Second Law of Thermodynamics

Reading: Chapter 20

One-way Processes

Examples
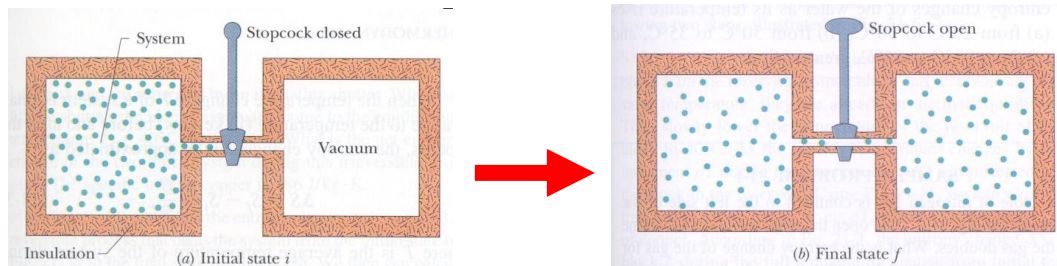## Irreversible process: free expansion

FIGURE 21-1 The free expansion of an ideal gas. (a) The gas is confined to the left half of an insulated container by a closed stopcock. (b) When the stopcock is opened, the gas rushes to fill the entire container. This process is irreversible; that is, it does not occur in reverse, with the gas spontaneously collecting itself in the left half of the container.
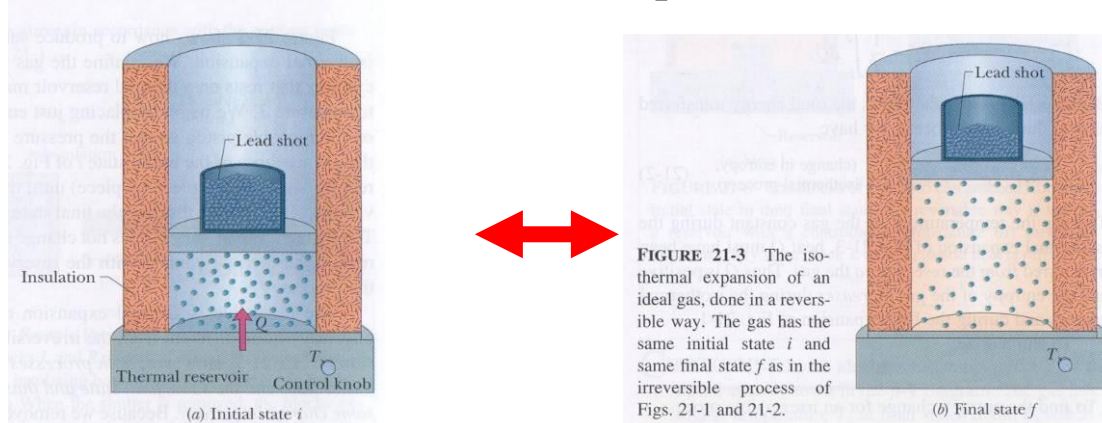
Reversible process: isothermal expansion

FIGURE 21-3 The iso-thermal expansion of an ideal gas, done in a reversible way. The gas has the same initial state i and same final state f as in the irreversible process of Figs. 21-1 and 21-2.

Change in Entropy

FIGURE 21-4 A *p-V* diagram for the reversible isothermal expansion of Fig. 21-3. The intermediate states, which are now equilibrium states, are shown.
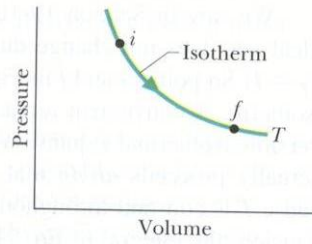
Suppose the initial state *i* and the final state *f* are connected by a reversible process. Then the change in entropy from state *i* to state *f* is

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}.$$

Although the heat transferred depends on the path connecting states *i* and *f*, it can be proved that the ΔS is independent of the path.
Hence the entropy is a *property of the state*.
When states *i* and *f* are connected by a reversible and an irreversible process, both processes *must have the same change in entropy*.

For isothermal expansion,

$$\Delta S = \frac{1}{T} \int_i^f dQ = \frac{Q}{T}.$$

For irreversible processes,

$$\Delta S > \int_i^f \frac{dQ}{T}.$$

Entropy as a State Function

Consider a reversible process of an ideal gas from initial state i to final state f. Using the first law of thermodynamics,

$$dQ = dE_{\text{int}} + dW.$$

Since $dW = p\,dV$ and $dE_{\text{int}} = nC_V\,dT$,

$$dQ = pdV + nC_V dT.$$

Using the ideal gas law, $p = nRT/V$. Hence

$$\frac{dQ}{T} = nR\frac{dV}{V} + nC_V\frac{dT}{T}.$$

Integrating,

$$\int_i^f \frac{dQ}{T} = \int_i^f nR\frac{dV}{V} + \int_i^f nC_V\frac{dT}{T}.$$

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} + nC_V\ln\frac{T_f}{T_i}.$$

Thus the entropy change between the initial and final states of an ideal gas depends only on properties of the initial state (V_i and T_i) and properties of the final state (V_f and T_f).

Examples

20-1 One mole of nitrogen gas is confined to the left side of the container in the figure. You open the stopcock and the volume of the gas doubles. What is the entropy change of the gas for this irreversible process? Treat the gas as ideal.

(a) Initial state i
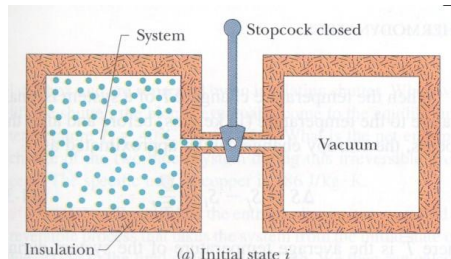
Replace the irreversible process with the isothermal expansion.

Heat absorbed by the gas:

$$Q = nRT \ln \frac{V_f}{V_i}.$$

Entropy change:

$$\Delta S = \frac{Q}{T} = nR \ln \frac{V_f}{V_i}$$

$$= (1)(8.31) \ln 2 = +5.76 \, \text{JK}^{-1} \quad \text{(ans)}$$

20-2 Consider two identical copper blocks, each of mass $m = 1.5$ kg: block L is at temperature $T_{iL} = 60^\circ$C and block R is at temperature $T_{iR} = 20^\circ$C. The blocks are in a thermally insulated box and are separated by an insulating shutter. When we lift the shutter, the blocks eventually come to the equilibrium temperature $T_f = 40^\circ$C. What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is 386 $\text{Jkg}^{-1}\text{K}^{-1}$.
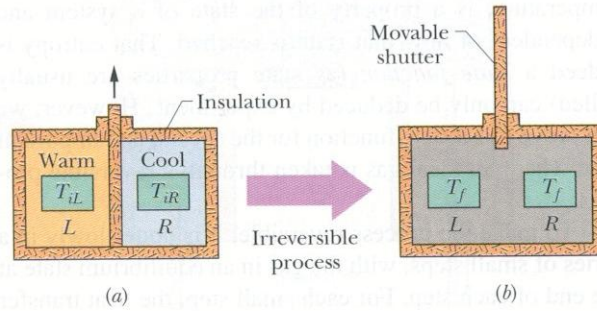
FIGURE 21-5 Sample Problem 21-2. (a) In the initial state, two copper blocks L and R, identical except for their temperatures, are in an insulating box and are separated by an insulating shutter. (b) When the shutter is removed, the blocks exchange heat and come to a final state, both with the same temperature T_f. The process is irreversible.

Replace the irreversible process by a reversible one which uses reservoirs with controllable temperatures.
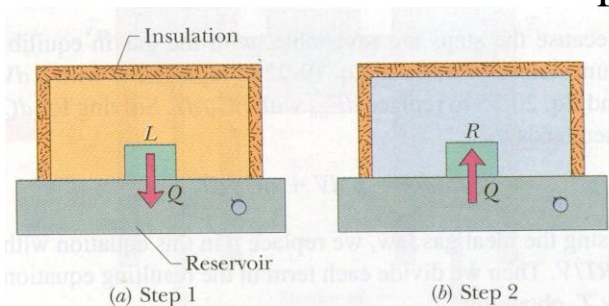
FIGURE 21-6 The blocks of Fig. 21-5 can proceed from their initial state to their final state in a reversible way if we use a reservoir with a controllable temperature (a) to extract heat reversibly from block L and (b) to add heat reversibly to block R.

Entropy change of block L:

$$\Delta S_L = \int_i^f \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{mcdT}{T} = mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln \frac{T_f}{T_{iL}}$$

$$= (1.5)(386) \ln \frac{40+273}{60+273} = -35.86 \, \text{JK}^{-1}.$$

Similarly, entropy change of block R:

$$\Delta S_R = (1.5)(386) \ln \frac{40+273}{20+273} = +38.23 \, \text{JK}^{-1}.$$
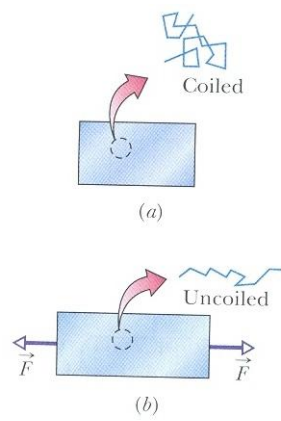
Net entropy change:

$$\Delta S = \Delta S_L + \Delta S_R = -35.86 + 38.23 = 2.4 \, \text{JK}^{-1}. \quad \text{(ans)}$$

The Second Law of thermodynamics

> If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. It never decreases.

$$\Delta S \geq 0.$$

The Rubber Band

FIG. 20-7   A section of a rubber band (*a*) unstretched and (*b*) stretched, and a polymer within it (*a*) coiled and (*b*) uncoiled.

Rubber consists of cross-linked polymer chains.
When the rubber band is at its rest length, the polymers are coiled up.
This is highly disordered and the rest state has a high entropy.
When the rubber band is stretched, the polymers are uncoiled.
This decreases the disorder and the entropy is reduced.
Implication: When the temperature increases, the rubber band tends to be shorter (the entropy increases).