Second and Third Laws of Thermodynamics

Chapter 5
Spontaneity of Changes

Real processes have a natural direction of change.

For example heat flows from hotter bodies to colder bodies, and gases mix rather than separate.

The state function that predicts the direction of spontaneous change is termed entropy, $S$.

For an isolated system, $S$ increases for a spontaneous change.

For a system that interacts with its environment, the sum of the entropy of the system and that of the surroundings increases.

The first law: in any process, the total energy of the universe remains constant.

If several possible energy conserving processes can occur, first law cannot predict which one is more likely to occur.

Some transformations/changes do not violate the first law of thermodynamics, however such changes (transformations) may not occur naturally.

Natural transformations, termed as spontaneous processes are processes that are extremely likely to happen. They would follow the first law.

Spontaneous processes has to satisfy the entropy requirement as well.

Spontaneity indicates nothing about the rate of occurrence of such transformations.

The concept of entropy has its origin in studies to maximize the ‘work’ output of heat engines. An idealized version of a heat engine has a ‘working substance’ heat source at $T_{hot}$ and a heat sink at $T_{cold}$.

The working substance is contained in a piston and cylinder assembly with diathermal walls. The expansion or contraction of the gas caused by changes in its temperature drives the piston in or out of the cylinder in a linear motion. The linear motion is converted to circular motion/rotary motion is employed to do work on the surroundings (heat to work!).
The P-V diagram for a reversible heat engine is shown below.

**Carnot Cycle**

- **a→b:** Rev. isothermal expansion - gas absorbs heat from the reservoir at $T_{\text{high}}$ and does work on the surroundings.
- **b→c:** Gas expands adiabatically - work done on the surroundings, gas has cooled to the temperature $T_{\text{cold}}$.
- **c→d:** An isothermal compression - surroundings do work on the system and heat is absorbed by the cold reservoir.
- **d→a:** Gas is compressed to its initial volume adiabatically - work is done on the system, temperature returns $T_{\text{high}}$, its initial value.

More heat absorbed from the hot source than lost to the surroundings.

Efficiency of a reversible heat engine: $\eta = \frac{W_{\text{net}}}{q_c}$

Entropy

Starting from efficiency expression:

$$\varepsilon = \frac{T_{hot} - T_{cold}}{T_{hot}} = \frac{q_{ab} + q_{cd}}{q_{ab}}$$

$$\Rightarrow 1 - \frac{T_{cold}}{T_{hot}} = 1 + \frac{q_{ab}}{q_{cd}}$$

$$\Rightarrow q_{ab} + q_{cd} = 0$$

The quantity $\frac{q}{T} = S$ for the reversible cycle would be $= 0$.

$$\int \frac{dq_{rev}}{T} = 0$$

Entropy

$$dS = \frac{dq_{rev}}{T} \Rightarrow \Delta S = \int \frac{dq_{rev}}{T}$$
The sum of the quantity \( \frac{q_{rev}}{T} \) around the Carnot cycle is zero. This is true for any reversible cycle, because any reversible cycle is made up of many incremental Carnot cycles.

\[
\Delta S_{\text{rev}} = \sum \left( \frac{q_{rev}}{T} \right)_{\text{rev}} = 0
\]

\[
\Delta S_{\text{irrev}} = 0
\]

Because \( S \) is a state function it is path independent. Therefore \( \Delta S \) is the same reversible or not, so for any process/change \( \Delta S \),

\[
\Delta S = \Delta S_{\text{rev}} = \Delta S_{\text{irrev}} = \int \frac{dq_{rev}}{T}
\]

Although \( dq \) is not an exact differential; division of \( T \) makes \( \frac{dq}{T} \) an exact differential!

\[
dS = \frac{dq}{T} \Rightarrow \Delta S = \int \frac{dq}{T}
\]

\( \Delta S \) Calculations: ideal gases

Any two macroscopic variables \( V, T, \) and \( P \) defines the state of an ideal gas.

1. \( \Delta S \) for the reversible isothermal expansion or compression of an ideal gas.

   \[
   P \text{ V T} \quad \Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{nRT \ln \frac{V_f}{V_i}}{T} \text{ d}T
   \]

2. \( \Delta S \) for an ideal gas that undergoes a reversible change in \( T \) at constant \( V \).

   \[
   P \text{ V T} \quad \Delta S = \int \frac{dq_{\text{rev}}}{T} = \int \frac{nC_p \Delta T}{T} = nC_p \ln \frac{T_f}{T_i}
   \]
3. \( \Delta S \) for an ideal gas that undergoes a reversible change in \( T \) at constant \( P \).

\[
\Delta S = \int \frac{\delta Q_{\text{rev}}}{T} = nC_v \ln \frac{T_f}{T_i}
\]

\( \Delta S = (S_f - S_i) \) for \( V_i T_i \rightarrow V_f T_f \)

\( \Delta S \) for \( V_i T_i \rightarrow V_f T_f = (\Delta S_1 \text{ for } V_i T_i \rightarrow V_i T_i) + \Delta S_2 \text{ for } (V_i T_i \rightarrow V_f T_f) \)

\( \Delta S \) Calculations: phase changes

- For vapor to liquid:

\[
\Delta S_{\text{vapor-liquid}} = \int \frac{\delta Q_{\text{vapor-liquid}}}{T} = \frac{q_{\text{vapor-liquid}}}{T_{\text{vapor-liquid}}} = \frac{\Delta H_{\text{vapor-liquid}}}{T_{\text{vapor-liquid}}}
\]

- For solid to liquid:

\[
\Delta S_{\text{solid-liquid}} = \int \frac{\delta Q_{\text{solid-liquid}}}{T} = \frac{q_{\text{solid-liquid}}}{T_{\text{solid-liquid}}} = \frac{\Delta H_{\text{solid-liquid}}}{T_{\text{solid-liquid}}}
\]
\[ \Delta S = \int \left( \frac{C_p}{T} \right) dT + \int \frac{\beta}{\rho n} dV = C_v \ln \frac{T_f}{T_i} + \beta(V_f - V_i) \]

\[ \Delta S = \int \left( \frac{C_p}{T} \right) dT + \int \frac{\beta}{\rho n} dV = C_v \ln \frac{T_f}{T_i} + \beta(V_f - V_i) \]

For an irreversible process in an isolated system, \( \Delta U = 0 \), \( q = -w \); there is a unique direction of spontaneous change: \( \Delta S > 0 \) for the spontaneous process; \( \Delta S < 0 \) for the opposite or nonspontaneous direction of change.

\[ \Delta S = \int \left( \frac{C_p}{T} \right) dT + \int \frac{\beta}{\rho n} dV = C_v \ln \frac{T_f}{T_i} + \beta(V_f - V_i) \]

\[ \Delta S = \int \left( \frac{C_p}{T} \right) dT + \int \frac{\beta}{\rho n} dV = C_v \ln \frac{T_f}{T_i} + \beta(V_f - V_i) \]

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\[ \Delta S = \int \left( \frac{C_p}{T} \right) dT + \int \frac{\beta}{\rho n} dV = C_v \ln \frac{T_f}{T_i} + \beta(V_f - V_i) \]

A process occurring in an isolated system is spontaneous and the system entropy increases, \( T_f > T_i \)

\[ \Delta S_{rev} = \Delta S_{irrev} \]

\[ \Delta S_{irrev} = \Delta S_{rev} < 0 \]

\[ \Delta S_{irrev} = \Delta S_{rev} > 0 \]

Ideal gas contracting to half its’ volume.

\[ \Delta S = \int \frac{dq}{T} = nR \ln \frac{V_f}{V_i} = -nR \ln 2 < 0 \]

\[ \Delta S_{rev} = \Delta S_{irrev} < 0 \]

Ideal gas expanding to double its’ volume.

\[ \Delta S = \int \frac{dq}{T} = nR \ln \frac{2V_f}{V_i} = nR \ln 2 > 0 \]

\[ \Delta S_{rev} = \Delta S_{irrev} > 0 \]

Irreversible process, spontaneous

A process occurring naturally in an isolated system is by definition spontaneous and results in an entropy increase. Whereas \( U \) can neither be created nor destroyed, \( S \) for an isolated system can be created \( \Delta S > 0 \), but not destroyed \( \Delta S < 0 \).
In a quasi-static reversible process, there is no direction of spontaneous change because the system is proceeding along a path, each step of which corresponds to an equilibrium state.

Ideal gas expanding to double its volume.

Entropy Change of System and Surroundings

For most situations both the system and the surrounding undergo changes during a process/change therefore the criterion for spontaneity should include entropy change in both the system and the surroundings.

The immediate surrounding is a large thermal reservoir at a temperature, say $T$, and in internal equilibrium with heat transfer.

Heat exchanges occur between the system and the surroundings.

If surrounding has a constant volume $q_{\text{surr}} = \Delta U_{\text{surr}}$ and if surrounding has at a constant pressure $q_{\text{surr}} = \Delta H_{\text{surr}}$.

For spontaneity: $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \Delta S_{\text{sys}} > 0$

That is, $\Delta S_{\text{sys}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

Process that occurs in the universe is by definition spontaneous and leads to an increase of $\Delta S_{\text{sys}}$. Therefore $\Delta S_{\text{sys}} > 0$ increases time increases, defining a unique direction of change with time.

Absolute Entropies and the Third Law Thermodynamics:

Matter exist in three different states of aggregation. Common behavior of matter is such that when solid phase temperature is increased to the melts, at constant temperature transitioning into the liquid phase. Further temperature increase further at constant temperature, liquid phase transitions into a gas phase at the boiling point.

At each transition point there will be an absorption of heat (latent heat) with no change of temperature.

The entropy of a pure, perfectly crystalline substance (element or compound) is zero at 0K: $S_m(0) = 0 \text{ kJ/mol-K}$.

The entropy of a pure substance increases with temperature $T$: $S_m(T)$. 
Third Law Thermodynamics: The entropy of a pure substance increases with temperature T, $S_m(T)$.

With relevant values of $C_p$, heats of transitions and transition temperatures one can calculate the molar entropy $S_m(T)$ at any T (and at $P = 1$ atm, conventionally)

$$S_m(T) = S_m(0K) + \sum \frac{\Delta H_{trans}}{T} + \int_{298.15}^{T} \frac{\Delta C_p}{T} dT$$

Oxygen

$C_p$ often vary with temperature.

$$S_p(T) = \frac{\Delta H_{trans}}{T} - \frac{5 \times 10^{-3}}{K} T - 3.9 \times 10^{-4} \frac{T^2}{K^2} + 9.54 \times 10^{-6} \frac{T^3}{K^3}$$

Entropy Changes in Chemical Reactions $\Delta S_R$

The entropy change in a chemical reaction is essential in determining the equilibrium concentration in a reaction mixture.

Calculating $\Delta S_R$ is similar to that of $\Delta H_R$ and $\Delta U_R$ for chemical reactions and is equal to the difference in the entropies of products and reactants.

$$\Delta S_R = \sum_{i} n_i \Delta S_{f_i}$$

Further at an arbitrary temperature, $\Delta S_{RT}$

$$\Delta S_{RT} = \Delta S_{RT,298.15} + \int_{S_{f_i}}^{T} \frac{\Delta C_p}{T} dT$$
Usually large and negative entropy change is mainly because net number of gaseous species from the reaction is negative (more gas molecules consumed in the reaction than generated). Entropy change is large and positive because net number of gaseous species is positive (more gas molecules produced in the reaction than consumed).

**Dependence of S on V and T (s,l,g) – Single Phase:**

\[
dU = TdS - PVdV \quad \Rightarrow \quad dS = \frac{1}{T}dU + \frac{P}{T}dV
\]

Expressing \( U \) as \( f(T,V) \):

\[
dS = \left( \frac{c_v}{c_p} \right)_V dT + \left( \frac{c_p}{c_v} \right)_V dV
\]

Substituting for \( dU \):

\[
dS = \frac{1}{T} \left[ c_v dT \left( \frac{dU}{dV} \right)_T \right] + \frac{P}{T}dV
\]

Expressing \( S \) as \( f(T,V) \):

\[
dS = \left( \frac{c_v}{c_p} \right)_V dT + \left( \frac{c_p}{c_v} \right)_V dV
\]

Because \( dS \) is an exact differential:

\[
\left( \frac{dS}{dT} \right)_V = \left( \frac{c_v}{c_p} \right)_V
\]

Also:

\[
\left( \frac{dS}{dV} \right)_T = \left( \frac{c_p}{c_v} \right)_V
\]

Left:

\[
\left( \frac{dS}{dT} \right)_V - \left( \frac{dS}{dV} \right)_T = \frac{c_v}{c_p} - \frac{c_p}{c_v}
\]

Right:

\[
\left( \frac{dS}{dT} \right)_V - \left( \frac{dS}{dV} \right)_T = \frac{c_v}{c_p} - \frac{c_p}{c_v}
\]
\[
\frac{1}{T} \left( \frac{\partial S}{\partial V} \right)_T - \frac{1}{T} \left( \frac{\partial P}{\partial V} \right)_T = \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_T - \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_P
\]

\[
P + \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{T} \left( p \left( \frac{\partial U}{\partial V} \right)_T \right) - \frac{1}{T} \left( \frac{\partial P}{\partial T} \right)_V.
\]

Again:
\[
\left( \frac{\partial S}{\partial V} \right)_T - \frac{1}{T} \left( \frac{\partial U}{\partial V} \right)_P = P,
\]

\[
\left( \frac{\partial S}{\partial V} \right)_T - \left( \frac{\partial P}{\partial T} \right)_V.
\]

\[
\frac{\partial S}{\partial T}_V = \frac{C_V}{T} \quad \frac{\partial S}{\partial V}_T = \frac{\beta}{\kappa}
\]

dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV

\[
\Delta S = \int_{V_1}^{V_f} \frac{C_V}{T} dT + \int_{V_1}^{V_f} \frac{\beta}{\kappa} dV
\]

Dependence of S on P and T \((s,l,g)\) – Single Phase:

\[
\delta S = \int \left( \frac{\partial S}{\partial T}_V \right)_P dT + \int \left( \frac{\partial S}{\partial V}_T \right)_P dV
\]

\[
\left( \frac{\partial S}{\partial T}_V \right)_P = \frac{C_V}{T} \quad \left( \frac{\partial S}{\partial V}_T \right)_P = \frac{\beta}{\kappa}
\]

dS = \frac{C_V}{T} dT + \frac{\beta}{\kappa} dV

\[
\Delta S = \int_{V_1}^{V_f} \frac{C_V}{T} dT + \int_{V_1}^{V_f} \frac{\beta}{\kappa} dV
\]

\[
\delta S = -1 \text{ cyclic rule}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_V = -1 \quad \left( \frac{\partial V}{\partial P} \right)_T = \frac{1}{\beta}
\]

and definition: isobaric expansion coefficient \( \beta = \frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \)

and definition: isothermal compressibility coefficient \( \kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \)

\[
\left( \frac{\partial S}{\partial T}_V \right)_P - \left( \frac{\partial P}{\partial T} \right)_V - \left( \frac{\partial V}{\partial P} \right)_T = \frac{\beta}{\kappa} - \frac{1}{\beta} \]

\[
\Delta S = \int_{P_1}^{P_f} \frac{C_V}{T} dT + \int_{P_1}^{P_f} \frac{\beta}{\kappa} dV
\]

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