Chapter 8. Spontaneous Processes and Thermodynamic Equilibrium
8.1 The nature of Spontaneous Processes

- A spontaneous change: given enough time, occur by itself without outside intervention, once conditions have been established for its initiation.
- Directionality of spontaneous change
  1. Heat flows from a hot body to a cold one
  2. A gas expanding from a higher pressure region into a lower pressure region
  3. Diffusion of an ink drop
  4. The sucrose dissolves to form a uniform solution
• Hydrogen and oxygen gas to water

• Sodium and chlorine to form sodium chloride

• Corrosion
• The direction of spontaneity of each of these processes is readily apparent from observation of the initial and final states, regardless of their paths.

• This suggests the existence of a new state function that indicates the directionality of spontaneous processes. \( \Rightarrow \) **entropy**: defined so that the sign of its change indicates the direction in which a proposed process will be spontaneous.

• Entropy change both in the system and surrounding should be considered to predict the spontaneity.

• Reaction: redistribution of the energy, volume, and matter between the system and surroundings.

• The thermodynamics universe is fixed.
8.2 Entropy and Spontaneity: A Molecular Statistical Interpretation

Thermodynamics
(macroscopic properties)

+ Microscopic molecular basis

\[ \text{probability theory} \]

Statistical thermodynamics
Spontaneity
Nothing in the laws of mechanics prevents a gas from compressing spontaneously, but the event is so improbable, it is not seen. The directionality of spontaneous change is a consequence of the large numbers of molecules in the macroscopic systems treated by thermodynamics.
Example 8.1

• Calculate the probability of a spontaneous compression of 1.00 mol of gas by 0.01%.
Relation of Entropy to the Number of Microstates

• **Entropy** of a macroscopic system: a measure of the range of possible motions

• The number of microstates, $\Omega$: counts all possible combinations of position and momentum available to the $N$ molecules in the system when the system has energy $E$ and volume $V$. 
Boltzmann Relation

The link between the macroscopic properties (thermodynamics) and the molecular world.
Example 8.2

- Consider the free expansion of one mole of gas from $V/2$ to $V$, illustrated in Figure 8.2. Use Boltzmann’s relation to estimate the change in entropy for this process.

So far, the microstates we have considered have involved only the positions of the molecules in a system. The distribution of energies and of bonding structures can also contribute to the number of microstates.
8.3 Entropy and Heat: Experimental basis of the Second Law of Thermodynamics

• In this section, we define the entropy function in terms of measurable macroscopic quantities so that you can calculate changes in entropy for specific processes.

• The definition is provided by the second law, which is stated as an abstraction and generalization of engineering observations on the efficiency of heat engines.
The Second Law of Thermodynamics

• The efficiency: the ratio of work accomplished by the engine in a cycle to the heat invested to drive that cycle
• Carnot’s conclusion: There is no device that can transfer heat from a colder to a warmer reservoir without net expenditure of work.
• Kelvin’s statement: There is no device that can transform heat withdrawn from a reservoir completely into work with no other effect.
Definition of Entropy
Calculation of $\Delta S = S_f - S_i$ for a specific process

1. Identify its initial and final equilibrium states $i$ and $j$.
2. Select any convenient reversible path between them along which $dq\textsubscript{rev}$ and $T$ are known.
3. Evaluate this integral along the selected path.

- It does not matter that the actual process of interest may be irreversible; because entropy is a state function, its change depends only on the initial and final states, not at all on the path.
- Therefore, we are free to choose any reversible path that connects the initial and final states, purely on grounds of convenience, for calculating $\Delta S$. 
8.5 Entropy Changes and Spontaneity

$\Delta S_{\text{sys}}$ for Isothermal Processes

-Compression/Expansion of an Ideal Gas

-Phase Transitions
Example 8.4

- Calculate the entropy change when 3.00 mol of benzene vaporizes reversibly at its normal boiling point of 80.1°C. The molar enthalpy of vaporization of benzene at this temperature is 30.8 kJ mol\(^{-1}\).

Trouton’s rule: \(\Delta S_{vap} = 88 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}\) for most liquids.
$\Delta S_{sys}$ for Processes with Changing Temperature

-For a reversible *adiabatic* process,

-For a reversible *isochoric* process, the volume is constant.

-For a reversible *isobaric* process, the pressure is constant.

Entropy always increases with increasing temperature.
• Entropy always increases with increasing temperature.

• Microscopic description: From the kinetic theory of gases, increasing the temperature of the gas increases the magnitude of the average kinetic energy per molecule and therefore the range of momentum available to molecules. This in turn increases $\Omega$ for the gas and, Boltzmann’s relation, the entropy of the gas.

• $\Delta S_p > \Delta S_v$
Example 8.5

(a) Calculate the entropy change for the process described in Example 7.9: 5.00 mol of argon expands reversibly at a constant temperature of 298 K from a pressure of 10.0 atm to 1.00 atm.

(b) Calculate the entropy change for the same initial and final states as in part (a) but along a different path. First the 5.00 mol of argon expands reversibly and adiabatically between the same two pressures. This is the path followed in Example 7.10; it causes the temperature to fall to 118.6 K. Then the gas is heated at constant pressure back to 298 K.
$\Delta S$ for Surroundings

$\Delta S_{\text{tot}}$ for System Plus Surroundings

-Spontaneous Cooling of a Hot Body
Example 8.6

A well-insulated ice-water bath at 0.0 °C contains 20 g ice. Throughout this experiment, the bath is maintained at the constant pressure of 1 atm. When a piece of nickel at 100 °C is dropped into the bath, 10.0 g of the ice melts. Calculate the total entropy change for the thermodynamic universe of this process. (Specific heats at constant P: nickel, 0.46 J K$^{-1}$g$^{-1}$; water, 4.18 J K$^{-1}$g$^{-1}$; ice, 2.09 J K$^{-1}$g$^{-1}$; Enthalpy of fusion of ice, 334 J g$^{-1}$.)
-Irreversible Expansion of an Ideal Gas

A reversible process is always more efficient than an irreversible one.

The heat absorbed is a maximum when the process is carried out reversibly.
Example 8.7

• Calculate the heat absorbed and the work done on a system of 5.00 mol of an ideal gas as it expands irreversibly at constant temperature $T = 298 \text{ K}$ from a pressure of 10.0 atm to 1.00 atm. The external pressure is held constant at 1.00 atm.
Inequality of Clausius states that in any spontaneous process the heat absorbed by the system from surroundings at the same temperature is always less than $T\Delta S$. In a reversible process, the heat absorbed is equal to $T\Delta S$.

For spontaneous processes within an *isolated* system,
The thermodynamic universe of a process (that is, a system plus its surroundings) is clearly an isolated system to which Clausius’s inequality can be applied.

1. In a reversible process the total entropy of a system pulse its surroundings is unchanged. ($\Delta S = 0$)
2. In a irreversible process the total entropy of a system pulse its surroundings must increase. ($\Delta S > 0$)
3. A process for which $\Delta S_{\text{total}} < 0$ is impossible.
Example 8.8

- Calculate $\Delta S_{\text{tot}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$ for the reversible and irreversible isothermal expansions of Examples 7.9 and 8.7
8.6 The Third Law of Thermodynamics

- Nernst heat theorem: In any thermodynamic process involving only pure phases in their equilibrium states, the entropy change $\Delta S$ approaches zero as $T$ approaches 0 K.
- Third law of thermodynamics: The entropy of any pure substance (element or compound) in its equilibrium state approaches zero at the absolute zero of temperature.
Standard-State Entropies

• At constant pressure,
Example 8.9

• Using the table of standard molar entropies in Appendix D, calculate \( \Delta S^\circ \) for the chemical reaction

\[
N_2(g) + 2 \text{O}_2(g) \rightarrow 2 \text{NO}_2(g)
\]

with reactants and products at a temperature of 25°C and a pressure of 1 atm.
8.7 The Gibbs Free Energy

\[ \Delta S_{\text{tot}} > 0 \quad \text{spontaneous} \]
\[ \Delta S_{\text{tot}} = 0 \quad \text{reversible} \]
\[ \Delta S_{\text{tot}} < 0 \quad \text{impossible} \]

- This requires calculation of the entropy change for the surroundings as well as the system. It is desirable to have a state function that predicts the feasibility of a process in the system without explicit calculations for the surroundings.
- For the special case of processes at constant temperature and pressure (the most important in Chemistry), such a state function called the Gibbs free energy and denoted by \( G \), exists.
Nature of Spontaneous Processes at Fixed T and P

Spontaneity of the process is determined by the change in Gibbs free energy of the system only, while T and P remain constant.
Development of the Gibbs Free Energy

\[ \Delta G_{\text{sys}} < 0 \quad \text{spontaneous} \]
\[ \Delta G_{\text{sys}} = 0 \quad \text{reversible} \]
\[ \Delta G_{\text{sys}} > 0 \quad \text{impossible} \]
The Gibbs Free Energy and Phase Transition

\[ \text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(s) \]
The Gibbs Free Energy and Chemical Reactions

Standard molar Gibbs free energy
Example 8.10

- Calculate $\Delta G^\circ$ for the following reaction, using tabulated values for $\Delta G_f^\circ$ from Appendix D.

\[ 3 \text{ NO(g)} \rightarrow \text{N}_2\text{O(g)} + \text{NO}_2\text{(g)} \]
Effects of Temperature on $\Delta G$