Exam-Copy

Second Law of Thermodynamics and Entropy

Some Things That Don't Happen

Consider the three things that never happen:

1. Coffee, resting quietly in your cup, never spontaneously cools down and starts to swirling around.
2. One end of a spoon resting on a table top never spontaneously gets hot while other end cools down.
3. The molecules of air in a room never all move to one corner and stay there.

The coffee could presumably get the kinetic energy for its swirling by cooling down. The hot end of the spoon could presumably gets energy from the cool end. And the molecules of air would not have to change their kinetic energies, just their positions.

The reverse of these three nonevents occur naturally and spontaneously. Coffee, swirling in your cup, will eventually stop swirling, its rotational energy changing into thermal energy and thus heating the coffee a little. Temperature differences set up between two ends of a spoon will tend to equalize. Air molecules will rush from one corner and fill the room uniformly.

The world is full of events that happen in one direction but never in the opposite way. The direction in which natural events happen is governed by the second law of thermodynamics. The law can be expressed in several equivalent forms, two of which involve simple statements about heat and work. A third formulation of the law is given in terms of a new and useful concept-entropy.

Engines

If you stir a cup of room-temperature coffee, your work on the spoon results in a transfer of energy to the coffee. The coffee then has kinetic energy-it swirls. As the swirls dies out, the excess energy becomes internal(or thermal) energy of the coffee. Since the temperature of the coffee is then (slightly) higher than that of the room, the coffee transfers its excess energy to the room as heat. In this process, you have the changed the work into completely and rather easily. The reverse process-changing heat into work-is quite another matter. Here as a challenge, is a formulation of the second law of thermodynamics.

Second law of thermodynamics (Kelvin-Planck statement)

It is impossible to change heat completely into work, with no change taking place.

Fig. 1 shows a cylinder containing an ideal gas and resting on a heat reservoir at temperature T. By

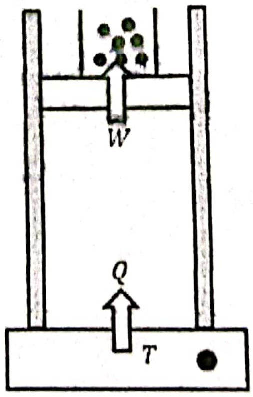

Figure 1: A gas in a cylinder of movable piston in upward direction.

removing weight gradually from the piston, we can permit the gas to expand. The gas remains at constant temperature while doing so, absorbing heat Q from the reservoir. The system(gas) follows the isotherm as shown in in Fig. 2 and-in lifting the weight-does work W as indicated by the area enclosed by the two dotted line, isotherm and line from V_i to V_f in the Figure 2. The internal energy E_{int}, which for an ideal gas depends only on the temperature-does not change during this isothermal expansion. From first law thermodynamics, $\Delta E_{int} = Q - W$, the work W is exactly equal to the heat Q extracted from the reservoir. Have we not turned

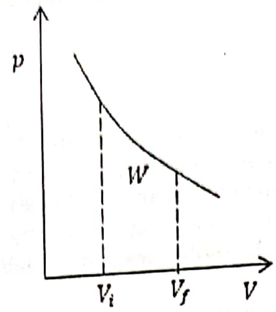

Figure 2: Work done by the gas in cylinder.

the that completely into work?

We have indeed done so, but we have not met the essential requirement **with no other change taking place.** Changes have taken place the gas in the cylinder is not in the same state as it was when started. Its volume has changed, for example, and so has its pressure. To meet our challenge, we must somehow restore the gas to its original condition. This means that the piston-cylinder arrangement must operate in a cycle, returning the gas to its original state at the end, of the cycle. A device that changes heat into work while operating in a cycle is called a heat engine or, more simply, an engine.

Fig. 1 suggests a generalized scheme of operation for an engine . during every cycle, energy is extracted as heat Q_H from a reservoir at temperature T_H, a portion is delivered to do useful work W, and the rest is discharged(lost) as heat Q_L to a reservoir at a lower temperature T_L.

Because an engine operates in a cycle, the internal energy E_{int} of the system, that is, of the gas in the cylinder, returns to its original value at the end of the cycle. Thus $\Delta E_{int} = 0$ and from the first law of thermodynamics ($\Delta E_{int} = Q - W$), the net work done per cycle by the system must equal to the net heat transferred per cycle. We write this is

$$|W| = |Q_H| - |Q_L| \tag{1}$$

We have chosen here to deal with the (positive) absolute values of Q and W, which we write as $|Q|$ and $|W|$,

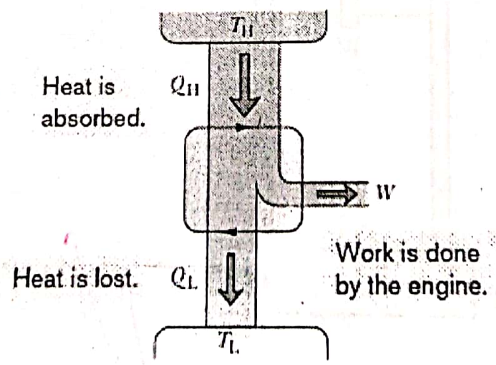

Figure 3: A schematic representation of heat engine.

respectively.

The purpose of an engine is to transform as much of the extracted heat Q_H into work as possible. We measure its success in doing so by its thermal efficiency e, defined as the ratio of the work it does per cycle-what you get-to the heat it absorbs per cycle-what you pay for. Using Eq. 1, we have

$$e = \frac{|W|}{|Q_H|} = \frac{|Q_H| - |Q_L|}{Q_H} \tag{2}$$

Eq. 2 shows that the efficiency of an engine can be unity, or 100%, only if $Q_L = 0$, that is, if no heat is delivered to the low-temperature reservoir. Fig. 4 is diagram of such a "perfect" engine. From accumulated experience to date, physicists have concluded that it is impossible to build such an engine. So, another way of expressing Kelvin-Planck statement is: *there are no perfect engines.*

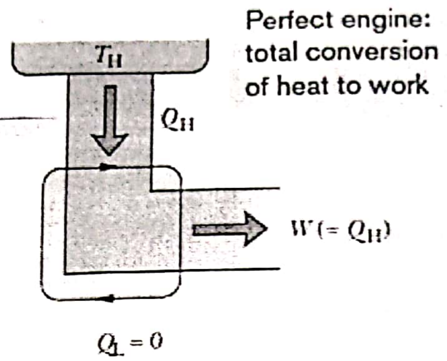

Figure 4: A schematic representation of perfect heat engine.

Second law of thermodynamics (Clausius Statement)

It is not possible for heat to be transferred from one body to another body that is at higher temperature, with no other change taking place.

A device that transfers energy as heat from a cold place to a warm place is called a refrigerator. Fig. 5 shows

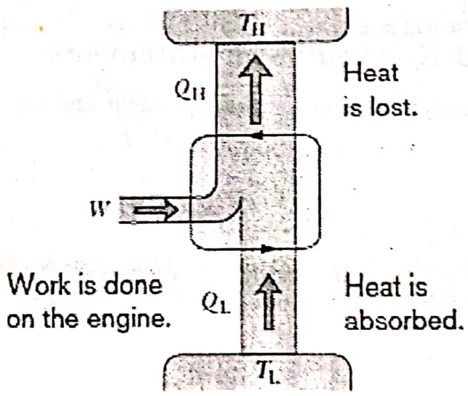

Figure 5: A schematic representation of refrigerator.

the heat and work transfers that occur. Heat Q_L is extracted from a low-temperature reservoir and some work W is done on the system by an external agent; the energies transferred as heat and as work are combined and discharged as heat Q_H to a high-temperature reservoir. [In our household refrigerator, the low-temperature reservoir is the cold chamber in which the food is stored. The high-temperature reservoir is the room in which the unit is housed. Work, which shows up on a utility bills, is done by the motor that drives the unit. In an air conditioner, the low-temperature reservoir is the room to be cooled, the high-temperature reservoir is the outside air, where the condenser coil are located, and again work is done by the motor that drives the unit.]

The purpose of both a refrigerator and an air conditioner is to transfer energy as heat from the low-temperature reservoir to high-temperature reservoir, doing a little work on the system as possible. We rate such unit by their coefficient of performance K, defined as

$$K = \frac{|Q_L|}{|W|} = \frac{|Q_L|}{|Q_H| - |Q_L|} \tag{3}$$

Engineers, and those who pay the utility bills, want the coefficient of performance of a refrigerator to be as high as possible. A value of 5 is typical for a household refrigerator, and a value in the range $2-3$ is typical for a room temperature.

Fi. 6 shows a perfect refrigerator-one that cools without the expenditure of work; it would have a coefficient

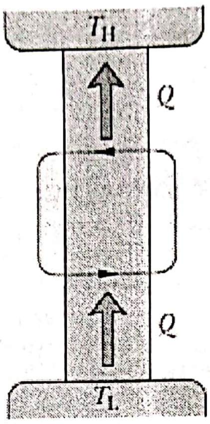

Figure 6: A schematic representation of perfect-refrigerator.

of performance of infinity. Long experience has shown that it is impossible to build such a device. So, another way to express the Clausius statement is: *there are no perfect refrigerators.*
The spontaneous arising of a temperature difference between the two ends of a spoon, energy would be transferred spontaneously as heat from a cool place to a warm place, a violation of the Clausius statement.

Equivalence of the Clausius and Kelvin-Planck statements

The two statements of second law of thermodynamics are not independent and are, in fact, entirely equivalent.

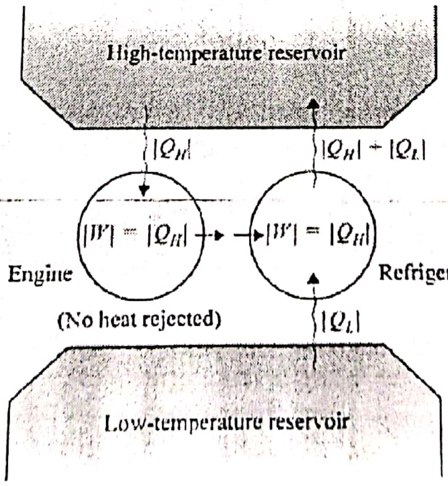

Figure 7: The heat engine on left side is violation of Kelvin-Planck statement; the heat engine and refrigerator acting together violate Clausius statement.

To show this, let us consider what would happen if the Kelvin-Planck statement were incorrect, and that we could build a perfect engine, converting heat Q_H entirely into work W. let us use this work W to derive a real refrigerator, as shown in Fig. 7 This refrigerator takes $|Q'_L|$ from the low temperature reservoir and pumps heat $|Q'_H| = |Q'_L| + |W|$ to the high-temperature reservoir. Let us regard the combination of the the perfect engine and the real refrigerator as a single device. The work W is an internal feature of this device and does not enter into any exchanges of energy with the environment. This device takes $|Q'_L|$ from the low temperature reservoir, and it transfers to the high-temperature reservoir a net amount of heat equal to $|Q'_H| - |Q_H|$. But $|Q_H| = |W|$, and so,

$$|Q'_H| - |Q_H| = |Q'_H| - |W| = |Q'_L| \tag{4}$$

Thus our combined device acts like a perfect refrigerator taking heat Q'_L from low-temperature reservoir and pumping heat Q'_L to the high-temperature reservoir, with no external work performed. This example shows that, if we can build a perfect engine, then we can build perfect refrigerator. That is, a violation of the Kelvin-Planck statement of the second law implies a violation of the Clausius statement and hence both statements are equivalent. In a similar manner, a perfect refrigerator allows us to turn a real heat engine into a perfect engine.

Reversible and Irreversible processes

A reversible process is one that is performed in such a way that, at the conclusion of the process, both the system and the local surroundings may be restored to their initial states **without producing any changes in the rest of the universe.** A process that does not fulfill these stringent requirements is said to be irreversible.

The Carnot engine

The second law of thermodynamics prevents us from building perfect heat engines and refrigerators. There is a fundamental limit to achieve perfection, and to consider it we discuss an engine that operates on a particular cycle, called Carnot engine.

In the Carnot cycle, an ideal gas is the working substance in our usual cylinder. we use two reservoirs, one at high-temperature T_H and another at the low-temperature T_L. The cycle consists of four reversible process, two isothermal and adiabatic. The sequence plotted on a PV diagram in Fig. 8, proceeds as follows:

Step 1 to 2: Put the cylinder on the high-temperature reservoir, with the gas in a state represented by

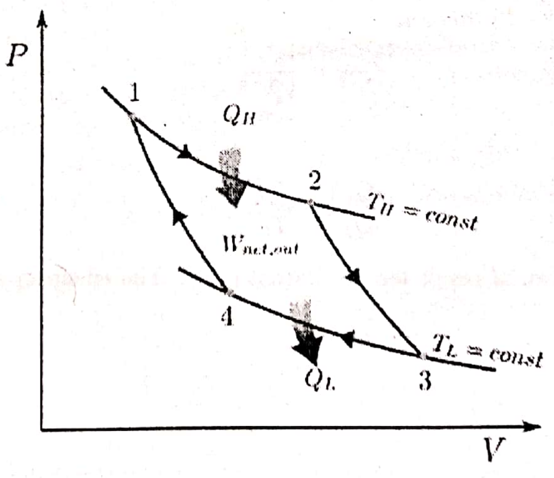

Figure 8: The Carnot cycle of real engine.

point $1(P_1, V_1, T_H)$ in Fig. 8. Gradually, remove some weights from the piston, allowing the gas to expand slowly to point $2(P_2, V_2, T_H)$. During this process, heat $Q_{in} = |Q_H|$ is absorbed by the gas from the high-temperature reservoir. Because this process is isothermal, the internal energy of the does not change ($\Delta E_{int} = 0$) and all the added heat is changed into the positive work done by the system(lifting the piston) during the expansion.

Step 2 to 3: Insulate the cylinder from the reservoir and, by incrementally removing more weight from the piston, allow the gas slowly to expand farther to the point $3(P_3, V_3, T_L)$ in Fig. 8. This expansion is adiabatic because no heat enters or leaves the system ($Q = 0$). The system does positive work in lifting the piston farther

and the temperature drops to T_L, the work must come from the internal energy of the system.
Step 3 to 4: put the cylinder on the low-temperature reservoir and, by gradually adding weight to the piston, compress the gas slowly to point $4(P_4, V_4, T_L)$ in Fig. 8. During this process, heat $Q_{out} = -|Q_L|$ is transferred from the gas to the reservoir. The compression is isothermal at temperature T_L, and Q_L is equal to the negative work done by the gas as the piston and load descend.
Step 4 to 1: Insulate the cylinder from the reservoir and, by adding still more weight, compress the gas slowly back to its initial point 1 of Fig. 8, thus completing the cycle. The compression is adiabatic because no heat enters and leaves. Negative work is done by the gas, and the temperature of the gas increases to T_H.

Let us now calculate the efficiency of a heat engine operating on the Carnot(reversible) cycle. Along the isothermal path 1 to 2 the temperature remains constant. Because the gas is ideal, its internal energy, which depends only on the temperature, also remains constant. With $\Delta E_{int} = 0$, the first law of thermodynamics requires that the heat Q_H from the high-temperature reservoir must equal to the magnitude of the W done on the expanding gas. The work done in isothermal process

$$|Q_H| = nRT_H ln\frac{V_2}{V_1} \tag{5}$$

Similarly, for the isothermal process 3 to 4 in Fig. 8, we can write

$$|Q_L| = nRT_L ln\frac{V_3}{V_4} \tag{6}$$

Dividing these two equations yields

$$\frac{|Q_H|}{|Q_L|} = \frac{|T_H|\, ln(V_2/V_1)}{|T_L|\, ln(V_3/V_4)} \tag{7}$$

For the two adiabatic process 2 to 3 and 4 to 1,

$$T_H V_2^{\gamma-1} = T_L V_3^{\gamma-1} \qquad \text{and} \qquad T_H V_1^{\gamma-1} = T_L V_4^{\gamma-1}$$

Dividing these two equations result in

$$\frac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = \frac{V_3^{\gamma-1}}{V_4^{\gamma-1}} \tag{8}$$

Combining Eqs. 7 and 8 yields

$$\frac{|Q_H|}{|Q_L|} = \frac{T_H}{T_L} \tag{9}$$

Eq. 9 is an important and fundamental result for the Carnot cycle. The efficiency of a heat engine operating on a Carnot cycle:

$$e = 1 - \frac{|Q_L|}{|Q_H|} = 1 - \frac{T_L}{T_H} = \frac{T_H - T_L}{T_H} \tag{10}$$

The efficiency of a Carnot engine depends only on the temperature of two reservoirs between which it operates. Note that the efficiency increases as T_L decreases, approaching 1 as T_L approaches 0. Since T_L can never reach 0, the efficiency must be less than 100%. A Carnot cycle, because it is reversible, can be run backward to make a refrigerator. The coefficient of performance of a Carnot refrigerator is

$$K = \frac{T_L}{T_H - T_L} \tag{11}$$

We have used an ideal gas as an example of working substance. The working substance can be anything at all, although the PV diagrams for other substances would be different. Although real heat engines do not operate on a reversible cycle, the Carnot cycle, which is reversible, gives useful information about the behavior of any heat engine. It is especially important because it sets upper limit on the performance of real engines.

Carnot theorem and second law of thermodynamics

Based on ideal reversible heat engine, Carnot develops a general theorem applicable to all heat engines:

The efficiency of any heat engine operating between two specified temperatures can never exceed the efficiency of a Carnot engine operating between the same two temperatures.

To show violating Carnot's theorem is also a violation of the second law, let us suppose we have an engine X, whose efficiency e_X exceeds the Carnot efficiency e. Now couple the engine X to a Carnot engine operating backward as a refrigerator, as shown in Fig. 9.

Engine X extracts heat Q'_H from the high-temperature reservoir and discharges heat Q'_L to the low-temperature

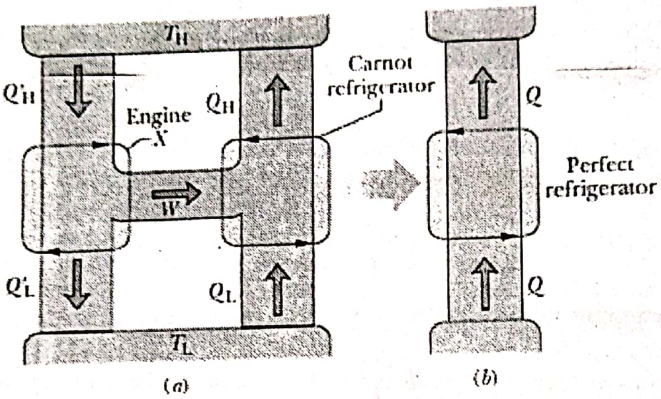

Figure 9: (a) Engine X drives a Carnot refrigerator, (b) Couple of Engine X and a Carnot refrigerator forms a perfect engine.

reservoir, doing work W in the process. Let this work W drive the Carnot refrigerator, which extracts heat Q_L from the low-temperature reservoir and discharges Q_H heat to the high-temperature reservoir.

The net heat that flows from the low-temperature reservoir to the low-temperature reservoir due to the combination of the two devices is $|Q'_L| - |Q_L|$ and the net heat delivered to the high-temperature reservoir is $|Q'_H| - |Q_H|$. Applying the first law to each device separately , we have $|W| = |Q_H| - |Q_L|$ for engine X and $|W| = |Q'_H| - |Q'_L|$ for the Carnot refrigerator. Equating these two expressions, we find

$$|W| = |Q_H| - |Q_L| = |Q'_H| - |Q'_L| \tag{12}$$

or, defining $Q = |Q'_H| - |Q_H| = |Q'_L| - |Q_L|$, our hypothesis is that efficiency of engine X can be exceed the Carnot efficiency; that is

$$e_X = e \tag{13}$$

our hypothesis is equivalent to

$$\frac{|W|}{|Q_H|} > \frac{|W|}{|Q'_H|} \tag{14}$$

or,

$$|Q'_H| > |Q_H| \qquad \text{(consequence of hypothesis)} \tag{15}$$

Comparing Eqs. 12 and 15, we see that $Q > 0$. Thus the combination of engine X and the Carnot refrigerator is equivalent to the perfect refrigerator without external work. This clearly violates the Clausius statement of the second law of thermodynamics.

If $e_x < e$, the Eq 15 would change to $|Q'_H| < |Q_H|$ and from Eq. 12 we would deduce $Q < 0$, the heat Q would be flowing from the high-temperature reservoir to the low-temperature reservoir, which is a natural process and violates no basic law. We can summarize Carnot's theorem as follows:

$$e = e_{carnot} \tag{16}$$

$$e < e_{carnot} \tag{17}$$

Eq. 16 is for the reversible processes. and on the other hand Eq. 17 is for the irreversible processes.

Entropy and Reversible process

The second law of thermodynamics is related to a thermodynamic variable called entropy, S, and that we can express the second law quantitatively in terms of this variable. We start by considering a Carnot cycle. For such a cycle

$$\frac{|Q_H|}{T_H} = \frac{|Q_L|}{T_L}$$

We now discard the absolute value notation, recognizing in this process whether the Carnot cycle is carried out clockwise, as an engine, or counterclockwise, as a refrigerator, Q_H and Q_L always have opposite signs. We can therefore write

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = 0 \tag{18}$$

This equation states that sum of the algebraic quantities $\frac{Q}{T}$ is zero for a Carnot cycle generally for any reversible cycle. We can write

$$\sum \frac{Q}{T} = 0 \tag{19}$$

or, in the limit infinitesimal temperature differences

$$\oint \frac{dQ}{T} = 0 \tag{20}$$

in which $\oint$ indicates that the integral is evaluated for a complete traversal of the cycle, starting and ending at the same arbitrary point of the cycle. We use dQ here to mean a small quantity of heat, not a true differential. If the integral of a variable around any closed path in a coordinate system is zero, then the value of that variable at point depends only on the coordinates of the point and not on the path by which we arrived at that point. Such a variable is often called a state variable. Therefore dQ/T must be differential change in a state variable. We call this new variable the entropy S, such that

$$dS = \frac{dQ}{T} \tag{21}$$

Eq. 20 becomes

$$\oint dS = 0 \tag{22}$$

The change in entropy between any two states i and f is then

$$\Delta S = S_f - S_i = \int_i^f dS = \int_i^f \frac{dQ}{T} \tag{23}$$

where the integral is evaluated over any reversible path connecting these two states.

Entropy and Irreversible process

There are no absolutely reversible process in nature. Friction and unwanted heat transfers always present, and we can seldom perform real processes in infinitesmall steps. Every thermodynamic process is therefore to some extent irreversible.

To find the entropy change for an irreversible path between two equilibrium states, find a reversible process connecting the same states, and calculate the entropy change for reversible path. We consider two examples:

Free expansion: Let an ideal gas double its volume by the expanding into an evacuated space. No work is done against the vacuum, so $W = 0$ and the gas is confined to an insulating container, so $Q = 0$. From the

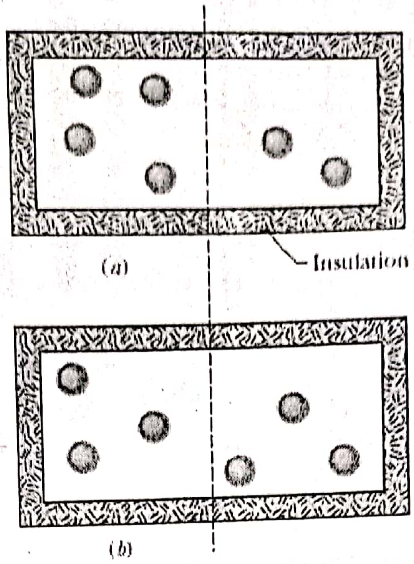

Figure 10: (a) Gas confined one compartments, (b) Gas occupies two compartments due to free expansion.

first law of thermodynamics, we must therefore have the $\Delta E_{int} = 0$. For an ideal gas, whose internal energy depends only on temperature, it follows that $T_i = T_f = T$.
The free expansion is certainly irreversible, because we lose control of the system once we open the valve that separates the compartments. There is an entropy difference between the initial and final states.
To find the entropy change, we choose a reversible path from i to f for which we can do this calculation. A convenient choice is an isothermal expansion that would take an ideal gas from the same initial point (P_i, V_i, T) to the some final point (P_f, V_f, T). It represents a procedure very different from that of the expansion, but it connects that same pair of equilibrium states.

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T} = \frac{1}{T}\int_i^f dQ = \frac{Q}{T} = \frac{W}{T}$$

Since $\Delta E_{int} = 0$, $Q = W$, we obtain

$$\Delta S = \frac{W}{T} = nR\ln\frac{V_f}{V_i} \tag{24}$$

This is equal to the entropy change for the irreversible free expansion. Note that ΔS is positive for the system. Because there is no energy transfer of any kind to the environment in the free expansion, the entropy change of the environment is zero. Thus the total entropy of *system + surrounding* increases during a free expansion.

Irreversible heat transfer: Consider two blocks, each of mass m and specific heat c, that are thermally insulated from each other within an insulating box. The blocks are alike in every way except that one is at a higher temperature than the other. If we remove the insulating barrier that separates the blocks and put them in the thermal contact, they will eventually reach a common temperature T. This process is reversible because we totally lose control of it once we put the blocks in thermal contact with each other.
To find the entropy change between the initial state and the final state, we must find a reversible process connecting these states. We can carry out a reversible process using a temperature reservoir of large heat capacity whose temperature is under our control, perhaps by turning a knob. We first adjust the reservoir temperature to $T + \Delta T$ the temperature of the block of the hotter block, we put that block in thermal contact with the reservoir. We then slowly (reversibly) lower the reservoir temperature from $T + \Delta T$ to T, extracting heat from the block. Because heat leaves the hot block, the entropy of that block decreases, the entropy change being

$$\Delta S_H = \int_i^f \frac{dQ}{T} = \int_{T+\Delta T}^{T} \frac{mcdT}{T} = mc\int_{T+\Delta T}^{T}\frac{dT}{T} = mc\ln\frac{T}{T+\Delta T} \tag{25}$$

Here we have replaced dQ, the heat extracted from the hot block as its temperature changes by dT, by $mcdT$. To continue the reversible process, we now adjust the reservoir temperature to $T - \Delta T$, the temperature of the cooler block, and put that block in thermal contact with the reservoir. We then slowly (reversibly) raise the temperature from $T - \Delta T$ to T, adding heat tio the cooler block. Because heat is added to it, the entropy of the block increases, the entropy change being

$$\Delta S_C = mc \ln \frac{T}{T - \Delta T} \tag{26}$$

Two blocks are now in their final equilibrium state and the reversible process is completed. The entropy change for system is

$$S_f - S_i = \Delta S_H - \Delta S_C = mc\ln \frac{T}{T + \Delta T} - mc\ln \frac{T}{T - \Delta T} = mc\ln \frac{T^2}{T^2 - \Delta T^2} \tag{27}$$

The quantity whose logarithm is taken in Eq. 27 is greater unity so that the entropy of the system increases during this irreversible heat transfer. Because the system is thermally isolated from the its surrounding, the entropy of the *system* + *surrounding* also increases during this irreversible process.

Entropy and the second law of thermodynamics

There is no way in which you can make the entropy of the *system* + *surrounding* decreases. It is true that the entropy of a system can be made to decrease, but that decrease must always be accompanied by an equal or greater increase in the entropy of the system's entropy.

The spontaneous movement of the air in the room to the one corner, is what we may call a free compression, the opposite of a free expansion is always accompanied by an increase of entropy for the system and surrounding. A free compression would result in an entropy decrease and would thus be a violation of the entropy form of second law of thermodynamics.

Let us now make sure that the entropy form of the second law is consistent with the two forms:

1. *There are no perfect engines:* For a perfect engine, the environment is the single reservoir and the entropy change is a decrease, because heat is withdrawn from the reservoir. Thus a perfect engine(which is a violation of the Kelvin-Planck statement) generates an entropy decrease, a violation of the entropy form of the second law of thermodynamics.
2. *There are no perfect refrigerators:* The environment is the two reservoirs and the entropy change is

$$\Delta S = \frac{Q}{T_H} - \frac{Q}{T_L}$$

Because $T_H > T_L$, this entropy change is negative. So, the perfect refrigerator(which violates the second form) also is a violation of the entropy form of the second law of thermodynamics.