Chemical Thermodynamics

Spontaneous Processes, Entropy and the Second Law of Thermodynamics

Review Reaction Rates, Energies, and Equilibrium

- Although a reaction may be energetically favorable (i.e. products have lower energy than reactants), reaction rates are largely determined by the magnitude of the activation energy barrier.
  - For example, molecules require a minimum kinetic energy to collide and react.
  - The higher the activation energy barrier, the fewer the molecules in the population with enough energy to overcome the barrier.
- At equilibrium, opposing reaction rates (e.g. forward and reverse reaction rates) are equal in magnitude.
  - Reaction rates are related to the product of an intrinsic rate constant and the concentration of reactant(s).
- If equilibrium is related to reaction rates and reaction rates are related to energy, then equilibrium must be related to energy in some way.
- We have used the magnitude and sign of reaction enthalpies to predict whether a reaction will proceed or not.
  - Reactions with negative enthalpies indicate heat release; the products are lower in energy than the reactants and the reaction will proceed.
  - Reactions with positive enthalpies indicate that heat must be input into the system for the reaction to proceed. The products are higher in energy than the reactants and the reaction will not usually proceed spontaneously.
- However, we have seen that a consideration of reaction enthalpies alone is not enough to predict whether a reaction (or physical process) will proceed.
  - $\text{NH}_4\text{SO}_3(s)$ dissolves in water spontaneously even though the enthalpy of solvation is positive (it absorbs heat and is the basis of instant ice packs).

In addition to enthalpy, we must consider the change in the randomness or disorder that accompanies a reaction or physical process.

**Spontaneous Processes**

The first law of thermodynamics:

- **The Law of Conservation of Energy**
  - Any energy lost by a system must be gained by the surroundings, and vice versa. Energy is neither created nor destroyed by a process (it is only transformed from one form to another).
  - Energy, $E$, can be associated with work, $w$ (i.e. $\text{force} \cdot \text{distance}$, in the displacement of an object) or the transfer of heat, $q$.

$$
\Delta E = q + w
$$

$\Delta E$ = the change in the internal energy of a system
$q$ = heat absorbed by the system from the surroundings
$w$ = the work done on the system by the surroundings

We can keep track of the work done on a system and the heat absorbed or emitted by a system, however, since the overall change in energy for (the system + surroundings) = 0, we cannot use the change in energy of a system to predict whether a reaction will occur.

- If the internal energy of a system is increased, then the energy of the surroundings must decrease, and vice versa.
• When the effects of the energy change of the surroundings are taken into account, the net energy change = 0

Some processes are known to always occur:

• **Highly ordered systems become more disordered**
  - Eggs have a tendency to break, yet I have never seen an intact egg spontaneously reassemble from a pile of egg bits.
  - A pile of leaves in my garden will eventually distribut themselves over my entire lawn. Unfortunately, I have never seen the leaves on my lawn spontaneously assemble into a nice neat pile by themselves.
  - I have seen ocean waves destroy an elaborate sand castle, but have never seen a sand castle spontaneously rise up and form out of the sandy surf.

  These spontaneous processes also have an intrinsic direction, even though there is no apparent net energy change

• By all accounts, in the absence of some outside influence, the above spontaneous processes are irreversible

Although a process may be spontaneous, that does not mean that it will necessarily be fast

• Thermodynamics provides information about the direction a reaction or process will proceed (i.e. which direction of a reaction is spontaneous, but not about how fast it will go)
• Spontaneity of a process depends not only upon the enthalpy change (e.g. exothermic) but also upon how the disorder of the system changes

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**Entropy and the Second Law**
Consider the following two experiments:
1. Behavior of gas in a container

   • I have two glass containers connect by a valve. In the left-hand side container I have a sample of nitrogen gas. In the right-hand side container there is nothing (i.e. a vacuum):

   ![Diagram of gas containers](image)

   • I then open the valve connecting the two containers. What happens?
There is a spontaneous process that involves the flow of gas molecules from the left chamber to fill in the empty right-hand side chamber
  - There was no work performed either on the system or on the surroundings (w = 0)
  - There was no heat input or output from the system to the surroundings (q = 0)
  - The spontaneous reaction results in pressure uniformity
    - Although the gases spontaneously moved from the left chamber to the right, it is highly unlikely (impossible) that the gases might spontaneously move back into the left-hand side chamber (to produce the original condition). Thus, the process appears to be spontaneous and irreversible (in the absence of some outside influence)

2. The behavior of objects of different temperature

I have two cubes of metal. One cube I stick in the oven until it gets red hot. The other I put in the freezer until it gets really cold. Then I put the two blocks next to each other:

Over time what will happen to the temperature of the two blocks?

There is a spontaneous process that involves the flow of heat energy from the hot block to the cold block (the net heat energy is unchanged, however)
  - There was no work performed either on the system or on the surroundings (w = 0)
  - There was no heat input or output from the system to the surroundings (q = 0)
  - The spontaneous reaction results in temperature uniformity
    - Although the heat energy spontaneously moved from the hot block to the cold block, it is highly unlikely (impossible) that heat energy might spontaneously move back into the left-hand side block (to produce the original condition). Thus, the process appears to be spontaneous and irreversible (in the absence of some outside influence)

In both of the above cases, we had a situation where the starting condition was highly ordered (gas on left, vacuum on right; hot block on left, cold block on right)

The final condition was one of uniformity (of pressure or temperature)

The spontaneity of the process appears to be associated with a highly ordered system going to a less-ordered, uniform state

The disorder is expressed by a thermodynamic quantity called entropy (S)
The more disordered a state, the larger its entropy (a large magnitude for $S$ means a lot of disorder)

- Entropy is a state function: $\Delta S = S_{\text{final}} - S_{\text{initial}}$
  - In other words, the pathway you choose to get to $S_{\text{final}}$ is not important, what is important is discussing the change in entropy of a system is a comparison of the initial and final values of the entropy
  - A positive value for $\Delta S$ indicates an increase in disorder. A negative value for $\Delta S$ indicates a decrease in disorder

How is the change in the enthalpy of a system ($\Delta S$) defined?

$$\Delta S = \frac{q_{\text{en}}}{T}$$

(where $T$ is some constant temperature)

- Obviously an enthalpy change is in some way proportional to some kind of energy term. If a system does not do any mechanical work, then heat energy must be involved. (Note: heat, like work, is not an entity but a method of energy transfer)
- If the system is at constant $T$, then the non-mechanical energy flow is not being used to change the temperature (it is associated with the changing order of the system)
- Why is $\Delta S$ inversely proportional to the absolute (K) temperature?
  - At high temperatures what will the system be like? It will be a highly energetic gas and it will be difficult to get much more disorder out of it (thus at high temperatures, the change in disorder ($\Delta S$) will be small for a given amount of non-mechanical energy transfer to the system.
  - At low temperatures the system will be more ordered (highest order is at absolute zero) and the change in disorder ($\Delta S$) will be larger for a given amount of non-mechanical energy transfer to the system

One of the classic examples of entropy changes in response to non-mechanical energy transfer at a constant temperature is the melting of ice at 0°C (i.e. 273K)

- At 0K liquid water is in equilibrium with solid (i.e. ice)
- Non-mechanical energy can be transferred into the system without raising the temperature (this is true as long as there is some ice and water present; if things get to the point where all the ice is melted, then the temperature will raise as you heat the water; if all the liquid water is frozen, then you lower the temperature of the ice as heat is removed; otherwise, the effect of energy flow into and out of the system results in either more or less ice being present, but no temperature change)
- The amount of heat transferred to the system during the fusion of ice is the heat of fusion, $\Delta H_{\text{fus}}$ (6.01kJ/mole). Thus,

$$\Delta S = 6.01\text{kJ/mol} / 273\text{K} = 22 \text{J/mol K}$$

- $\Delta S$ is positive, indicating that the liquid form of water has greater disorder compared to the solid form (ice) (Note: this is an equilibrium situation, not an irreversible spontaneous reaction. Thus, input energy must increase the disorder of the system)

We can also define the entropy change in relationship to expansion of a gas at constant $T$ (i.e. isothermal expansion

$$\Delta S = nR \ln \left( \frac{V_{\text{final}}}{V_{\text{initial}}} \right)$$

(for an ideal gas at some constant $T$)

The Second Law of Thermodynamics
The law that expresses the idea that there is an inherent direction in which processes occur is called the second law of thermodynamics.

We must consider the change in entropy of the system and the surroundings.

- Together, the system and the surroundings constitute the universe.

\[ \Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \]

- For an irreversible (spontaneous) process, we have an increase in entropy. Since it is irreversible, the Universe has gained entropy:

\[ \Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) > 0 \]

- For a reversible process (not spontaneous, but manipulable by heat flow) there is no net \( \Delta S \) as far as the Universe is concerned (i.e. if we input heat energy into the system, then the heat energy of the surroundings decreases):

\[ \Delta S_{\text{universe}} = (\Delta S_{\text{system}} + \Delta S_{\text{surroundings}}) = 0 \]

- Thus, there is no case where \( \Delta S \) of the universe decreases.

\( \Delta S \) universe is constantly increasing (the universe is moving towards greater and greater disorder).

Chemical reactions follow this same law.

- Consider an exothermic reaction that is less disordered when complete (\( \Delta S \) decreases; the disorder decreases):

\[ \text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{g}) \]

- Let's perform this reaction in the following way: We will keep the temperature constant. Since the reaction is exothermic, we do this by having the surroundings absorb the released heat.
  
  - The product is two molecules of water. The reactants comprise three molecules (one of \( \text{O}_2 \) and two of \( \text{H}_2 \)).
  
  - Since temperature is constant, the overall change in entropy of the system (reactants and products) is reduced (products are fewer gas molecules due to atoms being bonded together - this reduces the entropy of the atoms because since they are bonded together they are restricted in their movements).

- The released heat is taken up by the surroundings.
  
  - The surroundings are kept at same temperature.
  
  - Since temperature is constant, the energy absorbed by surroundings is manifest as increased disorder. The surroundings become more disordered.

\[ -q_{sy}/T = +q_{surr}/T \text{ (where } T \text{ is constant)} \]

in other words

the entropy lost by the system = entropy gained by surroundings

- If the entire process were reversible, \( \Delta S \) universe = 0
- If any small part is irreversible, \( \Delta S > 0 \)

Although the reaction results in a decrease in entropy, the net entropic change of the universe is either 0 or positive.
A Molecular Interpretation of Entropy

Many processes can lead to an increase in a system's entropy

- Increasing the volume that a gas can occupy will increase the disorder of a gas
- Dissolving a solute into a solution will increase the entropy of the solute - typically resulting in an increase in the entropy of the system. (Note: the solvation of a solute can sometimes result in a significant decrease in the solvent entropy - leading to a net decrease in entropy of the system)
- Phase changes from solid to liquid, or liquid to gas, lead to an increase in the entropy of the system

Some processes can lead to a decrease in the entropy of a system

- A gas molecule dissolved in a liquid is much more confined by neighboring molecules than when it is in the gaseous state. Thus, the entropy of the gas molecule will decrease when it is dissolved in a liquid
- A phase change from a liquid to a solid (i.e. freezing), or from a gas to a liquid (i.e. condensation) results in an decrease in the disorder of the substance, and a decrease in the entropy
- A chemical reaction between gas molecules that results in a net decrease in the overall number of gas molecules will decrease the disorder of the system, and result in a decrease in the entropy

\[ 2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g) \quad \Delta S < 0 \]

What is the molecular basis for the above observations for the change in entropy?

Let's first consider the last example, the decrease in entropy associated with a decrease in the number of gas molecules for a chemical reaction

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

- The product (NO\(_2\)) involves the formation of a new N-O bond. The O atoms, originally in a separate O\(_2\) molecule, are now connected to the NO molecule via a new N-O bond
  - Since they are now physically bonded to the other molecule (forming a new, larger, single molecule) the O atoms have less freedom to move around
  - The reaction has resulted in a loss of the degrees of freedom of the atoms (O atoms)
  - There is a reduction in the disorder of the system (i.e. due to the reduction in the degrees of freedom, the system is more ordered after the reaction). \( \Delta S < 0 \).

Degrees of Freedom of molecules

Individual molecules have degrees of freedom related to their motions within a substance

- Translational motion. The entire molecule can move in some direction in three dimensions
• **Rotational motion.** The entire molecule can rotate around any axis, (even though it may not actually change its position translationally)

<image>

• **Vibrational motion.** The atoms within a molecule have certain freedom of movement relative to each other; this displacement can be periodic motion like the vibration of a tuning fork

<image>

*These forms of motion are ways in which the molecule can store energy*

• The greater the energy that is stored in these motions, the greater the degrees of freedom, and the greater the entropy

**The Third Law of Thermodynamics**

If we lower the temperature of the system, the thermal energy decreases

• the energy stored in translational, rotational and vibrational motions decreases
  o the entropy of the system decreases

*The Third Law of Thermodynamics: The entropy of a pure crystalline substance at absolute zero (i.e. 0 Kelvin) is 0.*

• S = 0 corresponds to perfect order. The position of the atoms or molecules in the crystal would be perfectly defined
  o As the temperature increases, the entropy of the atoms in the lattice increase
  o Vibrational motions cause the atoms and molecules in the lattice to be less well ordered

Continued heating of a solid lattice

• In a solid lattice, neighboring molecules are constrained to a certain position in the lattice (that's what makes a solid a solid)
• In the liquid state, a molecule is free to move about the entire volume of the liquid
  o Molecules in a liquid have a higher degree of freedom than in a solid
  o The liquid has a higher entropy than a solid
• As we heat a solid, there is a gradual increase in the entropy of the system
  o At the melting point there is a dramatic increase in the entropy of the system as neighboring molecules are free to move past each other
  o After all the solid has melted, the system is in the liquid state
• As we heat the liquid, there is a graduate increase in the entropy
• In the vapor state, a molecule is free to move about the entire container (potentially the entire universe)
Molecules in the vapor state have a higher degree of freedom than in the liquid state. The vapor has a higher entropy than the liquid. At the boiling point there is a dramatic increase in the entropy of the system. After all the liquid has vaporized, the system is in a gaseous state.

- As we heat the gas, there is a gradual increase in the entropy of the system.

In general, the entropy is expected to increase for the following types of processes:

1. The melting of a solid to form a liquid
2. The vaporization of a liquid (or solid) to produce a gas
3. Chemical reactions that involve phase changes of solid → liquid/gas, or liquid → gas
4. Chemical reactions that result in an increase in the number of gaseous molecules
5. Any time the temperature of a substance is increased

Calculation of Entropy Changes

We have seen that the energy given off (or absorbed) by a reaction, and monitored by noting the change in temperature of the surroundings, can be used to determine the enthalpy of a reaction (e.g. by using a calorimeter).

Tragically, there is no comparable easy way to measure the change in entropy for a reaction.

- However, one thing to think about is the following: suppose we know that energy is going into a system (or coming out of it), and yet we do not observe any change in temperature. What is going on in such a situation?
- Changes in internal energy, that are not accompanied by a temperature change, might reflect changes in the entropy of the system.

For example, consider water at 0°C at 1atm pressure

- This is the temperature and pressure condition where liquid and solid phases of water are in equilibrium (also known as the melting point of ice)

\[
H_2O(s) \rightarrow H_2O(l)
\]

- At such a temperature and pressure we have a situation (by definition) where we have some ice and some liquid water
- If a small amount of energy is input into the system the equilibrium will shift slightly to the right (i.e. in favor of the liquid state)
Likewise if a small amount of energy is withdrawn from the system, the equilibrium will shift to the left (more ice)

However, in both of the above situations, the energy change is not accompanied by a change in temperature (the temperature will not change until we no longer have an equilibrium condition; i.e. all the ice has melted or all the liquid has frozen)

Since the quantitative term that relates the amount of heat energy input vs. the rise in temperature is the heat capacity, it would seem that in some way, information about the heat capacity (and how it changes with temperature) would allow us to determine the entropy change in a system

In fact, values for the "standard molar entropy" of a substance have units of J/mol K. The same units for molar heat capacity.

Standard Molar Entropy, $S^0$
The entropy of a substance has an absolute value of 0 entropy at 0K

- **Standard molar entropies** are listed for a reference temperature (like 298K) and 1 atm pressure (i.e. the entropy of a pure substance at 298K and 1 atm pressure). A table of standard molar entropies at 0K would be pretty useless because it would be 0 for every substance (duh!)
- When comparing standard molar entropies for a substance that is either a solid, liquid or gas at 298K and 1 atm pressure, the gas will have more entropy than the liquid, and the liquid will have more entropy than the solid
- Unlike enthalpies of formation, standard molar entropies of elements are not 0.

The entropy change in a chemical reaction is given by the sum of the entropies of the products minus the sum of the entropies of the reactants

- As with other calculations related to balanced equations, the coefficients of each component must be taken into account in the entropy calculation (the $n$ and $m$, terms below are there to indicate that the coefficients must be accounted for)

$$\Delta S^0 = \sum nS^0(\text{products}) - \sum mS^0(\text{reactants})$$

Calculate the change in entropy associated with the Haber process for the production of ammonia from nitrogen and hydrogen gas.
At 298K as a standard temperature:

\[
S^0(\text{NH}_3) = 192.5 \text{ J/mol K} \\
S^0(\text{H}_2) = 130.6 \text{ J/mol K} \\
S^0(\text{N}_2) = 191.5 \text{ J/mol K}
\]

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)
\]

From the balanced equation we can write the equation for $\Delta S^0$ (the change in the standard molar entropy for the reaction):

\[
\Delta S^0 = 2\times S^0(\text{NH}_3) - [S^0(\text{N}_2) + (3\times S^0(\text{H}_2))]
\]

\[
\Delta S^0 = 2\times 192.5 - [191.5 + (3\times 130.6)]
\]

\[
\Delta S^0 = -198.3 \text{ J/mol K}
\]

It would appear that the process results in a decrease in entropy - i.e. a decrease in disorder. This is expected because we are decreasing the number of gas molecules. In other words the \text{N}_2(g) used to float around independently of the \text{H}_2 gas molecules. After the reaction, the two are bonded together and can't float around freely from one another. (I guess you can consider marriage as a negative entropy process)
Gibbs Free Energy

J. Willard Gibbs was the first person to be awarded a Ph.D. in science from an American University (Yale, 1863)

Spontaneous reactions often have:

- A negative enthalpy (release of heat energy, $\Delta H < 0$).
- An increase in entropy (increase in disorder, $\Delta S > 0$)

*The spontaneity of a reaction appears to involve two thermodynamic properties: enthalpy and entropy*

- Furthermore, spontaneous reactions are those that go downhill in energetic terms. In other words, *the final state has a lower energy content than the initial state*

Gibbs came up with an equation, combining both enthalpy and entropy contributions, that provided a means to describe energy content and therefore a means to evaluate the spontaneity of a reaction when that energy content changes. The energy contents of a substance was termed the *Gibbs Free Energy* and it was defined by the *Gibbs Free Energy equation:*

$$G = H - T*S$$

*The free energy of a substance = stored heat energy - inherent disorder at a reference temperature*  
H is enthalpy, S is entropy and T is the temperature in Kelvin

- If there is a lot of stored heat energy, then the substance has a lot of free energy  
- The more disorder a substance has, the less free energy it has

Changes in a substance (as in a chemical reaction or physical phase change):  
$$\Delta G = \Delta H - T*\Delta S$$

- If the substance releases heat energy, then the product has a lower value of stored heat energy and $\Delta H < 0$. Such a change is downhill energetically (i.e. spontaneous)  
- If the disorder (entropy) increases, this is also a spontaneous process and $\Delta S > 0$. Since $\Delta S > 0$ this means that $(-T*\Delta S < 0$).
- Therefore, *both the enthalpic ($\Delta H$) and entropic (-T$\Delta S$) terms are negative* for processes that are spontaneous.

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How to quantitate the contribution of the entropic term to the free energy?

In "instant ice packs" a reaction occurs that is spontaneous, and yet is endothermic (i.e. it is "cold" due to absorption of heat energy). The absorption of heat energy is unfavorable and therefore must be "driven" by an increase in entropy (i.e. a large -T$\Delta S$ term).

*Therefore, the degree to which heat can be spontaneously absorbed is actually providing us with information regarding the magnitude of the entropic increase* (i.e. the entropic increase is what is "driving" the unfavorable heat absorption).

- Recall that entropy was defined previously as $q/T$ (i.e. non-mechanical energy transferred at a constant temperature). This definition is just a way of saying that if heat is absorbed but the temperature does not change, then the heat energy is being sucked in due to an entropic increase - and that entropic increases is energetically equal to the heat energy absorbed
- In such a case $\Delta S$ is positive, entropy increases, and (-T$\Delta S$) is negative (favoring spontaneous reaction)
• Heat absorbed at a fixed temperature is essentially an infinite heat capacity, and this is just to point out that entropy has units of J/mol K, like heat capacity values. A material with a high heat capacity has the ability to absorb a lot of heat energy with a small temperature change. It can do this because it is able to increase its internal disorder and "soak" up the heat energy and thus the temperature won't rise much. If a material cannot increase its internal disorder, then it will increase temperature in response to even a small amount of added heat energy.

For a process occurring at constant temperature, T:

• If \( \Delta G = 0 \), it means that the enthalpy change associated with a reaction is equal in magnitude (and opposite in sign) to the entropy change. For example, the process being considered may result in a reduction in entropy (i.e. more order) but it releases an amount of heat energy that exactly counteracts the effects of the \( T \Delta S \) term. Such a reaction is in equilibrium (i.e. no net reaction)
• If \( \Delta G < 0 \). This would occur for not only an exothermic reaction (\( \Delta H = \) negative) that overwhelms any unfavorable entropic effect. But potentially also for an endothermic process that has a significant increase in disorder (i.e. \( \Delta S \) is large, and thus, \( T \Delta S \) is large and negative). In either case, the process being considered has a net driving force (release of energy or increase in entropy) that indicates the reaction is spontaneous
• If \( \Delta G > 0 \). This will happen if the reaction is highly endothermic (\( \Delta H \) positive) and the entropic term is not so great. Or, if the reaction is exothermic (i.e. \( \Delta H \) is negative), but the process results in significant increase in order (i.e. the \( T \Delta S \) term ends up being a negative number, so that \(-T \Delta S\) is positive in magnitude). In any case, this is energetically an unfavorable process being considered. To move in the forward direction, energy must be supplied. If energy is not supplied, then the reaction will proceed spontaneously in the reverse direction.

Free energy and chemical reactions at equilibrium.
It would seem there are 4 possible types of reactions or processes with regard to the enthalpic and entropic contribution to the free energy change:

1. \( \Delta H = (-), -T \Delta S = (-) \). Favorable enthalpic change (exothermic) and favorable entropic change (disorder increases)
2. \( \Delta H = (+), -T \Delta S = (+) \). Unfavorable enthalpic change (endothermic) and unfavorable entropic change (disorder decreases)
3. \( \Delta H = (-), -T \Delta S = (+) \). Favorable enthalpic change (exothermic) and unfavorable entropic change (disorder decreases)
4. \( \Delta H = (+), -T \Delta S = (-) \). Unfavorable enthalpic change (endothermic) and favorable entropic change (disorder increases)

If you look at these four types of energy changes, you will notice that 1) and 2) are considering the same process, just from different directions. Likewise, with 3) and 4) (i.e. an exothermic process in one direction is endothermic in the opposite direction). So, in principle, we just have to understand two types of processes.

• For type 1) above, both enthalpy and entropy favor the forward direction. There would appear to be no energetic term favoring the reverse direction. Thus, this type of process would be expected to go to completion (i.e. no equilibrium condition because no reverse reaction occurs). Type 2) is the same situation, but viewed from the opposite direction.
• For type 3) above, enthalpy favors the forward direction but the energy associated with the entropic change favors the reverse direction. There are, therefore, energetic forces driving the process in opposite directions, and it would seem likely that an equilibrium condition might exist. Type 4) is the same situation, but viewed from the opposite direction.

Consider our old friend, the Haber reaction:
If we start with nothing but NH\(_3\) (g) in the sample, the reaction will proceed in the reverse direction to produce H\(_2\) (g) and N\(_2\) (g) (i.e. \(\Delta G\) for the reaction will be a positive value)

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)
\]

Or, \(\Delta G\) is negative for the following reaction (i.e. the following reaction is spontaneous):

\[
2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g)
\]

If we start with nothing but H\(_2\) (g) and N\(_2\) (g) in the sample, the reaction will proceed in the forward direction to produce NH\(_3\) (g) (i.e. \(\Delta G\) for the reaction will be a negative value)

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)
\]

If we start with concentrations of all components such that \(Q = K_c\), then the reaction is at equilibrium and \(\Delta G = 0\).

The reaction wants to be driven in a direction such that \(\Delta G\) goes to 0 (i.e. equilibrium) At equilibrium the free energy of the system is at a minimum. To produce either more product, or more reactants, requires an increase in free energy (i.e. some modification of heat or entropy properties)

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) + \Delta(\text{heat})
\]

**Standard Free-Energy Changes**

The free-energy term, \(G\), is a state function, thus values can be defined for substances at specific conditions of temperature and pressure known as the standard state. In this case, we will have \(\Delta G\) values associated with the formation of compounds from their elemental constituents, known as the standard free energy of formation, \(\Delta G_f^0\).

Standard conditions include:

- 1 atm pressure
- 1M concentration (solutions)
- Pure solid (if a solid) or pure liquid (if a liquid)
- For elements, the standard free energy of formation, \(\Delta G_f^0\) of an element in its normal state is 0
- There is no standard state for temperature. \(G\) will vary with temperature. 298K (i.e. 25°C) is a common temperature chosen for standard reference values of \(G\)

Standard free-energy values can be used to calculate the standard free energy change associated with a reaction:
\[ \Delta G^0 = \sum n \Delta G_i^0(\text{products}) - \sum m \Delta G_j^0(\text{reactants}) \]

What information will the calculation of \( \Delta G^0 \) provide?

- \( \Delta G^0 < 0 \), the reaction is spontaneous as written (i.e. goes to the right)
- \( \Delta G^0 > 0 \), the reaction will proceed to the left as written
- \( \Delta G^0 = 0 \), the reaction is at equilibrium

**Free Energy and Temperature**

**Free Energy and the Equilibrium Constant**

How is the change in free energy (i.e. \( \Delta G \)) as we go from state 1 to state 2 (or reactants to products) affected by temperature?

\[ \Delta G = \Delta H - T \Delta S \]

**The enthalpic term, \( \Delta H \)\**

*Exothermic* reactions release heat to the surroundings and have a negative value for \( \Delta H \)

- If there were no entropic considerations, all exothermic reactions would result in negative values of \( \Delta G \), and would define spontaneous reactions

**The entropic contribution, \( -T \Delta S \)\**

The value of \( \Delta S \) (the entropic change) may be either positive (products have a greater degree of disorder than reactants) or negative (products have a lesser degree of disorder than reactants)

- For those reactions where \( \Delta S \) is positive, the \( -T \Delta S \) term will be negative. This will contribute to the overall negative value (i.e. spontaneity) of \( \Delta G \)
- For those reactions where \( \Delta S \) is negative, the \( -T \Delta S \) term will be positive. This decrease in entropy will oppose spontaneity. This will reduce the magnitude of a negative value of \( \Delta G \) and may even cause \( \Delta G \) to be positive (indicating a non-spontaneous process)

What is the effect of temperature on \( \Delta H \) and \( \Delta S \) values, and \( \Delta G \)?

- Generally, \( \Delta H \) and \( \Delta S \) values do not change much with temperature
- Although the \( \Delta S \) term may not change much with temperature, the magnitude of the \( -T \Delta S \) term is obviously dependent upon the value of \( T \) (temperature). For an equivalent change in disorder, greater energy is absorbed at higher temperatures.

*The greater the temperature, the greater the magnitude of the \( -T \Delta S \) term*

If \( \Delta S \) is negative (i.e. unfavorable entropy change), the value of the \( -T \Delta S \) term is positive, and increasing the temperature will increase the magnitude of the positive value of the \( -T \Delta S \) term
• **At some high temperature**, the magnitude of the (positive) \(-T\Delta S\) term can *overwhelm the magnitude of an exothermic* (i.e. negative) \(\Delta H\) term. And even though the reaction is exothermic it *will not occur spontaneously* (i.e. \(\Delta G = \text{positive in value}\))

The opposite type of situation may occur: a reaction may be endothermic (\(\Delta H\) is *positive*), and have a *positive* value for \(\Delta S\)

• With a positive value for \(\Delta S\), the \(-T\Delta S\) term favors spontaneity. However, at low temperatures, its contribution will be small (magnitude of \(-T\Delta S\) at low temperatures is small). In this case \(\Delta H\) predominates and the reaction will be non-spontaneous \((\Delta G = \text{positive})\)

• **At higher temperatures**, the magnitude of the \(-T\Delta S\) term increases and *can overwhelm the (positive) \(\Delta H\) term*. In this case the \(-T\Delta S\) predominates and the reaction is spontaneous \((\Delta G = \text{negative at high temp})\)
Summary:

<table>
<thead>
<tr>
<th>ΔH</th>
<th>ΔS</th>
<th>-TΔS</th>
<th>ΔG</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(exothermic)</td>
<td>(products more disordered)</td>
<td>(favors spontaneity)</td>
<td>(spontaneous at all T)</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>(exothermic)</td>
<td>(products less disordered)</td>
<td>(opposes spontaneity)</td>
<td>(spontaneous at low T) + (non-spontaneous) at high T</td>
</tr>
<tr>
<td>&quot;Enthalpically-driven process&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
</tr>
<tr>
<td>(endothermic)</td>
<td>(products more disordered)</td>
<td>(favors spontaneity)</td>
<td>(non-spontaneous at low T) - (spontaneous) at high T</td>
</tr>
<tr>
<td>&quot;Entropically-driven process&quot;</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+</td>
<td>-</td>
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<td>+</td>
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<tr>
<td>(endothermic)</td>
<td>(products less disordered)</td>
<td>(opposes spontaneity)</td>
<td>(non-spontaneous at all T)</td>
</tr>
</tbody>
</table>
Consider the following possible states for two different types of molecules with some attractive force:

- There would appear to be greater entropy on the left (state 1) than on the right (state 2). Thus the entropic change for the reaction as written (i.e. going to the right) would be (-) in magnitude, and the energetic contribution to the free energy change would be (+) (i.e. unfavorable) for the reaction as written.
- In going to the right, there is an attractive force and the molecules adjacent to each other is a lower energy state (heat energy, q, is liberated). To go to the left, we have to overcome this attractive force (input heat energy) and the left direction is unfavorable with regard to heat energy q. The change in enthalpy is (-) in going to the right (q released), and this enthalpy change is negative (-) in going to the right (and (+) in going to the left).
- This reaction as written, is therefore, enthalpically favorable, and entropically unfavorable. It is **enthalpically driven**.
- From the above table, it would appear that we might be able to get the reaction to go to the right at low temperatures (low temperature would minimize the energetic contribution of the entropic change).

Looking at the same process from an opposite direction:

- This reaction as written, is entropically favorable, and enthalpically unfavorable. It is **entropically driven**.
- From the above table, it would appear that we might be able to get the reaction to go to the right at high temperatures (high temperature would increase the energetic contribution of the entropic change).

**Free Energy and the Equilibrium Constant**

Recall that standard free-energy of formation values from tables can be used to calculate the standard free energy change associated with a reaction:

$$ \Delta G^0 = \sum n \Delta G_f^0(\text{products}) - \sum m \Delta G_f^0(\text{reactants}) $$

- These tabulated $\Delta G_f^0$ values are for standard conditions and a defined temperature
- Often we are interested in the value of $\Delta G^0$ for a reaction that is not under standard conditions (e.g. other concentrations than standard conditions of 1 atm for a gas, or 1M for a solution)
The general relationship between the free-energy change under standard conditions (i.e. \( \Delta G^0 \)) and the free-energy change under any other conditions, (i.e. \( \Delta G \)), is defined as:

\[
\Delta G (\text{e.g. under non-standard conditions of conc.}) = \Delta G^0 + RT \ln Q
\]

- \( R \) is the gas constant, 8.314 J/mol K
- \( T \) is absolute temperature (K)
- \( Q \) is the calculated reaction quotient

\( Q \) reflects the ratios of the various components under starting conditions. \( K \) reflects their ratios at equilibrium.

- If the starting system is at equilibrium, then \( Q = K \)
- At equilibrium \( \Delta G = 0 \) (no spontaneous reaction in either direction)

Therefore:

\[
\Delta G = \Delta G^0 + RT \ln Q
\]

at \textit{equilibrium} becomes

\[
\Delta G = \Delta G^0 + RT \ln K
\]

and

\[
0 = \Delta G^0 + RT \ln K
\]

or

\[
\Delta G^0 = -RT \ln K
\]

- If \( K > 1 \) it means the equilibrium favors the products (i.e. spontaneity to the right). In this case \( \ln K \) will be \textit{positive} and therefore \( \Delta G^0 \) will be negative (again spontaneity to the right)
- If \( K < 1 \) it means the equilibrium favors the reactants (i.e. spontaneity to the left). In this case \( \ln K \) will be negative and therefore \( \Delta G^0 \) will be positive
- If \( K = 1 \), \( \ln K \) will be zero and so will \( \Delta G^0 \). The reaction is at equilibrium

The above equation also allows us to calculate \( K \) if we know \( \Delta G^0 \):

\[
K = e^{-\Delta G^0 / RT}
\]