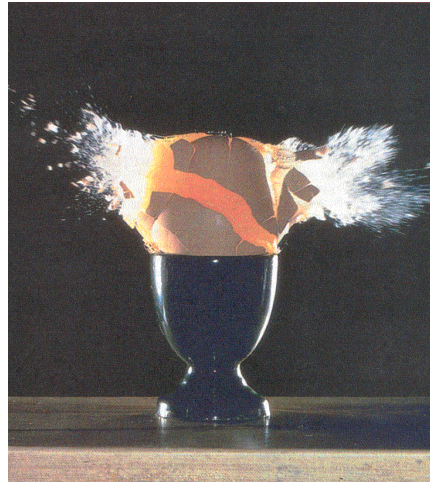


Second Law of Thermodynamics

Reading: Chapter 20

One-way Processes



Examples

Irreversible process: free expansion

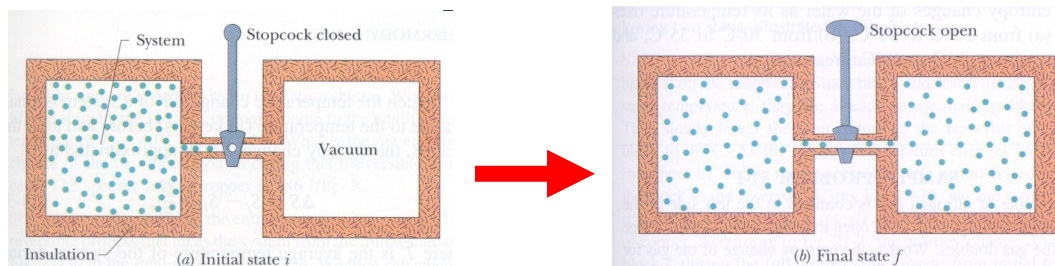


FIGURE 21-1 The free expansion of an ideal gas. (a) The gas is confined to the left half of an insulated container by a closed stopcock. (b) When the stopcock is opened, the gas rushes to fill the entire container. This process is irreversible; that is, it does not occur in reverse, with the gas spontaneously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

Reversible process: isothermal expansion

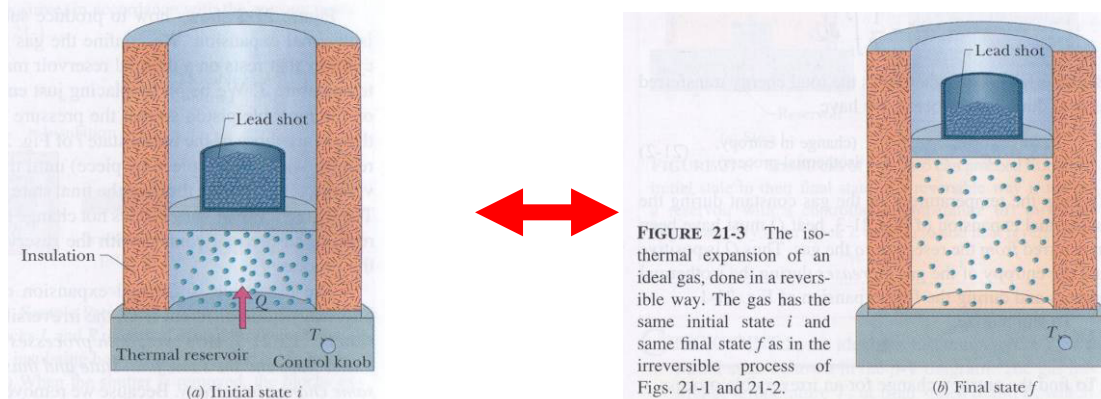
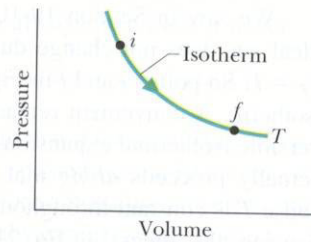


FIGURE 21-3 The isothermal expansion of an ideal gas, done in a reversible way. The gas has the same initial state i and same final state f as in the irreversible process of Figs. 21-1 and 21-2.

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

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

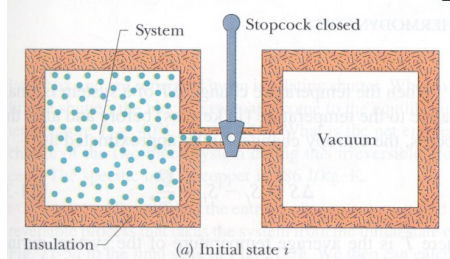
Integrating,

$$\int_i^f \frac{dQ}{T} = \int_i^f nR \frac{dV}{V} + \int_i^f nC_V \frac{dT}{T}.$$
$$\Delta S = S_f - S_i = nR \ln \frac{V_f}{V_i} + nC_V \ln \frac{T_f}{T_i}.$$

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.



Replace the irreversible process with the isothermal expansion.

Heat absorbed by the gas:

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

Entropy change:

$$\begin{aligned} \Delta S &= \frac{Q}{T} = nR \ln \frac{V_f}{V_i} \\ &= (1)(8.31) \ln 2 = +5.76 \text{ JK}^{-1} \quad (\text{ans}) \end{aligned}$$

20-2 Consider two identical copper blocks, each of mass $m = 1.5 \text{ kg}$: block L is at temperature $T_{iL} = 60^\circ\text{C}$ and block R is at temperature $T_{iR} = 20^\circ\text{C}$. 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 $T_f = 40^\circ\text{C}$. What is the net entropy change of the two-block system during this irreversible process? The specific heat of copper is $386 \text{ Jkg}^{-1}\text{K}^{-1}$.

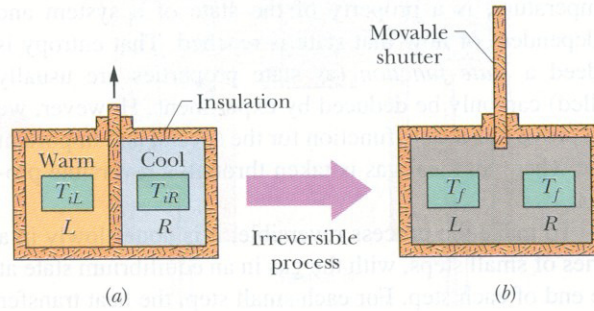


FIGURE 21-5 Sample Problem 21-2. (a) In the initial state, two copper blocks L and R , identical except for their temperatures, are in an insulating box and are separated by an insulating shutter. (b) When the shutter is removed, the blocks exchange heat and come to a final state, both with the same temperature T_f . The process is irreversible.

Replace the irreversible process by a reversible one which uses reservoirs with controllable temperatures.

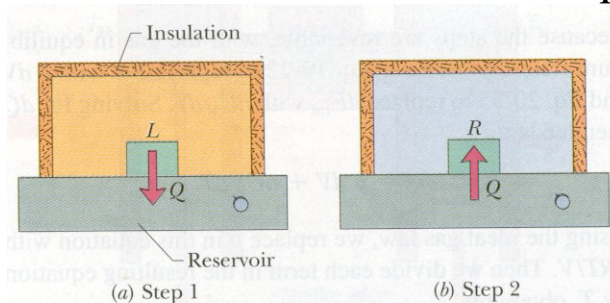


FIGURE 21-6 The blocks of Fig. 21-5 can proceed from their initial state to their final state in a reversible way if we use a reservoir with a controllable temperature (a) to extract heat reversibly from block L and (b) to add heat reversibly to block R .

Entropy change of block L :

$$\begin{aligned}\Delta S_L &= \int_i^f \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{mcdT}{T} = mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln \frac{T_f}{T_{iL}} \\ &= (1.5)(386) \ln \frac{40 + 273}{60 + 273} = -35.86 \text{ JK}^{-1}.\end{aligned}$$

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

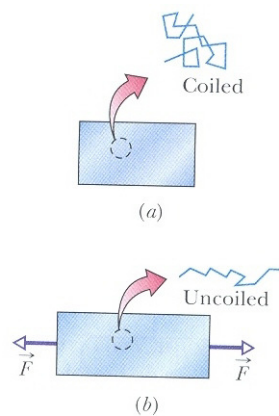


FIG. 20-7 A section of a rubber band (a) unstretched and (b) stretched, and a polymer within it (a) coiled and (b) uncoiled.

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).

Heat Engines

A heat engine is a device that extracts heat and does work as it continuously repeats a set sequence of processes.

Carnot Engine

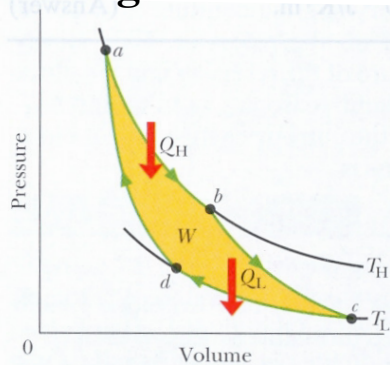


FIG. 20-9 A pressure–volume plot of the cycle followed by the working substance of the Carnot engine in Fig. 20-8. The cycle consists of two isothermal (ab and cd) and two adiabatic processes (bc and da). The shaded area enclosed by the cycle is equal to the work W per cycle done by the Carnot engine.

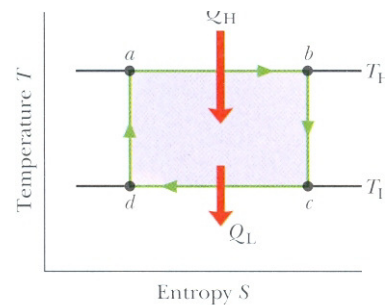


FIG. 20-10 The Carnot cycle of Fig. 20-9 plotted on a temperature–entropy diagram. During processes ab and cd the temperature remains constant. During processes bc and da the entropy remains constant.

A Carnot engine is an ideal engine: all processes are reversible and no energy is wasted due to friction and turbulence. Its cycle operates in the following 4 steps:

ab : Isothermal expansion at T_H (Q_H is absorbed)

bc : Adiabatic expansion from T_H to T_L

cd : Isothermal compression at T_C (Q_L is discharged)

da : Adiabatic compression from T_L to T_H

Efficiency

$$\varepsilon = \frac{\text{energy we get}}{\text{energy we pay for}} = \frac{W}{Q_H}.$$

Efficiency of an Ideal Engine

Since the engine returns to its original state at the end of each cycle, $\Delta E_{\text{int}} = 0$. The first law of thermodynamics:

$$0 = Q_H - Q_L - W.$$

$$\varepsilon = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H}.$$

Since all the engine processes are reversible, the net entropy change per cycle for the entire system must be zero.

$$\Delta S = -\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0, \quad \frac{Q_L}{Q_H} = \frac{T_L}{T_H}.$$

$$\varepsilon = \frac{T_H - T_L}{T_H}.$$

In *real* engines, there are wasteful energy transfers and irreversible processes. Their efficiency is therefore lower than the ideal efficiency.

Car engine: ideal efficiency about 55%, actual efficiency about 25%.

Since T_H and T_C are finite, there are no *perfect* engines with 100% efficiency.

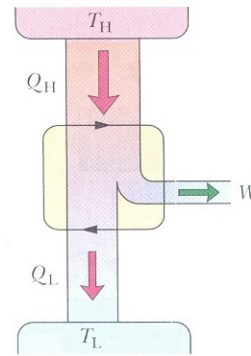


FIG. 20-8 The elements of a Carnot engine. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p - V plot. Energy $|Q_H|$ is transferred as heat from the high-temperature reservoir at temperature T_H to the working substance. Energy $|Q_L|$ is transferred as heat from the working substance to the low-temperature reservoir at temperature T_L . Work W is done by the engine (actually by the working substance) on something in the environment.

Examples

20-4 Imagine a Carnot engine that operates between the temperatures $T_H = 850 \text{ K}$ and $T_L = 300 \text{ K}$. The engine performs 1200 J of work each cycle, which takes 0.25 s.

- What is the efficiency of this engine?
- What is the average power of this engine?
- How much energy $|Q_H|$ is extracted as heat from the high-temperature reservoir every cycle?
- How much energy $|Q_L|$ is delivered as heat to the low-temperature reservoir every cycle?
- By how much does the entropy of the working substance change as a result of the energy transferred to it from the high-temperature reservoir? From it to the low-temperature reservoir?

$$(a) \quad \varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{300}{850} = 0.647 \approx 65\% \quad (\text{ans})$$

$$(b) \quad P = \frac{W}{t} = \frac{1200}{0.25} = 4800 \text{ W} = 4.8 \text{ kW} \quad (\text{ans})$$

$$(c) \quad \text{Since } \varepsilon = \frac{W}{|Q_H|},$$

$$|Q_H| = \frac{W}{\varepsilon} = \frac{1200}{0.647} = 1855 \text{ J} \quad (\text{ans})$$

$$(d) \quad |Q_L| = |Q_H| - W \\ = 1855 - 1200 = 655 \text{ J} \quad (\text{ans})$$

$$(e) \quad \Delta S_H = \frac{Q_H}{T_H} = \frac{1855}{850} = +2.18 \text{ JK}^{-1} \quad (\text{ans})$$

$$\Delta S_L = \frac{Q_L}{T_L} = \frac{-655}{300} = -2.18 \text{ JK}^{-1} \quad (\text{ans})$$

20-5 An inventor claims to have constructed an engine that has an efficiency of 75% when operated between the boiling and freezing points of water. Is that possible?

Efficiency of a Carnot engine operating between the same temperatures

$$\varepsilon = 1 - \frac{T_L}{T_H} = 1 - \frac{273}{373} = 0.268 \approx 27\%$$

Therefore, the efficiency of 75% is not possible. (ans)

Second Law of Thermodynamics (2nd alternative form)

No series of processes is possible whose sole result is the absorption of heat from a thermal reservoir and the complete conversion of this energy to work.

There are no *perfect engines*.

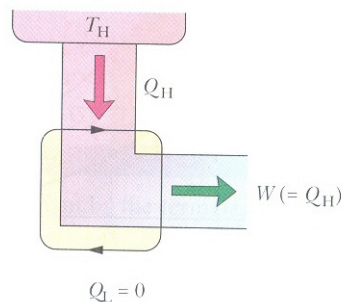


FIG. 20-11 The elements of a perfect engine—that is, one that converts heat Q_H from a high-temperature reservoir directly to work W with 100% efficiency.

Refrigerators

A refrigerator is a device that uses work to heat energy from a low-temperature reservoir to a high-temperature reservoir.

Coefficient of performance

$$K = \frac{\text{energy extracted}}{\text{energy we pay for}} = \frac{Q_L}{W}.$$

First law of thermodynamics:

$$W = Q_H - Q_L.$$

$$K = \frac{Q_L}{Q_H - Q_L}.$$

Since an ideal refrigerator is an ideal engine in reverse,

$$K = \frac{T_L}{T_H - T_L}.$$

Typical room air conditioners: $K \approx 2.5$

Household refrigerators: $K \approx 5$.

Second law of thermodynamics (3rd alternative form)

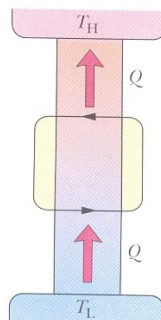


FIG. 20-15 The elements of a perfect refrigerator—that is, one that transfers energy from a low-temperature reservoir to a high-temperature reservoir without any input of work.

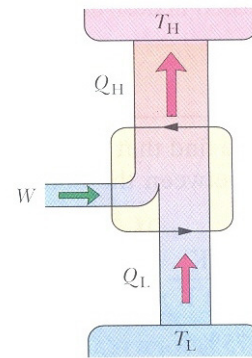


FIG. 20-14 The elements of a refrigerator. The two black arrowheads on the central loop suggest the working substance operating in a cycle, as if on a p - V plot. Energy is transferred as heat Q_L to the working substance from the low-temperature reservoir. Energy is transferred as heat Q_H to the high-temperature reservoir from the working substance. Work W is done on the refrigerator (on the working substance) by something in the environment.

No series of processes is possible whose sole result is the transfer of heat from a reservoir at a given temperature to a reservoir at a higher temperature.

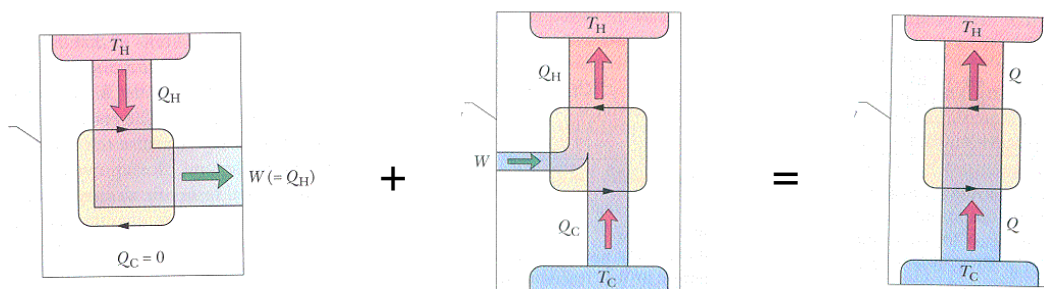
There are no *perfect refrigerators*.

Entropy change of a perfect refrigerator ($T_L < T_H$):

$$\Delta S = -\frac{Q}{T_L} + \frac{Q}{T_H} < 0!!!$$

This violates the 1st form of the second law of thermodynamics.

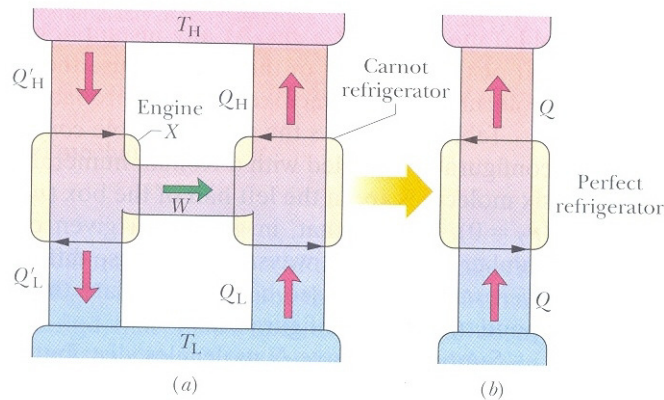
Equivalence with the 2nd Alternative Form



1. Suppose the 2nd alternative form of the second law of thermodynamics is invalid, that is, we can find a heat engine that can completely change heat energy from a hot reservoir into mechanical energy.
2. Then we can use the mechanical energy of this heat engine to drive a refrigerator that transports heat energy from a cold reservoir back to the hot reservoir.
3. The net effect of this engine-fridge system is thus to transport heat energy from the cold reservoir to the hot reservoir, which violates the 3rd alternative form of the second law of thermodynamics.

Real Engines vs Carnot Engines

FIG. 20-16 (a) Engine X drives a Carnot refrigerator. (b) If, as claimed, engine X is more efficient than a Carnot engine, then the combination shown in (a) is equivalent to the perfect refrigerator shown here. This violates the second law of thermodynamics, so we conclude that engine X cannot be more efficient than a Carnot engine.



1. Let \mathcal{E}_C be the efficiency of a Carnot engine operating between T_H and T_L .

Suppose there exists an engine X with

$$\mathcal{E}_X > \mathcal{E}_C$$

2. Then we can use the mechanical energy of this engine to drive a Carnot refrigerator, and we have

$$\frac{W}{Q'_H} > \frac{W}{Q_H} \Rightarrow Q_H > Q'_H$$

3. The net effect of this engine-fridge system is thus to transport heat energy $Q = Q_H - Q'_H > 0$ from the cold reservoir to the hot reservoir. This violates the 3rd alternative form of the second law of thermodynamics.

Conclusion: No real engine can have an efficiency greater than that of a Carnot engine working between the same two temperatures.

A Statistical View of Entropy

Consider a box containing 4 identical gas molecules.

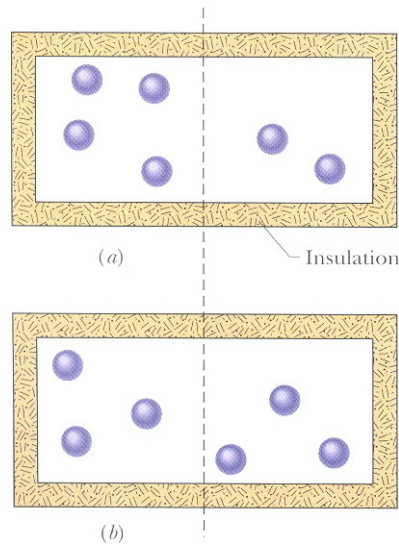


FIG. 20-17 An insulated box contains six gas molecules. Each molecule has the same probability of being in the left half of the box as in the right half. The arrangement in (a) corresponds to configuration III in Table 20-1, and that in (b) corresponds to configuration IV.

a	b	c	d	config	Degeneracy	entropy
L	L	L	L	I	1	0
R	L	L	L	II	4	1.39k
L	R	L	L			
L	L	R	L			
L	L	L	R			
L	L	R	R	III	6	1.79k
L	R	L	R			
R	L	L	R			
L	R	R	L			
R	L	R	L			
R	R	L	L			
L	R	R	R			

R	L	R	R	IV	4	1.39k
R	R	L	R			
R	R	R	L			
R	R	R	R	V	1	0

There are 16 *microstates*.

There are 5 *macrostates*.

The *degeneracy* (multiplicity) of each of the 5 macrostates is 1, 4, 6, 4, 1 respectively.

Note that macrostates with a fair distribution between L and R have the largest degeneracy.

Terms

Microstate = the detailed specification of the state of a collection of particles, particle-by-particle

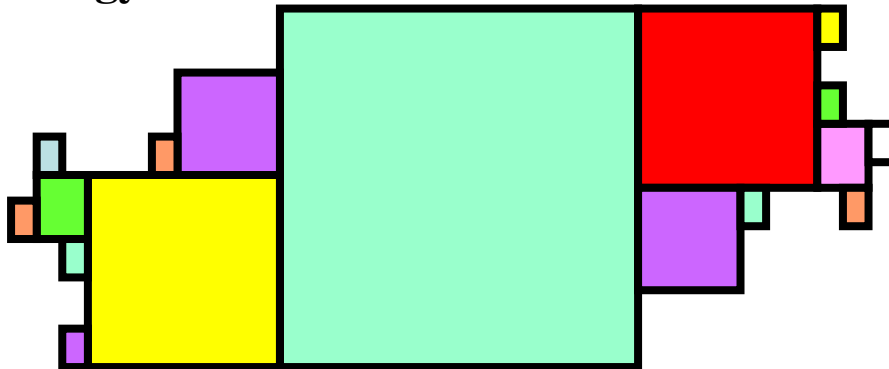
Macrostate = the overall specification of the state of a collection of particles, irrespective of the detailed information of individual particles

Degeneracy = the number of microstates belonging to a macrostate

Basic Assumption of Statistical Mechanics

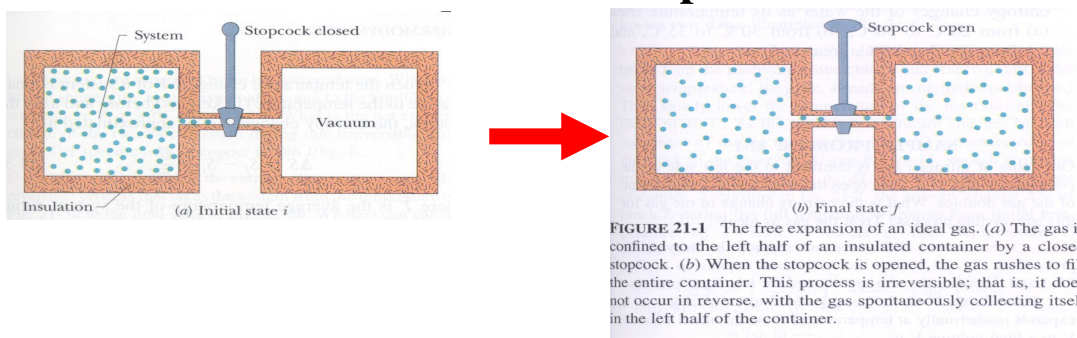
All microstates are equally probable, hence the macrostate with the highest degeneracy is the most probable one.

An Analogy: The Haunted Castle



- The situation is like a drunken ghost wondering inside a haunted castle with many rooms of different sizes. (It can penetrate all walls.)
- Even if he starts from a small room, he will most likely be located in the room with the largest area after a long time.
- The largest room corresponds to the macrostate having the largest number of microstates.

Statistical Mechanics of Free Expansion



The macrostate with molecules filling only the left box has a low degeneracy.

The macrostate with molecules filling both the left and right boxes has a high degeneracy.

Hence given enough time, the gas will reach the macrostate which fills both left and right boxes.

The macrostate which only fills the left box is not completely impossible, but it is highly improbable.

The Large N Limit

For a general N , the degeneracy W of a configuration:

$$W = \frac{N!}{n_L!n_R!}$$

No. of atoms	Deg (half L, half R)	Deg (all left)
4	6	1
10	252	1
100	10^{29}	1

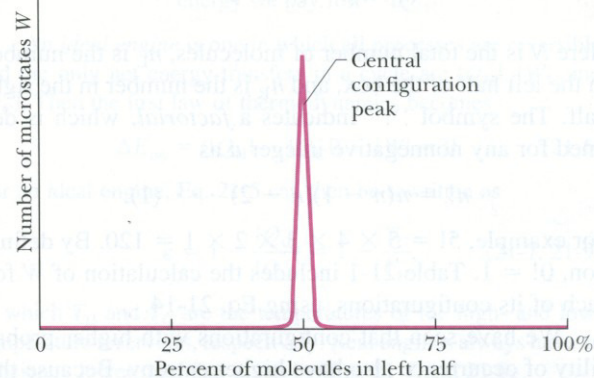


FIGURE 21-15 For a *large* number of molecules in a box, a plot of the number of microstates that require various percentages of the molecules to be in the left half of the box. Nearly all the microstates correspond to an approximately equal sharing of the molecules between the two halves of the box; those microstates form the central *configuration peak* on the plot. For $N \approx 10^{22}$, the central configuration peak would be much too narrow to be drawn on this plot.

When N is large, nearly all microstates correspond to roughly equal division of molecules between left and right.

Boltzman's Entropy Equation

$$S = k \ln W.$$

$k = 1.38 \times 10^{-23}$ J/K is the Boltzmann constant.

This equation is engraved on Boltzmann's tombstone.

Stirling's Approximation

Stirling's approximation is used to find the logarithms of the factorials of large numbers, which are usually encountered in entropy calculations:

$$\boxed{\ln N! = N \ln N - N.}$$

Example

20-7 When n moles of an ideal gas doubles its volume in a free expansion, the entropy increase from the initial state i to the final state f is $S_f - S_i = nR \ln 2$. Derive this result with statistical mechanics.

Let N be the number of molecules in n moles of gas. In the initial state, when all N molecules are in the left half of the container,

$$W_i = \frac{N!}{N!0!} = 1 \Rightarrow S_i = k \ln W_i = 0.$$

In the final state,

$$W_f = \frac{N!}{(N/2)!(N/2)!}.$$

$$\begin{aligned} S_f &= k \ln W_f = k \ln(N!) - 2k \ln[(N/2)!] \\ &= k[N \ln N - N] - 2k[(N/2) \ln(N/2) - (N/2)] \\ &= k[N \ln N - \cancel{N} - N \ln(N/2) + \cancel{N}] \\ &= k[\cancel{N \ln N} - \cancel{N \ln N} + N \ln 2] = kN \ln 2. \end{aligned}$$

Since $k = R/N_A$ and $N = nN_A$,

$$S = S_f - S_i = kN \ln 2 - 0 = kN \ln 2 = nR \ln 2. \quad (\text{ans})$$

