Module 2 Thermal Physics

Chapter 18    Second Law of Thermodynamics

ENTROPY

References: 18.9    18.10
Examples:   18.5   18.6   18.7   18.9   18.10   18.13   18.14

Checklist

- **Entropy and disorder**
  
  Quantitative measure of disorder – when a gas is heated and expands, the gas is in a more disordered state after the expansion than before since the molecules are moving in a larger volume and have more randomness of position.

  Infinitesimal reversible change
  \[ dS = \frac{dQ}{T} \]  
  (Eq. 18.17)  

  Reversible isothermal change
  \[ \Delta S = \frac{Q}{T} \]  
  (Eq. 18.18)  

  Entropy change in a reversible process
  \[ \Delta S = \int_1^2 \frac{dQ}{T} \]  
  (Eq. 18.19)  

  The entropy has a definite value for a particular state. When a change occurs from state 1 to state 2, the change in entropy is the same for all possible paths 1 to 2. This fact can be used to determine the entropy change for an irreversible process – simply invent a path from 1 to 2 that consists of entirely reversible processes.

- **Entropy changes**

  Reversible cyclic process
  \[ \Delta S = \oint \frac{dQ}{T} = 0 \]  
  (Eq. 18.21)  

  All irreversible changes \( \Delta S > 0 \) ⇒ entropy is not a conserved quantity
Second law – when all systems taking part in a process are included, the entropy remains constant or increases $\Leftrightarrow$ no process is possible in which the total entropy decreases, when all systems taking part in the process are included

For all processes $\Delta S_{\text{total}} \geq 0$

- **Entropy – microscopic view**
  Microscopic states, macroscopic states.
  Much greater number of possible microscopic states $\Rightarrow$ much greater probability of macroscopic state $\Rightarrow$ much greater disorder $\Rightarrow$ much greater entropy.

**Equilibrium state – most probable macroscopic state – most number of microscopic states – greatest disorder – greatest entropy.**

Configurations associated with large numbers of microstates are said to be more complex or more disordered than those with fewer microstates. The equilibrium state of a system is the most disordered configuration available. The Austrian physicist Ludwig Boltzmann introduced a measure of disorder called the entropy defined by

$$S = k \ln(w)$$  \hspace{1cm} (Eq. 18.22)

$$\Delta S = S_2 - S_1 = k \ln \left( \frac{w_2}{w_1} \right)$$  \hspace{1cm} (Eq. 18.23)

$w$ is the number of possible microscopic states for a given macroscopic state, $k$ is the Boltzmann constant and $\ln$ is the natural logarithm ($\log_e$).

A closed system can never spontaneously undergo a process that decreases the total number of microscopic states.
Entropy – macroscopic view

Assume a small amount of heat added to a system at a temperature \( T \) (measured in K) during a reversible process. Change in entropy of the system is defined to be

\[
\Delta S = \frac{\Delta Q}{T}
\]

For a large quantity of heat transfer, approximate it by a large number of reversible processes

\[
\Delta S = \sum \left\{ \frac{\Delta Q}{T} \right\} \rightarrow \int \left\{ \frac{dQ}{T} \right\}
\]

\( \Delta Q > 0 \) when heated added to a system
\( \Delta Q < 0 \) when heated removed from a system
SI unit for entropy J.K\(^{-1}\)

Irreversible processes - by definition, irreversible processes involve an increase in entropy and \( \Delta S \) is calculated by considering reversible processes that would bring the system to the same final state i.e., in calculating changes in entropy we are only interested in the initial and final states of the system, not in the way the system changed.

Law of Nature: part of the energy surrounding us is completely useless - this energy is the energy of the thermal motion of the molecules - it is not possible to simply extract this energy and converting it into useful mechanical work \( \Rightarrow \) no perpetual motion machines by just removing heat.

Second Law of Thermodynamics (Closed or isolated system)

- reversible process (system can return to its original state with no net change in the system or surroundings) \( \Delta S = 0 \)
- Irreversible process (e.g., smashing an egg, opening a bottle of perfume, rubbing your hands together) \( \Delta S > 0 \)

The Second Law sets limits on the efficiency of converting thermal energy to work that is independent of the materials used in the process - heat engines can not be 100% efficient in converting heat energy into work- all the energy liberated by burning petrol in a car does NOT go into making the car move. The Second Law enables us to calculate the efficiency of engines.

Cyclic process

A cyclic process is one in which a system goes through certain changes and returns to its original state. The changes may involve heat flowing to or from the system and work being done on or by the system. Examples of such processes occur with a car engine or the human body. Heat flows to the engine from burning petrol or to the body from oxidation of food. In both cases work is done on the surroundings. Schematically these examples might be drawn as
The diagram above indicates that all the energy from the burning petrol or the oxidising food has been transformed to useful work. This is possible on energy conservation considerations, but are there other constraints that prevent it from happening? We use the Second Law and entropy calculations to answer this question.

Entropy change in engine = 0 (since the initial and final states of the engine are the same cyclic process - no heat exchange to surroundings).

- Entropy change in engine (cyclic process) = 0
- Entropy change in heat reservoir = \(-\frac{Q}{T}\) (a decrease in entropy because there is a flow of heat from the reservoir).
- Entropy change in surrounding = 0 (there is no heat flow to the surroundings).
- Net entropy change = \(-\frac{Q}{T}\)

The Second Law states that such a decrease of entropy in the universe (system plus reservoir plus surroundings) is impossible. So the above diagram represents an impossible situation and must be amended.

Here, some energy is discharged to a lower temperature reservoir. Only part of the energy from the burning petrol or oxidising food is transformed to useful work.

For one cycle:

1. **First Law**: \(\Delta U = 0\) and \(Q = Q_H - Q_C\) \(\Rightarrow\) \(W = Q_H - Q_C\)
2. **Entropy change in engine (cyclic process)** = 0
3. **Entropy change in surroundings (only work is done on surroundings)** = 0
4. **Entropy change in hot reservoir** = \(-\frac{Q_H}{T_H}\)
5. **Entropy change in cold reservoir** = \(\frac{Q_C}{T_C}\)
6. **Change in entropy of system** = \(-\frac{Q_H}{T_H} + \frac{Q_C}{T_C}\)
As long as $Q_H / T_H < Q_C / T_C$, useful work can be done on the surroundings while the cyclic process goes on. Note that because $Q_C$ is smaller than $Q_H$, $T_C$ must be smaller than $T_H$. Both a hot temperature reservoir and a cold temperature reservoir are needed. Most work done on surroundings occurs when $\Delta S = 0$ and $Q_H / T_H = Q_C / T_C$. This gives the maximum efficiency of a heat engine $e$ as

$$e = \frac{W}{Q_H} = \left( \frac{Q_H - Q_C}{Q_H} \right) / \frac{Q_H}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

For an engine the above represents a **Carnot Cycle** where all processes are reversible.

### Calculating $\Delta S$

#### Isothermal Process: $T$ constant

$\Delta S = \int \frac{dQ}{T}$

$\Delta S = \frac{Q}{T}$

In an isothermal expansion, heat $Q$ must be added to keep $T$ constant, in a process where $\Delta T$ is small

$\Delta S \sim \frac{Q}{T_{avg}}$

$Q = n R T \ln(V_f / V_i)$

$\Delta S \sim n R \ln(V_f / V_i)$

For an adiabatic process: $Q = 0$

$Q = 0 \Rightarrow \Delta S = 0$

**Change in entropy object** - heating results in an increase in temperature of object with mass $m$ and specific heat capacity $c$

$Q = m c \Delta T$

$\Delta S = \int \frac{dQ}{T} = \int m c \frac{dT}{T} = m c \int \frac{dT}{T}$

$\Delta S = m c \ln(T_f / T_i)$

**Change in entropy of an ideal gas for a reversible process**

$\Delta U = Q - W$

process - small steps passing through equilibrium states - reversible

$W = p \Delta V$

$\Delta U = n C_V \Delta T$

$Q = n C_V \Delta T + p \Delta V$

$p = n R T / V$

$\Delta S = \int \frac{dQ}{T} = \int \{ n C_V \frac{dT}{T} + n R \frac{dV}{V} \}$

$\Delta S = n C_V \ln(T_f / T_i) + n R \ln(V_f / V_i)$

$\Rightarrow \Delta S$ depends only on initial and final states - path independent - is a state variable.

### Example 1

A mug of coffee cools from 100 °C to room temperature 20 °C. The mass of the coffee is 0.25 kg and its specific heat capacity may be assumed to be equal to that of water.
4200 J.kg\(^{-1}\).K\(^{-1}\). Calculate the change in entropy of the coffee, of the surroundings and of the coffee plus the surroundings (the "universe").

The entropy of the coffee and of the surroundings will both change. In each case we consider the system of interest (first the coffee, second the surroundings) and look at the corresponding reversible change that takes the system from its initial to its final state. Note well that we are not claiming that the change occurred reversibly, we are just imagining the reversible change so that we can calculate the entropy change in the real situation.

**Coffee**: The coffee cools from 100 °C to 20 °C, i.e. from \(T_H = 373\) K to \(T_C = 293\) K.

The transfer of energy as \(\Delta Q\), from the coffee is given by the relation

\[
\Delta Q = m \cdot c \cdot \Delta T,
\]

where \(m\) is the mass of the coffee, \(c\) the specific heat capacity of the coffee and \(\Delta T\) the change in temperature of the coffee while in contact with that reservoir.

\[
\Delta S = \sum (m \cdot c \cdot \Delta T / T) = \int (m \cdot c \cdot dT / T) = m \cdot c \cdot \ln(T_C / T_H)
\]

\[
\Delta S = (0.25)(4200)\ln(293/373) = -253\ J.K^{-1}
\]

**Surroundings**: These remain at temperature 293 K while an irreversible flow of \(m \cdot c \cdot \Delta T\) occurs. Note that this heat flow is calculated indirectly, in terms of coffee, where data needed for this calculation is available, rather than from values directly associated with the surroundings.

\[
\Delta S = \Delta Q / T = (m \cdot c \cdot \Delta T) / T
\]

\[
\Delta S = (0.25)(4200)(373 - 293)/293 = 287\ J.K^{-1}
\]

This will be positive, as to be expected since heat flows into the surroundings.

**Coffee plus surroundings**: \n
\[
\Delta S = \Delta S(\text{coffee}) + \Delta S(\text{surroundings}) = -253 + 287
\]

\[
\Delta S = 34\ J.K^{-1}
\]

As for all naturally occurring processes the net change in entropy is positive.

**Example 2**

*A stone of mass 1.0 kg is dropped into a lake of water from a height of 3.0 m. Calculate the changes in entropy of the stone and of the lake.*

At first sight, this might seem to be a mechanics sum. But there will be an energy transfer: potential energy of the stone to kinetic energy of stone to internal energy of the lake. Changes in entropy are associated with the energy transfers. Because of the size of the lake, its temperature is effectively unchanged. We also assume that there is no difference between the temperatures of the air and the lake, so the temperature of the stone is also unchanged.

**Stone**: The initial and final thermal states (internal energy, temperature, volume, etc.) are identical. The corresponding reversible change to be considered is extremely simple - no change. This means that the entropy change of the stone is zero.
The energy that is transferred from the stone to the lake, as flow, is equal to the original potential energy of the stone. The corresponding reversible change is the transfer as heat flow to the lake

\[ \Delta S = \frac{mg}{T} \]

Assume \( T = 300 \text{ K} \), \( m = 1.0 \text{ kg} \), \( g = 10 \text{ m.s}^{-2} \) and \( h = 3.0 \text{ m} \)

\[ \Delta S = \frac{(1.0)(10)(3.0)}{300} = 0.10 \text{ J.K}^{-1} \]

**Example 3**

A current of 4.0 A passes through a 60 \( \Omega \) resistor in 5 minutes. The resistor is cooled by the continuous passage of fast running water (enough water so that its temperature essentially remains constant). The temperature of the room is 290 K. Calculate the rate of change of entropy of the resistor and the surroundings.

\[ I = 4.0 \text{ A}, R = 60 \text{ \Omega}, t = 5 \text{ min} = (5)(60) = 300 \text{ s}, T = 290 \text{ K} \]

Rate of energy supply = \( I^2 R = (4.0)^2(60) = 960 \text{ W} \)

When the resistor is cooled by a continuous supply of running water, it remains at room temperature. The thermal state of the resistor is unchanged and there is a flow of heat at a rate of 960 W into the running water. We assume that the water flow is fast enough so that the water temperature is unchanged, so the only thermal effect is the flow of 960 W into the water without changing its temperature

Rate of entropy increase of water = \( \frac{\Delta Q}{T} = \frac{960}{290} = 3.3 \text{ W.K}^{-1} \)

**Example 4**

Consider two engines, the details of which are given in the following diagrams. For both engines

(a) Calculate the heat flow to the cold reservoir.

(b) The changes in entropy of the hot reservoir, cold reservoir and engine.

(c) Which engine violates the Second Law?

(d) What is the efficiency of the working engine?

<table>
<thead>
<tr>
<th>Engine 1</th>
<th>Engine 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_H = 400 \text{ K} )</td>
<td>( T_H = 400 \text{ K} )</td>
</tr>
<tr>
<td>( T_C = 300 \text{ K} )</td>
<td>( T_C = 300 \text{ K} )</td>
</tr>
<tr>
<td>( Q_H = 1000 \text{ J} )</td>
<td>( Q_H = 1000 \text{ J} )</td>
</tr>
</tbody>
</table>
\[ W = 200 \text{ J} \quad W = 300 \text{ J} \]

\[ Q_C = ? \text{ J} \quad \Delta S = ? \text{ J.K}^{-1} \quad e = ? \]

(a) First Law: \( \Delta U = Q - W \)
\[ Q = Q_H - Q_C \]

Engine - cyclic process \( \Delta U = 0 \) \( \Rightarrow Q = W \Rightarrow Q_H = Q_C = W \Rightarrow Q_C = Q_H - W \)

Engine 1: \( Q_C = 1000 - 200 = 800 \text{ J} \)

Engine 2: \( Q_C = 1000 - 300 = 700 \text{ J} \)

(b) Change in entropy
\[ \Delta S = \frac{\Delta Q}{T} \]

Surroundings: No heat flows to the surroundings, \( \Delta S = 0 \)

Hot reservoir (heat removed from reservoir): \( \Delta S = -\frac{Q_H}{T_H} \)

Engines 1 and 2: \( \Delta S = -\frac{1000}{400} = -2.5 \text{ J.K}^{-1} \)

Cold reservoir (heat added to reservoir): \( \Delta S = \frac{Q_C}{T_C} \)

Engine 1: \( \Delta S = \frac{800}{300} = +2.7 \text{ J.K}^{-1} \)

Engine 2: \( \Delta S = \frac{700}{300} = +2.3 \text{ J.K}^{-1} \)

Change in entropy of the engines: \( \Delta S = 0 \iff \text{undergo continuous cycles} \)

Change in entropy of the "universe":
\[ \Delta S = \Delta S(\text{hot reservoir}) + \Delta S(\text{cold reservoir}) + \Delta S(\text{surroundings}) + \Delta S(\text{engine}) \]

Engine 1: \( \Delta S = -2.5 + 2.7 + 0 = +0.2 \text{ J.K}^{-1} > 0 \Rightarrow \text{Second Law validated} \)

Engine 2: \( \Delta S = -2.5 + 2.3 + 0 = -0.2 \text{ J.K}^{-1} < 0 \Rightarrow \text{Second Law not validated} \)

(d) Engine 1 is the working engine;

\[ e = \left( \frac{\text{work out}}{\text{energy input}} \right) \times 100 \quad e = \left( \frac{200}{1000} \right)\times 100 = 20\% \]

Note: The working substance in the engine goes around a cycle, therefore, no change in entropy for the engine.

Example 5

A thermally insulated box is divided by a partition into two compartments, each having a volume \( V \). Initially, one compartment contains \( n \) moles of an ideal gas at temperature \( T \) and the other compartment is evacuated. We then break the partition and the gas expands to fill both compartments. What is the increase in entropy?

The process is a free expansion, \( Q = 0, W = 0 \) and \( \Delta U = 0 \) and therefore, because the system is an ideal gas \( \Delta T = 0 \). The entropy change is not zero even though no heat exchange occurs because the process is not reversible. The change in entropy only depends on the initial and final states and not the process. We can devise a reversible process that has the same end points and hence calculate the change in entropy. We can consider an isothermal expansion from \( V \) to \( 2V \) at a temperature \( T \). The gas does work during this expansion and so heat must be supplied to keep the internal energy constant (\( \Delta T = 0 \)).
For an isothermal expansion

\[ W = Q = n R T \ln(\frac{V_f}{V_i}) = n R T \ln(2) \]

Thus the change in entropy is

\[ \Delta S = \frac{Q}{T} = n R \ln(2) \]
\[ \Delta S = (1)(8.315)\ln(2) \]
\[ \Delta S = 5.8 \text{ J.K}^{-1} \]

**Entropy – microscopic view**

\[ S = k \ln(w) \]

Consider a game of throwing coins into the air and then counting the number of heads and tails. We can start with throwing 4 coins (5 macroscopic states and 16 microscopic states).

Macroscopic state **1**: 4 H / 0 T, microscopic state \( w = 1 \), prob = 1/16, \( S = k \ln(1) = 0 \)
- microscopic state 1: H H H H

Macroscopic state **2**: 3 H / 1 T, microscopic states \( w = 4 \), prob = 4/16, \( S = k \ln(4) \)
- microscopic state 2: H H H T
- microscopic state 3: H H T H
- microscopic state 4: H T H H
- microscopic state 5: T H H H

Macroscopic state **3**: 2 H / 2 T, microscopic states \( w = 6 \), prob = 6/16, \( S = k \ln(6) \)
- microscopic state 6: H H T T
- microscopic state 7: H T T H
- microscopic state 8: T T H H
- microscopic state 9: T H T H
- microscopic state 10: H T H T T
- microscopic state 11: T H H T

Macroscopic state **4**: 1 H / 3 T, microscopic states \( w = 4 \), prob = 4/16, \( S = k \ln(4) \)
- microscopic state 12: T T T H
- microscopic state 13: T T H T
- microscopic state 14: T H T T
- microscopic state 15: H T T T

Macroscopic state **5**: 0 H / 4 T, microscopic state \( w = 1 \), prob = 1/16, \( S = k \ln(1) = 0 \)
- microscopic state 16: T T T T
Most probable macroscopic state is the state with the greatest probability of occurrence, state with the greatest disorder and the state with the greatest entropy, it is macroscopic state 3 (2 H / 2 T).

For \( N \) coins, the total number of microscopic states = \( 2^N \)

For \( h \) heads and \( t \) tails, the number of microscopic states = \( (h + t)! / h! \ t! = N! / h! \ t! \)

Probability of a macroscopic state
\[
= \text{no. of microscopic states} / \text{total no. microscopic state}
\]
\[
= \frac{N!}{(h+t)!} \quad 2^N
\]

\( N = 4 \), macroscopic state (3 H / 1T): \( h = 3 \) and \( t = 1 \)

\[
\text{prob} = \frac{4!}{(3!+1!)} = \frac{4}{16}
\]

\( N = 4 \), macroscopic state (2 H / 2T): \( h = 2 \) and \( t = 2 \)

\[
\text{prob} = \frac{4!}{(2!+2!)} = \frac{6}{16} \quad \text{this is the most probable state}
\]

–state with greatest entropy

---

![Graph showing probability distribution for 40 coins](attachment:image.png)
Macrosstates: no of heads

No. of coins $N = 80$

Macrostates: no of heads

No. of coins $N = 160$

$x \times 10^{46}$

No. of coins $N = 160$

No. of microstates

Macrostate: no. of heads
**Card playing:** Consider the following set of cards dealt to a group of 4 persons

<table>
<thead>
<tr>
<th></th>
<th>Jill</th>
<th>Jack</th>
<th>Jan</th>
<th>John</th>
</tr>
</thead>
<tbody>
<tr>
<td>clubs</td>
<td>AKQJ1098765432</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diamonds</td>
<td>AKQJ1098765432</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hearts</td>
<td></td>
<td>AKQJ1098765432</td>
<td></td>
<td></td>
</tr>
<tr>
<td>spades</td>
<td></td>
<td></td>
<td>AKQJ1098765432</td>
<td></td>
</tr>
</tbody>
</table>

This set of cards is well-ordered and it would be very surprising to see such an arrangement. The chance of getting this arrangement is 1 in $2 \times 10^{27}$.

<table>
<thead>
<tr>
<th></th>
<th>Jill</th>
<th>Jack</th>
<th>Jan</th>
<th>John</th>
</tr>
</thead>
<tbody>
<tr>
<td>clubs</td>
<td>AJ65</td>
<td>K97</td>
<td>1032</td>
<td>Q84</td>
</tr>
<tr>
<td>diamonds</td>
<td>K75</td>
<td>QJ8</td>
<td>432</td>
<td>A1096</td>
</tr>
<tr>
<td>hearts</td>
<td>Q62</td>
<td>J875</td>
<td>K109</td>
<td>A43</td>
</tr>
<tr>
<td>spades</td>
<td>863</td>
<td>KJ4</td>
<td>A752</td>
<td>Q109</td>
</tr>
</tbody>
</table>

This set of cards is disordered and is the type of arrangement that one commonly sees. The chance of getting arrangement 2 is 1 in $2 \times 10^{27}$.

Both arrangements dealt have the same probability, but arrangement 2 is normal and arrangement 1 is very, very, … rare. Although the arrangement 2 is improbable as any other, it is representative of a large number of hands of the type 4 of one suit and 3 of the other suits. A single hand such as 4/3/3/3 can be obtained in any one of $1.7 \times 10^{10}$ ways. This means that if we play many games of bridge we see many occurrences of this 4/3/3/3 arrangement.

Now, consider the situation with a large number of molecules of air in a box. There are too many molecules to use the laws of motion to keep track of them – a statistical or probability approach must be used. How do we expect the molecules to spread out? There is no fundamental law of physics that says they must be evenly distributed – rather, it is a matter of probabilities.

<table>
<thead>
<tr>
<th>Box size</th>
<th>1 m$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. of molecules</td>
<td>$10^{25}$</td>
</tr>
<tr>
<td>Size of cell</td>
<td>$10^{-6}$ m$^3$</td>
</tr>
<tr>
<td>No. of cells</td>
<td>$10^6$</td>
</tr>
</tbody>
</table>

No. of ways of getting all molecules into a single cell = 1
Entropy $S = k \ln(w)$  \( w = 1 \quad S = 0 \)

No. of ways of arranging molecules evenly among cells ($10^{19}$ in each cell) is

\[
\left(10^6\right)^{10^{25}}
\]

Entropy $S = k \ln(w)$  \( w = \left(10^6\right)^{10^{25}} \quad k = 1.38 \times 10^{-3}$ J.K$^{-1}$

\[
S = (1.38 \times 10^{-3}$ J.K$^{-1})(10^{25}) \ln(10^6) = 2000$ J.K$^{-1}$
Discerning the arrow of time

In the movies of the type, “Perils of Pauline”, a scene often appears where the heroine is tied to the railway tracks and a train comes to a halt just before it cuts her into three. If you watch such a scene (diverting your attention from the heroine) and should pick up a clue to the fact the film is actually being shown in reverse (less heroines are lost this way). What is the clue?

There is no phenomena whereby an object will spontaneously leave a state of equilibrium. All natural processes proceed in such a way that the probability of the state increases – law of increasing entropy – it is on of the most important laws of nature – the Second Law of Thermodynamics.