and
- evaluating factors limiting attainment of the theoretical performance.

The Second Law can also be used for,

- defining a temperature scale independent of a substance or class of substances, and
- evaluation of thermodynamic properties.

The Second Law of Thermodynamics has been stated in several ways. The three common statements are,

(1) the Clausius Statement,
(2) the Kelvin-Planck Statement, and
(3) entropy.

We'll discuss the first two statements now, but leave the discussion of entropy for later.

3.6.1. The Clausius Statement of the Second Law of Thermodynamics

It is impossible for any system to operate in such a way that the sole result is the transfer of heat from a cooler object to a hotter object (refer to Figure 3.30 for an illustration).

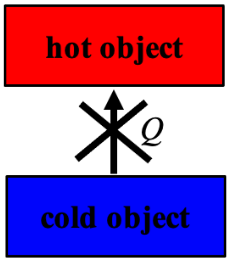


Figure 3.30. An illustration of the Clausius statement of the Second Law of Thermodynamics.

Note:

- It is certainly possible to transfer heat from cold objects to hot objects, e.g., refrigerators and heat pumps do this, but their operation doesn't violate the Clausius statement since the heat transfer isn't the sole effect. Refrigerators and heat pumps require the input of work to make the heat transfer occur.

3.6.2. The Kelvin-Planck Statement of the Second Law of Thermodynamics

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 (refer to Figure 3.31 for an illustration).

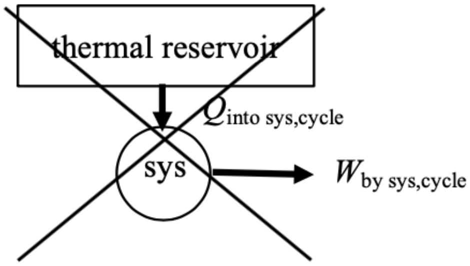


Figure 3.31. An illustration of the Kelvin-Planck statement of the Second Law of Thermodynamics.

Notes:

1. A thermal reservoir is a body that is sufficiently large so that its temperature remains essentially unchanged despite a transfer of heat to or from it. Thermal reservoirs can be either heat sinks or heat sources, i.e., heat can be transferred to them or from them, respectively, without changing the thermal reservoir's temperature. The defining characteristic of a thermal reservoir is its temperature.
2. Recall from earlier work that the thermal efficiency of a power cycle, for example, is,

   $$\eta = 1 - \frac{Q_{C,\text{cycle}}}{Q_{H,\text{cycle}}}. \tag{3.102}$$

   The Kelvin-Planck statement indicates that $Q_{C,\text{cycle}} \neq 0$ which implies that the efficiency cannot be 100%.
3. Mathematically, the Kelvin-Planck statement may be written as,

   $$W_{\substack{\text{by sys,}\\ \text{cycle}}} \leq 0 \quad \text{(single reservoir)}. \tag{3.103}$$

   In other words, when there is heat exchange with just a single reservoir (hence the "single reservoir" comment in parentheses), the work done by the system over a cycle cannot be positive (as given by Kelvin-Planck). We can put work into the system or produce no work, but no work can be done by the system.
4. The Clausius and Kelvin-Planck statements are equivalent. This fact can be shown by considering the following scenario (Figure 3.32).
   - (a) Assume the system on the left transfers energy Q_C from the cold reservoir to the hot reservoir, which we know is a violation of the Clausius Statement of the Second Law.
   - (b) The system on the right operates over a cycle and produces work. This power cycle does not violate the Second Law.
   - (c) The combined system within the dotted line consists of a cold reservoir and two devices (left and right dashed objects). This combined system (dotted line) executes a cycle while receiving energy by heat transfer from a single hot reservoir ($Q_H - Q_C$) and produces work. Thus, this dotted line cycle violates the Kelvin-Planck Statement of the Second Law.
   - (d) Thus, we observe that a violation of the Clausius Statement results in a violation of the Kelvin-Planck Statement. A similar argument can be performed in reverse to demonstrate that a violation of the Kelvin-Planck Statement results in a violation of the Clausius Statement.

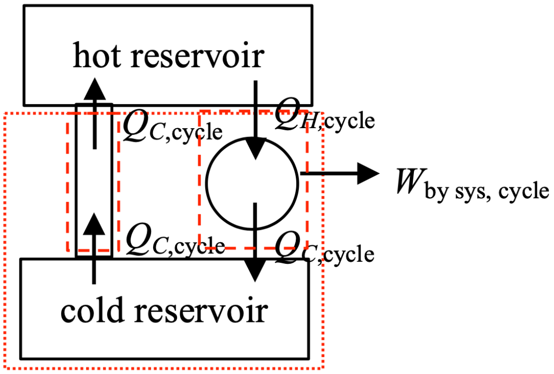


Figure 3.32. A schematic illustrating the equivalence of the Clausius and Kelvin-Planck statements of the Second Law.

Since a violation of one results in a violation of the other, we conclude that the statements are equivalent.

3.6.3. Reversible and Irreversible Processes

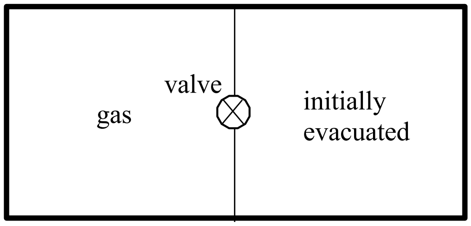
A reversible process is one in which the system is in a state of equilibrium at all points in its path. In a reversible process, the system and the surroundings can be restored exactly to their initial states.

An irreversible process is one where the system is not in a state of equilibrium at all points in its path. The system and surroundings cannot be returned to their exact initial states in an irreversible process. Note that all natural processes are irreversible.

Notes:

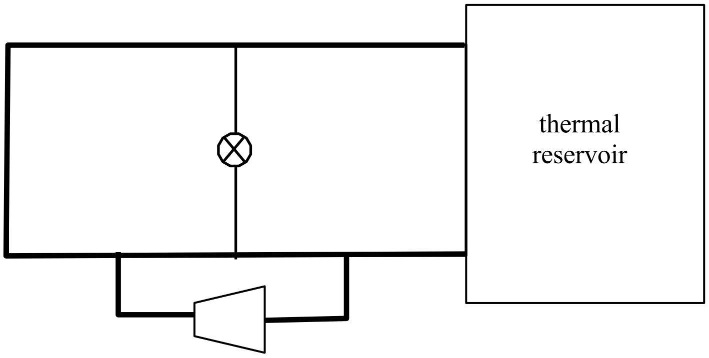
1. Examples of reversible processes include frictionless pendulums and adiabatic expansion/compression occurring slowly in a frictionless piston-cylinder.
2. Thermal reservoirs are considered to be reversible.
3. All real-world processes are irreversible.
4. Examples of irreversibilities include: heat transfer through a finite temperature gradient, unrestrained expansion of a gas or liquid, spontaneous chemical reaction, spontaneous mixing, friction, electric current flow through a resistance, and inelastic deformation.
5. Irreversibility can occur within a system, in the surroundings, or both. If a system has no dissipative internal processes, then it's considered internally reversible. For an internally reversible process, Eq. (3.103) becomes $W_{\text{by cycle}} = 0$ (single reservoir). If the surroundings have no dissipative processes, it is considered externally reversible. For an internally irreversible process, then Eq. (3.103) becomes $W_{\text{by cycle}} < 0$ (single reservoir).
6. Proofs to determine if a process is irreversible typically rely on proof by contradiction. The process is assumed to be reversible and then combined with one or more other reversible processes to form a thermodynamic cycle. Next, it is shown that the cycle violates the Kelvin-Planck statement of the Second Law.

A rigid insulated tank is divided into halves by a partition. On one side of the partition is a gas. The other side is initially evacuated. A valve in the partition is opened and the gas expands to fill the entire volume. Using the Kelvin-Planck statement of the 2nd Law, demonstrate that this process is irreversible.



SOLUTION:
Note that since the tank is well insulated and rigid, there is no heat transfer into the tank nor is there any work. Furthermore, the kinetic energy at the beginning and end of the process is zero and there is no change in potential energy. Hence, from the 1st Law,

$$\Delta E_{\text{sys}} = Q_{\substack{\text{into}\\ \text{sys}}} + W_{\substack{\text{on}\\ \text{sys}}} \Rightarrow U_f = U_i \,. \tag{1}$$



Process 1. Assume that the process is reversible, meaning that the system can start with the gas in both chambers and the gas can spontaneously move from the right chamber into the left. Note that the pressure in the left chamber will now be larger than the pressure in the right chamber.

Process 2. Let part of the gas pass from the left chamber through a turbine into the right chamber until the pressure in both chambers is the same. Since there has been some work done,

$$U < U_i \tag{2}$$

Process 3. Remove part of the tank insulation and add energy into the system from a thermal reservoir until the system's energy returns to U_i. Since the system is back to its original state, we have completed a cycle.

The net result of this cycle is to draw energy from a single reservoir by heat transfer and produce an equivalent amount of work. Such a cycle violates the Kelvin-Planck statement of the 2nd Law. Since extracting energy from a turbine (Process 2) and heat transfer from a thermal reservoir (Process 3) are possible, Process 1 must be impossible. Thus, gas spontaneously expanding from one tank into another, lower pressure tank must be an irreversible process.