

Chemistry 331

Lecture 14

Entropy and the Second Law

NC State University

Spontaneity of Chemical Reactions

One might be tempted based on the results of thermochemistry to predict that all exothermic reactions would be spontaneous. The corollary this would be the statement that no endothermic reactions are spontaneous. However, this is not the case. There are numerous examples of endothermic reactions that are spontaneous. Of course, heat must be taken up from the surroundings in order for such processes to occur. Nonetheless, the enthalpy of the reaction does not determine whether or not the reaction will occur, only how much heat will be required or generated by the reaction. The observation that gases expand to fill a vacuum and that different substances spontaneously mix when introduced into the same vessel are further examples that require quantitative explanation.

Spontaneity of Chemical Reactions

As you might guess by now, we are going to define a new state function that will explain all of these observations and define the direction of spontaneous processes.

This state function is the entropy.

Entropy is related to heat and heat flow and yet heat is not a state function. Recall that q is a path function. It turns out that the state function needed to describe spontaneous change is the heat divided by the temperature.

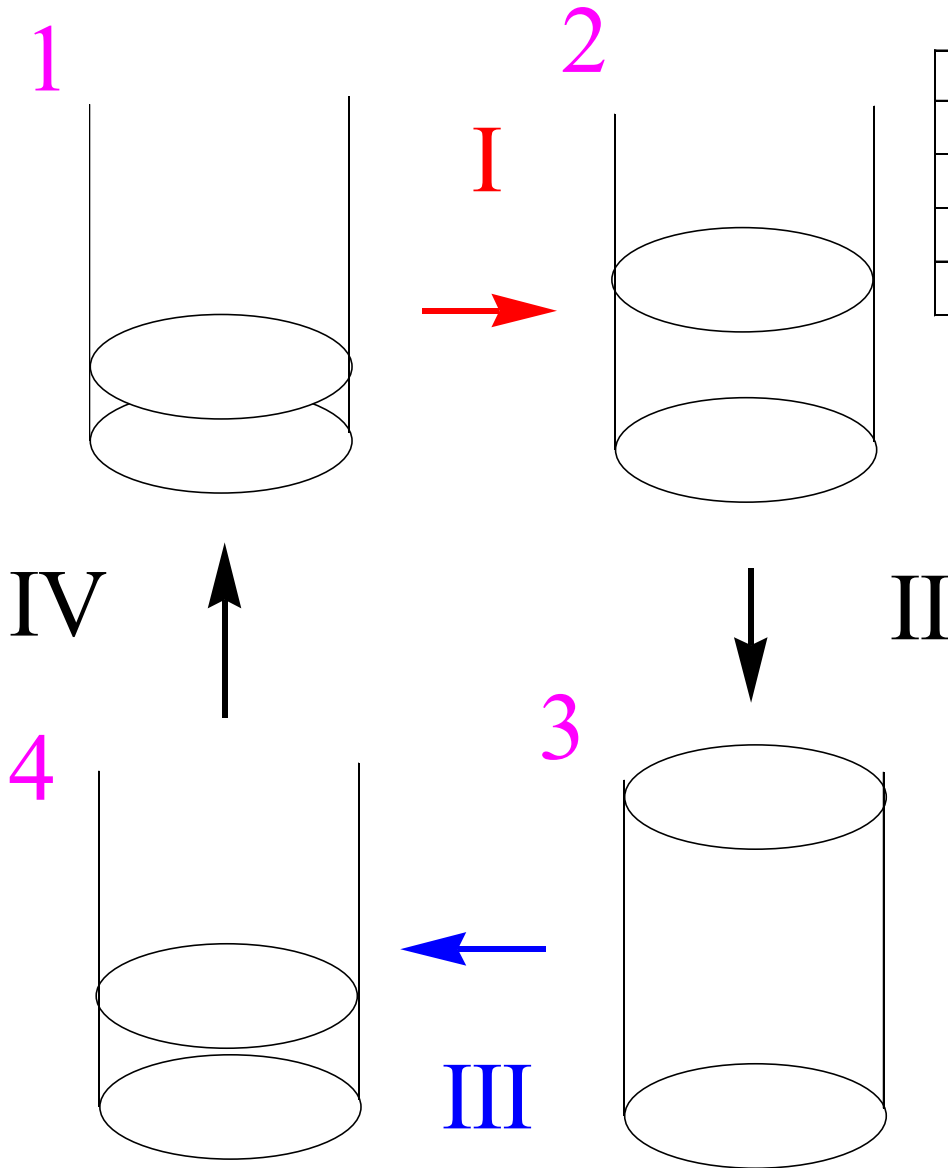
Here we simply state this result.

$$\Delta S = \frac{q_{rev}}{T}$$

Engines

Historically, people were interested in understanding the efficiency with which heat is converted into work. This was a very important question at the dawn of the industrial revolution since it was easy to conceive of an engine powered by steam, but it turned out to be quite difficult to build one that was efficient enough to get anything done! In an engine, there is a cycle in which fuel is burned to heat gas inside the piston. The expansion of the piston leads to cooling and work. Compression readies the piston for the next cycle. A state function should have zero net change for the cycle. It is only the state that matters to such a function, not the path required to get there. Heat is a path function. As we all know in an internal combustion engine (or a steam engine), there is a net release of heat. Therefore, we all understand that $\delta q \neq 0$ for the cycle.

A cyclic heat engine



Phase	Transition	Path	Condition
I.	1→2	Isothermal	$w = -q$
II.	2→3	Adiabatic	$\Delta U = w$
III.	3→4	Isothermal	$w = -q$
IV.	4→1	Adiabatic	$\Delta U = w$

The work is

$$w = w_I + w_{II} + w_{III} + w_{IV}$$

$$q = q_I + q_{III}$$

$$= -w_I - w_{III}$$

For the adiabatic steps

$$q_{II} = q_{IV} = 0$$

For the isothermal steps

$$\Delta U = 0$$

Work and Heat for the Cycle

Neither the work nor the heat is a state function. Neither one is zero for the cycle as should be the case for a state function.

The work is:

$$\begin{aligned}w &= w_I + w_{II} + w_{III} + w_{IV} \\&= -nRT_{\text{hot}} \ln(V_2/V_1) - C_v(T_{\text{cold}} - T_{\text{hot}}) - nRT_{\text{cold}} \ln(V_4/V_3) - C_v(T_{\text{hot}} - T_{\text{cold}}) \\w &= -nRT_{\text{hot}} \ln(V_2/V_1) - nRT_{\text{cold}} \ln(V_4/V_3) \text{ [since } w_{II} = -w_{IV}\text{]} \\w &= -nRT_{\text{hot}} \ln(V_2/V_1) - nRT_{\text{cold}} \ln(V_1/V_2) \text{ [since } V_4/V_3 = V_1/V_2\text{]} \\w &= -nRT_{\text{hot}} \ln(V_2/V_1) + nRT_{\text{cold}} \ln(V_2/V_1) \text{ [property of logarithms]}\end{aligned}$$

The heat is:

$$\begin{aligned}q &= q_I + q_{III} \text{ [since } \delta w_{II} = \delta w_{IV} = 0\text{]} \\&= -w_I - w_{III} \text{ [since } dU = 0 \text{ for isothermal steps]} \\q &= nRT_{\text{hot}} \ln(V_2/V_1) + nRT_{\text{cold}} \ln(V_4/V_3) \\q &= nRT_{\text{hot}} \ln(V_2/V_1) + nRT_{\text{cold}} \ln(V_1/V_2) \text{ [since } V_4/V_3 = V_1/V_2\text{]} \\q &= nRT_{\text{hot}} \ln(V_2/V_1) - nRT_{\text{cold}} \ln(V_2/V_1) \text{ [property of logarithms]}\end{aligned}$$

A new state function: Entropy

The heat is not a state function. The sum $q_I + q_{III}$ is not zero. From this point on we will make the following definitions:

$$q_I = q_{hot} \quad q_{III} = q_{cold}$$

$$q = q_{hot} + q_{cold} = nRT_{hot} \ln \left(\frac{V_2}{V_1} \right) - nRT_{cold} \ln \left(\frac{V_2}{V_1} \right) \neq 0$$

$$\frac{q_{rev}}{T} = \frac{q_{hot}}{T_{hot}} + \frac{q_{cold}}{T_{cold}} = nR \ln \left(\frac{V_2}{V_1} \right) - nR \ln \left(\frac{V_2}{V_1} \right) = 0$$

However, the heat divided by temperature is a state function. This reasoning leads to the idea of a state function called the entropy. We can write:

$$\Delta S = \frac{q_{rev}}{T}$$

Thermodynamics of an Engine

The cycle just described could be the cycle for a piston in a steam engine or in an internal combustion engine. The hot gas that expands following combustion of a small quantity of fossil fuel drives the cycle. If you think about the fact that the piston is connected to the crankshaft you will realize that the external pressure on the piston is changing as a function of time and is helping to realize an expansion that as close to an ideal reversible expansion as the designers can get. If we ignore friction and assume that the expansion is perfectly reversible we can apply the above reasoning to your car. The formalism above for the entropy can be used to tell us the thermodynamic efficiency of the engine.

Thermodynamic Efficiency

We define the efficiency as the work extracted divided by the total heat input.

$$\text{efficiency} = \frac{\text{work done}}{\text{heat used}}$$

$$\eta = \frac{|w_{total}|}{q_{hot}} = \frac{|nR(T_{cold} - T_{hot})\ln(V_2 / V_1)|}{nRT_{hot}\ln(V_2 / V_1)} = \frac{T_{hot} - T_{cold}}{T_{hot}}$$

The efficiency defined here is the ideal best case. It assumes a reversible process with no losses due to friction. The temperature T_{hot} is the temperature of the expansion in the engine. The temperature T_{cold} is the temperature of the exhaust. T_{cold} cannot be less than the temperature of the surroundings.

Question

Your car has an operating temperature of 400 K. If the ambient temperature is 300 K, what is the thermodynamic efficiency of the the engine?

- A. 75%
- B. 50%
- C. 25%
- D. 5%

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$$\eta = \frac{|w_{total}|}{q_{hot}} = \frac{T_{hot} - T_{cold}}{T_{hot}} = 1 - \frac{T_{cold}}{T_{hot}} = 1 - \frac{300K}{400K} = 0.25$$

Question

The thermodynamic cycle was derived for reversible expansions. What are the consequences if the cycle is not perfectly reversible?

- A. The work of expansion will decrease
- B. The work of compression will decrease
- C. There will be no adiabatic expansion
- D. There can be no cycle

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The Thermodynamic Temperature Scale

The definition of entropy is $q_{\text{hot}}/T_{\text{hot}} + q_{\text{cold}}/T_{\text{cold}} = 0$.

We can write this as

$$q_{\text{hot}}/T_{\text{hot}} = -q_{\text{cold}}/T_{\text{cold}}$$

Since q_{cold} is negative we can combine the minus sign with q_{cold} and write the expression as

$$|q_{\text{hot}}|/T_{\text{hot}} = |q_{\text{cold}}|/T_{\text{cold}}$$

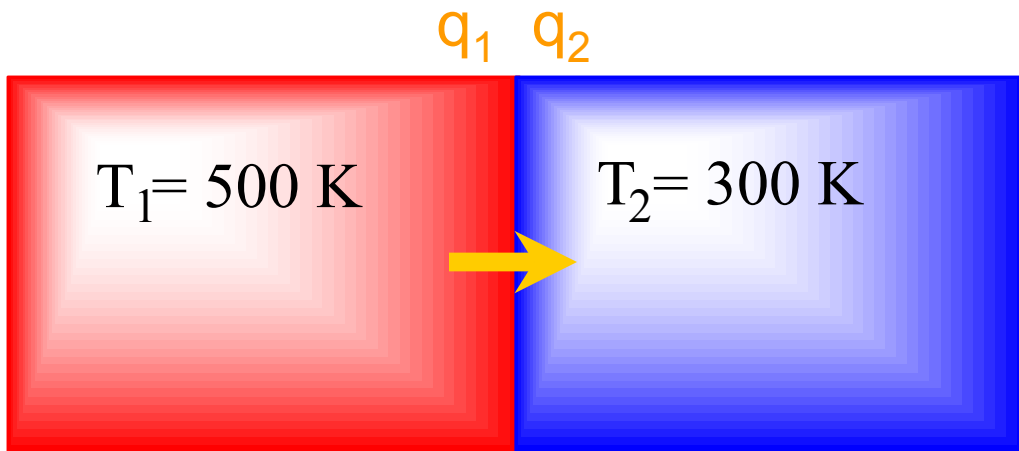
and finally

$$|q_{\text{hot}}|/|q_{\text{cold}}| = T_{\text{hot}}/T_{\text{cold}}$$

The ratio of the heats is equal to the ratio of temperatures for two steps in a thermodynamic cycle. This defines a temperature scale and allows one to measure temperature as well (i.e. this scheme represents a thermometer). Both this expression and the thermodynamic efficiency further imply that there is an absolute zero of temperature.

Heat Transfer

To examine the function that we have just defined, let us imagine that we place two identical metal bricks in contact with one another. If one of the bricks is at equilibrium at 300 K and the other at 500 K, what will the new equilibrium temperature be? Intuitively, you would say 400 K and you would imagine that heat flows spontaneously from the warmer brick to the colder brick. The entropy function makes these ideas quantitative.



$$\Delta S = \frac{q_2}{T_2} + \frac{q_1}{T_1}$$

Using this definition of entropy change as the heat flow divided by the temperature.

Heat Transfer

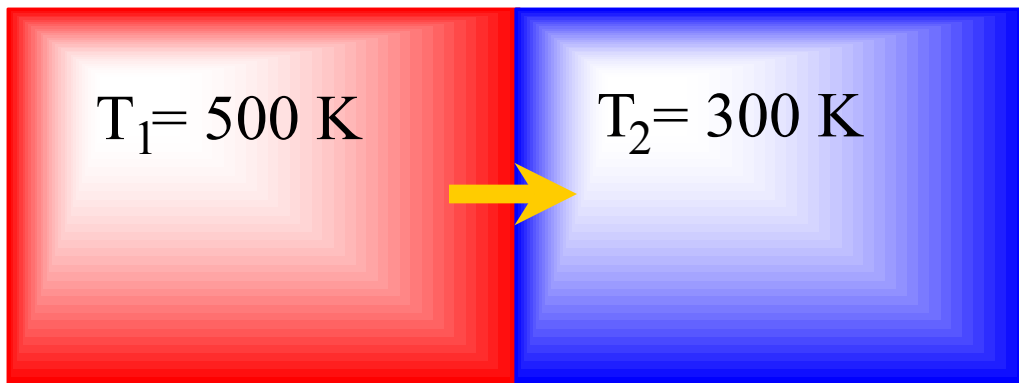
Let's assume that heat flows from the hot body to the cold body. Then q_1 is negative (the flow from the hot body) and q_2 is positive (the flow into the cold body). Moreover,

$$q_2 = -q_1 = q$$

This means that we can substitute in q to obtain:

$$\Delta S = \frac{q}{T_2} - \frac{q}{T_1} = q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) = q \left(\frac{1}{300} - \frac{1}{500} \right) = 0.0013 q$$

q



Using this definition $\Delta S > 0$, which says that the process is spontaneous.

Calculating reversible and irreversible paths

It is important to reiterate that the calculation of the entropy of the system always follows a reversible path.

You might ask, well what happens if the process is not reversible?

To consider this let us take the example of expansion of gas in a cylinder. The process can occur along different paths.

- a. constant pressure expansion, $w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$
- b. reversible isothermal expansion the work $w = -nRT\ln(V_f/V_i)$.

For both a. (irreversible) and b. (reversible) we will calculate the entropy along a reversible path.

$$\Delta S_{\text{sys}} = q/T = -w/T = nR\ln(V_f/V_i)$$

For the reversible path, we can use the fact that $\Delta S_{\text{surr}} = -\Delta S_{\text{sys}}$ to obtain $\Delta S_{\text{surr}} = -nR\ln(V_f/V_i)$.

System and surroundings

The heat transfer example shows us that we always must consider the surroundings. Any time the system releases heat it goes into the surroundings and this contributes to the overall entropy change. Thus, the total entropy is:

$$\Delta S_{\text{total}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}}$$

For a reversible process the total entropy is zero. If a process is irreversible and spontaneous the entropy change is positive. This implies that we must treat the system and the surroundings differently when we calculate entropy.

The rule is: always calculate the entropy of the system along a reversible path.

If the process is truly reversible then:

$$\Delta S_{\text{total}} = 0 \quad \text{and} \quad \Delta S_{\text{surr}} = - \Delta S_{\text{sys}}$$

Understanding the irreversible path

For the irreversible path we use the actual work of the constant pressure expansion, $w = -P_{\text{ext}}\Delta V = -P_{\text{ext}}(V_f - V_i)$ to calculate $\Delta S_{\text{surr}} = -q/T = w/T = -P_{\text{ext}}(V_f - V_i)/T$ where T is the same temperature we used for the isothermal expansion. Note that the sign is opposite since the heat is flowing into the surroundings (and out of the system).

We see that in this case the entropy change ΔS_{surr} is smaller in magnitude than ΔS_{sys} . We know this from the first law where we saw that the irreversible work of expansion is always less than the reversible work of expansion. Thus,

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

for the irreversible process.

The dependence of the entropy on volume

For a constant temperature (isothermal) expansion we have:

$$dS = \delta q_{\text{rev}}/T = -\delta w_{\text{rev}}/T.$$

The logic behind this statement is that the internal energy change is zero for a constant temperature process and so $\delta q_{\text{rev}} = -\delta w_{\text{rev}}$. To calculate the reversible work we simply plug in $\delta w_{\text{rev}} = -PdV$. According to the ideal gas law $P = nRT/V$ so $dS = nRdV/V$.

$$\int_{S_1}^{S_2} dS = nR \int_{V_1}^{V_2} \frac{dV}{V}$$

The result of this equation is that $\Delta S = nR \ln(V_2/V_1)$ at constant temperature.

The dependence of the entropy on temperature

The entropy change as a function of the temperature is derived at constant volume using the fact that

$$dU = \delta q_V = nC_V dT.$$

The reversible heat in this case, q_{rev} , is a constant volume heat and so it can be replaced by

$$dS = \delta q_{\text{rev}}/T = nC_V dT/T \text{ at constant volume}$$

To obtain ΔS we need to integrate both sides

$$\int_{S_1}^{S_2} dS = nC_V \int_{T_1}^{T_2} \frac{dT}{T}$$

We obtain:

$$\Delta S = S_2 - S_1 = nC_V \ln(T_2/T_1).$$

Exactly the same reasoning applies at constant pressure, so that $\Delta S = nC_p \ln(T_2/T_1)$.