The Second Law: The Concepts

Chapter 4 of Atkins: The Second Law: The Concepts
Sections 4.1 and 4.2

Direction of Spontaneous Change
Dispersal of Energy
Entropy
Thermodynamic definition
Entropy as a State Function
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First vs. Second Law

First Law of Thermodynamics:
The energy of the universe is constant - energy is conserved
• This law tells us nothing about the spontaneity of physical and chemical transformations

Consider the formation of water:
H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)
\Delta_fH = -286 kJ mol^{-1}

Using the first law, it is easy to calculate \Delta U and \Delta H associated with this spontaneous reaction - we can also calculate \Delta U and \Delta H for the reverse reaction, which we know does not occur spontaneously.

What about gases? We know that gases expand spontaneously to fill a container - we know that the opposite does not happen - unless some sort of work is done to bring about this reverse change.

Neither the sign nor the magnitude of \Delta U and \Delta H tells us which way the reaction will go - however, we can get this information from the Second Law of Thermodynamics.

Statements of the Second Law

Elements in a closed system tend to seek their most probable distribution; in a closed system entropy always increases.

1. Clausius (1822-1880) It is impossible that, at the end of a cycle of changes, heat has been transferred from a colder to a hotter body without at the same time converting a certain amount of work into heat.

2. Lord Kelvin (1824-1907) In a cycle of processes, it is impossible to transfer heat from a heat reservoir and convert it all into work, without at the same time transferring a certain amount of heat from a hotter to a colder body.

3. Ludwig Boltzmann (1844-1906) For an adiabatically enclosed system, the entropy can never decrease. Therefore, a high level of organization is very improbable.

4. Max Planck (1858-1947) A perpetual motion machine of the second kind is impossible.

5. Caratheodory (1885-1955) Arbitrarily near to any given state there exist states which cannot be reached by means of adiabatic processes.

First vs. Second Law

The first law gives us no clue as to what processes will actually occur and which ones will not. For that matter, why does anything ever happen at all? The universe is an isolated system after all. There is no change in internal energy. There is no heat transferred in or out and no work is done on or by the system as a whole. q=0; w=0; \Delta U=0.

With only the first law, and without the second law:
The universe is a boring place.

Yet, the universe is not a boring place:
• Stars come into existence and blow up into oblivion
• Planets are created and hurl around stars
• Life exists amid all of this turmoil on these planets

Why? What is driving all of this?

These processes do not lead to a lower energy for the universe as a whole. So what is going on?
The Second Law of Thermodynamics

The second law of thermodynamics can be stated in a number of equivalent ways; an early statement of the law from Lord Kelvin says:

No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

All heat engines have a source of heat and a cold sink, into which some heat is always discarded and not converted into work.

The engine on the left violates the second law - this is equivalent to a ball initially at rest on a heated surface starting to bounce (i.e., heat absorbed from this surface is converted into orderly work) - this has not been observed.

What determines how physical and chemical processes proceed spontaneously? Energy? Tendency towards minimum energy?

Simple Processes

Process 1: First Law fulfilled
- A perfectly elastic ball in a vacuum is dropped from some height with an initial potential energy.
- When it strikes the ground (h=0), all energy has been converted into kinetic energy.
- The ball bounces back to the original height, where all of the kinetic energy is converted back to the original potential energy.

Process 2: Why doesn’t the egg bounce?
- An egg is dropped from the same height as the ball.
- Initial and final states are not the same - seem to have lost energy!
- First Law: we cannot lose energy - where did it go?
  - Converted into random molecular motion and heat
  - We wound up with a more disorganized form of matter
- The universe tends to more random disorganized states

Dispersal of Energy

Spontaneous changes are accompanied by dispersal of energy into a more disordered form.

Bounding ball:
- Ball does not return to original height, as energy is redistributed to molecules in the floor and ball as heat - inelastic energy losses.
- Ball eventually comes to rest, losing all energy into thermal motion of atoms in the floor - the reverse process will never occur!

Heated floor and ball:
- Molecules and atoms in the floor (and ball) undergo thermal (random) motion.
- In order for the ball to spontaneously localize some of this motion into upward motion of all of the atoms, it must be in a virtually impossible process.

* * * Boltzmann paradox: could happen!
Cornerstone of the Second Law: Entropy

The universe tends towards more random, disorganized states. This is a rather loose statement of the second law of thermodynamics and our way of quantitating the disorder and randomized motion in one state versus another is a state function called entropy:

Increasing entropy means increasing disorder and randomized motion.

Irony of the Second Law:

Without the Second Law, nothing would happen. With it, the universe will progress to the point where the entropy is maximized, and hence nothing will ever happen again.

General Thoughts on Second Law

Signpost for spontaneous change:
Direction of change that leads to general chaotic dispersal of total energy of an isolated system

Ball will bounce and come to rest
Gas spontaneously expands, does not spontaneously contract
Object does not suddenly become warmer than its surroundings for no reason at all - random vibration of atoms will not suddenly lead to an excess of thermal motion (and therefore heating) - however, the object does spontaneously release energy into the surroundings as thermal motion (consequence of chaos...)

Puzzling thought:
The fall into disorder can result in highly ordered substances such as crystals, proteins, life, etc.: organized structures and patterns can emerge as energy and matter disperse (i.e., the entropy increases)
Check out: http://www.secondlaw.com
http://www.2ndlaw.com

Spontaneity & Reversibility

Spontaneous:
It has little to do with an impromptu gesture, a witty saying or impulsive shopping. It means a process that results in a change from one state to another in an irreversible way. Anything that happens in the universe that results in an irreversible change in state is spontaneous.

Reversible Change (Not Spontaneous):
Truly reversible processes do not happen in reality, because in a truly reversible process all forces would be perfectly balanced and there would be no driving force for the system to move. By moving things very slowly always keeping forces in near perfect balance, we can approximate reversible processes to whatever degree we like. For example, during reversible expansion of a gas, we keep the pressures essentially the same on the inside and the outside - if this was strictly true, the gas would not have any driving force to expand and nothing would ever happen. However, we can make it as close to true as we like by making the imbalance as small as we want.

Irreversible Change (Spontaneous):
All processes that really happen are irreversible, forces driving process are substantially out of balance.

Second Law and Entropy

The law used to identify spontaneous change, and can be quantified in terms of a state function known as entropy, S:

First Law
Uses internal energy, U, to identify permissible changes

Second Law
Uses entropy, S, to identify the spontaneous (irreversible) changes among the permissible changes

The entropy of an isolated system increases in the course of spontaneous change

$$\Delta S_{\text{total}} > 0$$

where $S_{\text{total}}$ is the total entropy of a system and its surroundings.
Thermodynamic Definition of Entropy

An infinitesimal change in entropy is $dS$, and this can occur as a result of a chemical or physical process. The thermodynamic definition of entropy:

$$ dS = \frac{dq_{rev}}{T} $$

If we perform some process along a reversible path, then the entropy produced should be proportional to the amount of heat produced (or consumed) and inversely proportional to the temperature.

Measurable entropy difference between two states, $\Delta S$: find a reversible path, calculate heat supplied at each stage of the path divided by temperature at which heat is supplied.

Why is this? The change in the extent to which energy is dispersed in a random disorderly manner depends on the amount of energy transferred as heat (creates random "thermal" motion). Work is not accompanied by increase in random motion, but rather, implies uniform motion, and is therefore not accompanied by changes in entropy.

$$ \Delta S = \frac{dq_{rev}}{T} \text{ if } \int dS = \frac{dq_{rev}}{T} $$

Surroundings

Surroundings are treated in a manner similar to the system, except that surroundings are so large that we consider them to be isothermal and (generally) at constant pressure. Thus, $dq_{sur} = \Delta H_{sur}$ (recall, $\Delta H = q_p$).

Therefore, heat transferred to the surroundings is equal to a state function and is independent of the path that the heat used to get out into the surroundings: it has been transferred by a reversible path.

Another view: the surroundings are generally assumed not to change state when something happens in the system, thus transfer of heat to and from the surroundings is effectively reversible (since there is no change of state, we cannot say that the change was irreversible):

$$ dS_{sur} = \frac{dq_{sur}}{T_{sur}} - \frac{dq_{sur}}{T_{sur}} $$

Since the surroundings are isothermal:

$$ \Delta S_{sur} = \frac{q_{sur}}{T_{sur}} \text{ and } \Delta S_{sur} = 0 $$

Entropy Example: Isothermal Expansion

Consider reversible isothermal expansion of a perfect gas ($pV = nRT$)

$$ p = p_{ex} \quad \Delta T = 0 \quad \Delta V = V_f - V_i > 0 \quad w < 0 $$

In an isothermal expansion, $\Delta U = 0$, so $q = -w$

Since $T$ is constant:

$$ \Delta S = \frac{1}{T} \int dq_{rev} = \frac{q_{rev}}{T} $$

We know the work of this type of expansion, so

$$ q_{sur} = -w_{rev} = nRT \ln \frac{V_f}{V_i} $$

Thus, it follows that

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

Entropy as a State Function

In order to prove that entropy is a state function, the integral of $dS$ must be independent of path:

$$ \oint \frac{dq_{rev}}{T_{sur}} = 0 $$

Where the integration is about a closed path.

If the integration of the above equation around an arbitrary cycle (cyclic system) is zero, this will show that the entropy of the system in the initial and final states is the same, regardless of the path taken.

In a thermodynamic cycle, the overall change in a state function is zero, and is independent of path.
Carnot Cycle

The **Carnot cycle**, named after Sadi Carnot, has four reversible stages:

1. Reversible isothermal expansion from A to B at $T_h$, $\Delta S = q_h/T_h$, $q_h$ is heat supplied from a hot source, and is positive.
2. Reversible adiabatic expansion from B to C, no heat leaves system ($\Delta S = 0$), temperature falls from $T_h$ to $T_c$, where $T_c$ is the temperature of the cold sink.
3. Reversible isothermal compression from C to D, $\Delta S = q_c/T_c$, $q_c$ is heat released into a cold sink, and is negative.
4. Reversible adiabatic compression from D to A, no heat enters the system ($\Delta S = 0$), temperature rises from $T_c$ to $T_h$.

Total entropy change

$$\int dS = q_h/T_h + q_c/T_c$$

This will be zero if:

$$\frac{q_h}{T_h} = \frac{q_c}{T_c}$$

Efficiency

The same calculation just completed for gases applies to all types of materials and systems. We define the **efficiency**, $\varepsilon$, of a heat engine:

$$\varepsilon = \frac{\text{work performed}}{\text{heat absorbed}}$$

The greater the work output from a given supply of heat, the greater the efficiency of the engine.

Work performed by the engine is the difference between heat supplied from the heat source and returned to the cold sink:

$$\varepsilon = 1 - \frac{q_c}{q_h}$$

Since $q_c < 0$, then for an ideal gas,

$$\varepsilon_{\text{rev}} = 1 - \frac{T_c}{T_h}$$

Carnot Cycles and Engines (Generalization)

Second Law: all reversible engines have the same efficiency regardless of construction - Two engines A and B, assume A more efficient than B, coupled together using the same reservoirs.

A: takes heat $q_h$, releases heat $q_c$; B: takes heat $q_c$ releases $q_h$. Since A more efficient than B, not all work A produces is needed for this process, and difference can be used to do work.

Net result: hot reservoir stays the same, hot reservoir loses energy, and work has been produced.

**Problem**: heat (disordered thermal motion) has been converted directly into work (ordered molecular motion) without the need for a cold sink - assumption that engines have different efficiencies is false!

Relationship between heat transfers and temperatures must be independent of working materials - BUT results are therefore the same as for an ideal gas.
Carnot Cycles: S is a State Function

Any reversible cycle can be thought of as a collection of Carnot cycles - this approximation becomes exact as cycles become infinitesimal.

Entropy change around an individual cycle is zero.

Sum of entropy changes over all cycles is zero.

In interior, entropy change along any path is cancelled by the entropy change along the path shared with its neighbor.

Thus, all entropy changes cancel except those along the perimeter of the entire cycle - but the sum of the paths along the perimeter, if the paths are infinitesimal in size, match the overall cycle exactly, so

\[ \sum \frac{dS}{T} = \sum \frac{dS}{T} = 0 \]

This is an exact differential and therefore S is a state function.

The Clausius Inequality I

Isothermal expansion of a perfect gas:

Case 1: reversible (p_{rev} = p_{rev,iso})

Case 2: irreversible (p_{irrev} = p_{irrev,iso})

\[ W_{isothermal, irrevers} = -p_{irrev} \Delta V = \frac{nRT}{V_f} \Delta V \]

\[ W_{isothermal, revers} = -p_{rev} \Delta V = \frac{nRT}{V_f} \Delta V \]

- Take: \( V_f = 2V_i \); \( w_{rev} = -0.5nRT \), and \( w_{irrev} = -0.693nRT \) (more work done on surroundings by irreversible expansion).
- Since isothermal expansion, \( \Delta U = 0 \), and \( q = -w \).
- This means that \( q_{irrev} > q_{rev} \).
- \( S_{sys} \) is state function, independent of path; \( \Delta S_{sys} = q_{rev}/T = (0.693)nRT \).
- \( S_{sur} \) depends on amount of heat transferred:
  \[ \Delta S_{sur, irrevers} = -0.5nRT \]

The Clausius Inequality II

- In the reversible case, \( \Delta S_{sys} = 0 \), since the entropy change of system and surroundings will have opposite signs.
- In the irreversible case, \( \Delta S_{sys} = 0.193nR \).

This is a general result: all irreversible reactions are spontaneous and have a total entropy change which is greater than zero.

For system in mechanical and thermal contact with surroundings, at some temperature, \( T \), there may not be mechanical equilibrium. Any change in state has entropy changes \( dS \) (system) and \( dS_{sur} \) (surroundings). The process may be irreversible, and then total entropy will increase:

\[ dS + dS_{sur} \geq 0 \]

Since \( \Delta S_{sys} = dS - dS_{sur} \), where \( dS \) is the heat provided to the system during the process, and \( dS_{sur} = -dq/T \). Then for any change

\[ dS \geq \frac{dq}{T} \]

(system isolated from surroundings)

The Clausius Inequality III

This is our signpost of spontaneous change: in an isolated system the entropy of the system alone cannot decrease due to spontaneous change.

**Example 1:** Irreversible adiabatic change, \( dq = 0 \), and therefore \( dS \geq 0 \). Entropy of system increases, entropy of surroundings stays constant (since no heat transfer has occurred), \( dS_{sur} \geq 0 \).

**Example 2:** Irreversible isothermal expansion of perfect gas, \( dq = -dw \) if into a vacuum, \( w = q \), so \( dS \leq 0 \), \( dS_{sur} = 0 \) and \( dS_{sys} \geq 0 \).

**Example 3:** Spontaneous cooling

\[ dS = \frac{dq}{T_f} \left[ \frac{1}{T_f} - \frac{1}{T_i} \right] \]

\( dS > 0 \), since \( T_i > T_f \) so cooling is spontaneous - if two temperatures are equal then \( dS = 0 \).