

Entropy

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1 Introduction

Entropy is the amount of disorder in a system/surrounding. If a system has a high entropy, there is a lot of disorder. If a system has a low entropy, there is less disorder, meaning that there is more order.

2 Theory

The concept of entropy is based around the second law of thermodynamics:

For a process to be spontaneous, the amount of entropy in the universe must increase. It is the conversion of ordered motion and energy to disordered motion and energy.

S represents the amount of entropy, and the amount of it in the universe increases. The units of entropy, S are $\text{Jmol}^{-1}\text{K}^{-1}$.

In nature, systems and surroundings will move spontaneously from order to disorder. This is because there are many more ways to reach a disordered state than an ordered state, therefore the probability of this occurring becomes very large. For example, a diatomic molecule such as H_2 will have two quanta (limited set amounts) of vibrational energy.

Energy Level	H_1	H_2
5e		
4e		
3e		
2e	•	•
1e		

If energy is transferred from H_1 to H_2 , such that H_1 will have an energy level of 1e and that H_2 will have an energy level of 3e, we can say that this system will have a total of 5 combinations of each particle having different energy levels that add up to a total of 4e. Increasing amounts of possible energy levels (increasing heat) and increasing amount of particles increases the amount of possible combinations. The larger the amount of combinations, the higher the disorder. Put simply, \uparrow Heat, and \uparrow No. of particles will result in $\uparrow S$. This poly-atomic molecule disorder can be calculated using the following equation:

$$W = \frac{(N + q - 1)!}{q!(N - 1)!} \quad (1)$$

Where W is the number of combinations, N is the number of atoms, and q is the number of quanta of energy that can be calculated with the following simple equation:

$$q = q_1 + q_2 + q_3 \dots \quad (2)$$

It is important to note that the lowest vibrational energy is $1e$ (zero point energy) , not $0e$, as particles at $0K$ violate Heisenberg's uncertainty principle. In all chemical reactions there are entropy changes, both in the reaction system, as well as the surrounding system. From this we can say that the total entropy change is:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \quad (3)$$

For example, the chemical equation below:



This is a reaction that has a negative value for ΔS_{system} , however, this reaction produces heat, so the value of $\Delta S_{\text{surroundings}}$ is positive to a degree that ΔS_{total} is positive. $\Delta S_{\text{surroundings}}$ is calculated by how much it changes the temperature of the surroundings during the reaction. It can be calculated using the following equation:

$$\Delta S_{\text{surroundings}} = -\frac{\Delta H}{T} \quad (4)$$

Where ΔH is the enthalpy change of the reaction and T is the temperature of the surroundings in Kelvin. Using these two equations, we can calculate the equation for the Gibb's Free Energy, which is an equation that can determine the spontaneity of a reaction at a certain temperature. Substituting equation (4) into equation (3), we get the following equation:

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \frac{\Delta H}{T} \quad (5)$$

Multiplying the entire expression by T , we get:

$$T\Delta S_{\text{total}} = T\Delta S_{\text{system}} - \Delta H \quad (6)$$

Multiplying the entire expression by -1 , we get:

$$-T\Delta S_{\text{total}} = \Delta H - T\Delta S_{\text{system}} \quad (7)$$

And since the Gibb's free energy is described as such:

$$\Delta G = -T\Delta S_{\text{total}} \quad (8)$$

We can substitute equation (8) into equation (7) to get:

$$\Delta G = \Delta H - T\Delta S_{\text{system}} \quad (9)$$

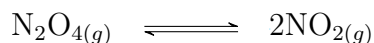
Which is the Gibb's free energy equation. If (ΔG) is negative, the reaction is spontaneous. However, even if a reaction is spontaneous, it might not take place since the kinetics of the reaction may be too slow. From this we can make a table on the spontaneity of a reaction based on the positivity of ΔS_{system} and ΔH :

Positivity	$\Delta H = -\text{ve}$	$\Delta H = +\text{ve}$
$\Delta S = -\text{ve}$	Spontaneous at low temperatures	ΔG positive at all temperatures, process never spontaneous
$\Delta S = +\text{ve}$	ΔG negative at all temperatures, process always spontaneous	Spontaneous at high temperatures

It is also possible to calculate the value of ΔS_{system} from the standard values of entropy found in most chemical data books using the following equation:

$$\Delta S_{\text{system}} = \sum S_{\text{products}} - \sum S_{\text{reactants}} \quad (10)$$

This equation can be used for calculating precise value for ΔS_{system} , however there are good ways to predict the positivity of ΔS_{system} by considering the number of molecules formed from the reactants, as well as the phases of all the molecules in the reaction. For example:



The chemical equation shown above shows a reaction in which the forward reaction doubles the amount of particles, while the reverse reaction halves the amount of particles. It is more likely for the forward reaction to take place since the forward reaction produces more particles, and there are more possible configurations for those particles to be in with larger amounts of particles, as seen in equation (1). The forward reaction therefore increases the amount of entropy in the system, and the reverse reaction decreases the amount of entropy in the system.



In the above reaction, where ice melts to water (the forward reaction), entropy increases since the energy of the particles has increased, creating more ways for the particles to be arranged at different energy levels.

In reversible reactions, when the mixture reaches equilibrium, we say that the forward reaction is going at the same rate as the reverse reaction, meaning the mixture is in a dynamic equilibrium. This therefore means that the forward and backward reactions must both be spontaneous, meaning that ΔS_{total} must be positive in both cases. The only way the forward and backward reaction can both be spontaneous, and not break the second law of thermodynamics, is if the value of ΔS_{total} for both reactions is 0. This makes intuitive sense since there cannot be an actual increase in the amount of entropy if the amounts of all the molecules remain constant and the temperature remains constant. Therefore, we can conclude that when a system is in dynamic equilibrium:

$$\Delta S_{\text{total}}[\text{forward reaction}] = \Delta S_{\text{total}}[\text{backward reaction}] = 0 \quad (11)$$

The spontaneous direction of change in a reversible reaction is determined by its total entropy change. The direction and extent of a change in a reversible reaction is determined by the equilibrium constant for that change. The connection between these two statements can be expressed like so:

$$\Delta S_{\text{total}} = R \ln K \quad (12)$$

Where K can be K_c or K_p , and where R is the gas constant. The following table shows rough guidelines to the extent of the reaction which can be determined by the different values of ΔS_{total} :

$\Delta S_{\text{total}}/\text{Jmol}^{-1}\text{K}^{-1}$	Extent of Reaction
+40 to -40	Mixture of reactants and products
>+200	Reaction is complete, and all the reactants turned to products
<-200	No evidence of products and the reaction does not take place

It is important to note that for exothermic reactions, an increase in temperature decreases the value of ΔS_{total} since it reduces the positivity of the $\Delta S_{\text{surroundings}}$ term due to the division by a larger number. An increase in temperature does not significantly affect the value of ΔS_{system} . This means that an increase in temperature decreases the spontaneity of the reaction, but it will not make it negative.