Investigating Entropy in Chemical Reactions Using ChemReaX™

A tutorial from ScienceBySimulation

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Introduction

Entropy is one of the trickiest topics for students to master in undergraduate and high-school AP chemistry courses. Entropy can appear very theoretical and abstract to the beginning chemistry student, and measurement of entropy is complicated. In this article, we will use our free online chemistry simulation app, ChemReaX, to conduct a series of virtual experiments to shed some light on the role of entropy in chemical reactions and generate useful insights that the student can add to his/her toolkit. The examples in this article can be used as a template for designing course-specific lab activities and exercises to investigate entropy and related topics.

It's all about the entropy[1]

Consider a reaction system at constant pressure and temperature. The criterion for spontaneous change in this system is that the change in the reaction free energy, $\Delta_r G$, is negative or zero: $\Delta_r G = \Delta_r H - T\Delta S <= 0$, where $\Delta_r H$ is the reaction enthalpy change and ΔS is the entropy change.

In an exothermic reaction, the enthalpy change, $\Delta_r H$, is negative and the reaction is spontaneous as long as this enthalpy reduction can overcome any entropy reduction (i.e., if ΔS is negative and the $-T\Delta S$ term is positive). There is no natural tendency for the system to simply sink to lower levels of enthalpy. A negative enthalpy change at constant temperature T really implies that the entropy of the surroundings increases by $\Delta_r H/T$ due to the energy transfer (in the amount of $\Delta_r H$) from the system to the surroundings. As long as the entropy of the surroundings increases more than any reduction in the entropy of the system (i.e., $-\Delta_r H/T > -\Delta S$), the total entropy of the universe increases and the reaction is spontaneous in converting reactants to products.

The enthalpy change in an endothermic reaction is positive, but this system too can spontaneously convert reactants to products if the system entropy increases more than the reduction in the entropy of the surroundings (i.e., $\Delta S > \Delta_r H/T$) such that the total entropy of the universe increases.

Thus the only consideration in assessing the spontaneity of any reaction is whether it causes the total entropy of the universe to increase or not. This perspective also easily explains why the equilibrium point is dependent on the temperature. As temperature increases, an exothermic reaction causes the entropy of the surroundings to *increase less* (since T is in the denominator), and therefore the equilibrium shifts to the left more towards the reactants (the amount of shift depending on the actual values involved). On the other hand, for an endothermic reaction, the entropy of the surroundings *decreases less* at higher temperatures, shifting the equilibrium to the right more towards the products. In both scenarios, the reaction system moves to the equilibrium point that maximally increases the total entropy of the universe.

Let us now look at concrete examples through simulation to make these concepts real.

[1] This section is largely based on the excellent discussion of entropy in Atkins & Paula, 2014.

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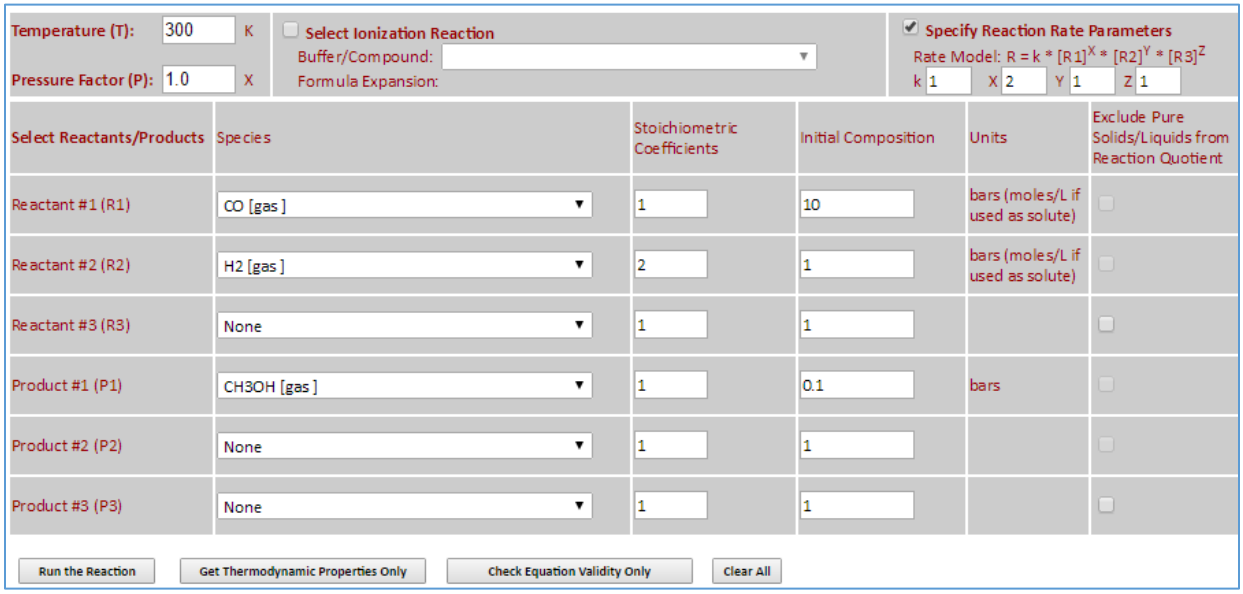
An exothermic reaction

Consider the exothermic synthesis of methanol from carbon monoxide and hydrogen:

$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$

This reaction can be set up as shown in the dashboard below, where the reactants and products are selected from the dropdown lists. The reaction must be balanced by setting the stoichiometric coefficients and initial compositions of all species must be specified. The temperature will be a variable in our experiment and the dashboard shows one of the temperatures of interest (300K).



The results panel below shows that the standard enthalpy change $\Delta_r H^o$ and the standard free-energy change $\Delta_r G^o$ are both negative for this exothermic reaction at 300K. For the initial composition shown in the dashboard, the initial reaction free-energy change ($\Delta_r G = \Delta_r G^o + R\ T\ \ln Q$, where Q is the reaction quotient) is negative as well, strongly pushing the reaction to the right towards the products. The results panel also shows the simulated final composition of the reactants and products at equilibrium.

Now if we vary the temperature from 200K to 600K and run the simulation at temperature increments of 100K and graph the final equilibrium composition at each temperature, we can see clearly that the equilibrium for this exothermic reaction shifts to the left as temperature increases. While the final state is made up entirely of the product at low temperatures, it almost exclusively consists of the reactants at high temperatures. Digging into this more, the simulations also show that the standard free-energy change $\Delta_r G^o$ becomes positive at higher temperatures, indicating that the reverse reaction will be spontaneous.

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Thermodynamics: (@ T = *300.00* K)

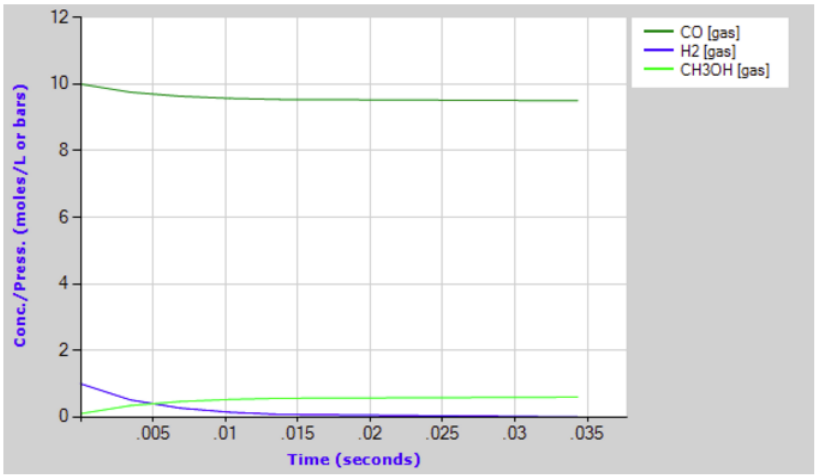
Standard Enthalpy of Formation and Entropy	$\Delta_f H^o(T)$ (KJ/mol)	$S^o(T)$ (J/mol.K)
CO [gas]	-110.48	197.84
H2 [gas]	0.05	130.86
CH3OH [gas]	-200.86	240.08

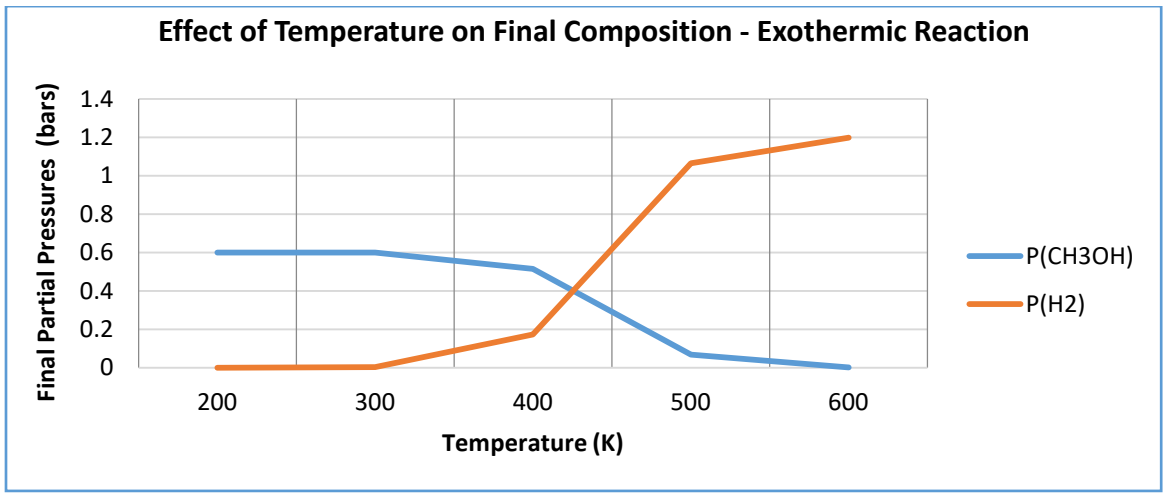
Reaction Thermodynamics & Equilibrium	Value	
Standard enthalpy change, $\Delta_r H^o(T)$	-90.49	KJ
Standard entropy change, $\Delta S^o(T)$	-0.22	KJ
Standard reaction free energy change, $\Delta_r G^o(T)$	-24.65	KJ
Reaction free energy change at initial composition, $\Delta_r G(T)$	-36.13	KJ
Equilibrium constant, K	1.955669e+004	

Data sources: NASA

Simulated Final State: (@ T = *300.00* K ; P = *1.00* X)

Reactants, Products	Final Composition	Pressure-adjusted Composition	Units
CO [gas]	9.50091e+000	9.50091e+000	bars (moles/L if used as solute)
H2 [gas]	1.82841e-003	1.82841e-003	bars (moles/L if used as solute)
CH3OH [gas]	5.99086e-001	5.99086e-001	bars





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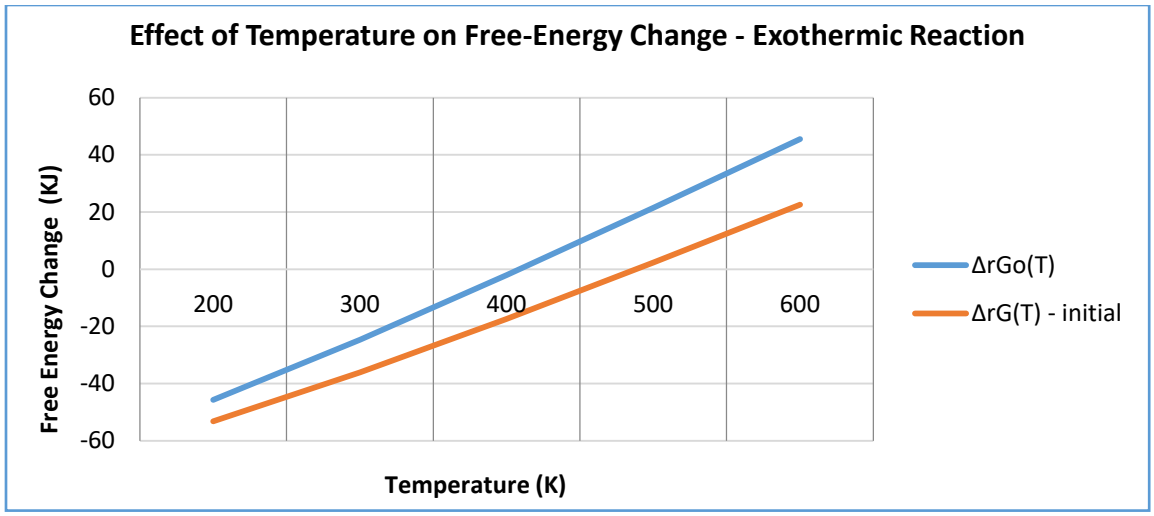
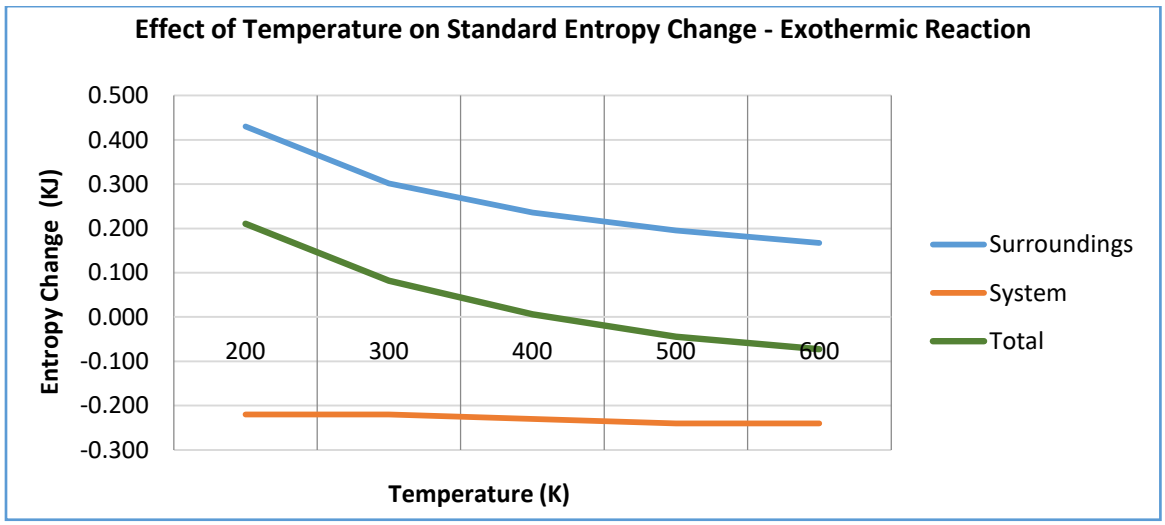


The final piece of the puzzle is the entropy, which is the underlying cause of the change in the direction of spontaneity. The chart below uses data from the simulations to show the standard entropy change of the surroundings ($-\Delta_r H^o/T$), the standard entropy change of the system (ΔS^o), and the total entropy change of the universe. As the temperature increases, the total entropy change decreases until it becomes negative – at that point, the forward reaction is no longer spontaneous. This crossover occurs at a temperature of just over 400K in our series of simulations. This is also the exact point at which the standard free-energy change becomes positive and the final composition indicates more reactants than product. We have now used simulation results to show how the direction of spontaneity is directly related to the sign of the total standard-state entropy change, as expected from the theory described earlier. An interesting point that we will come back to in the next sections is that the crossover point is independent of the initial composition and can be predicted based on standard-state entropies alone.



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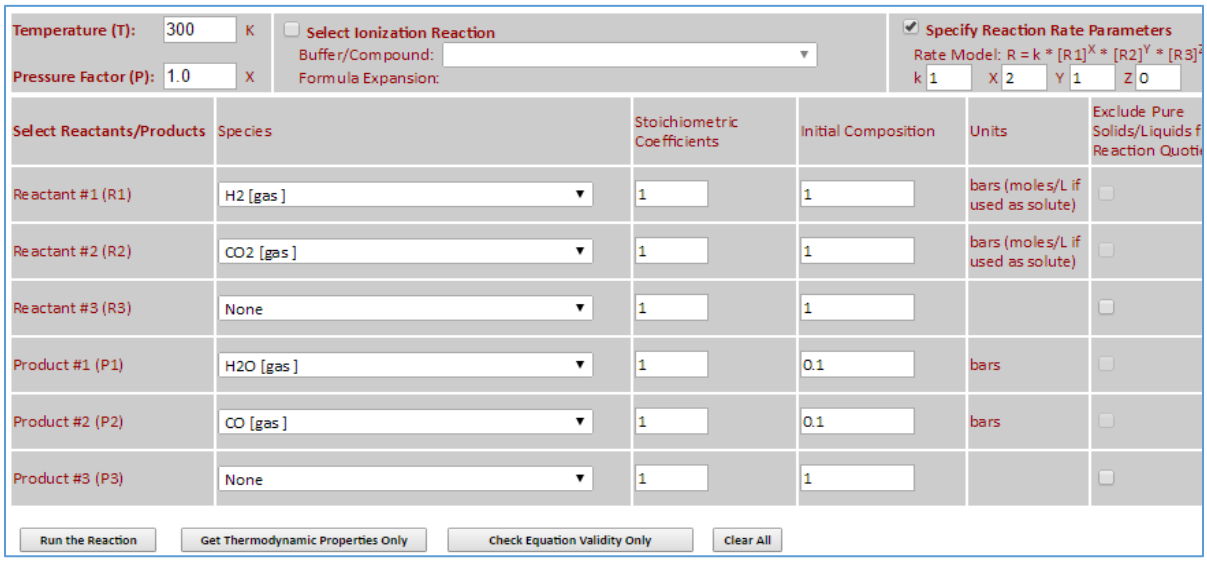
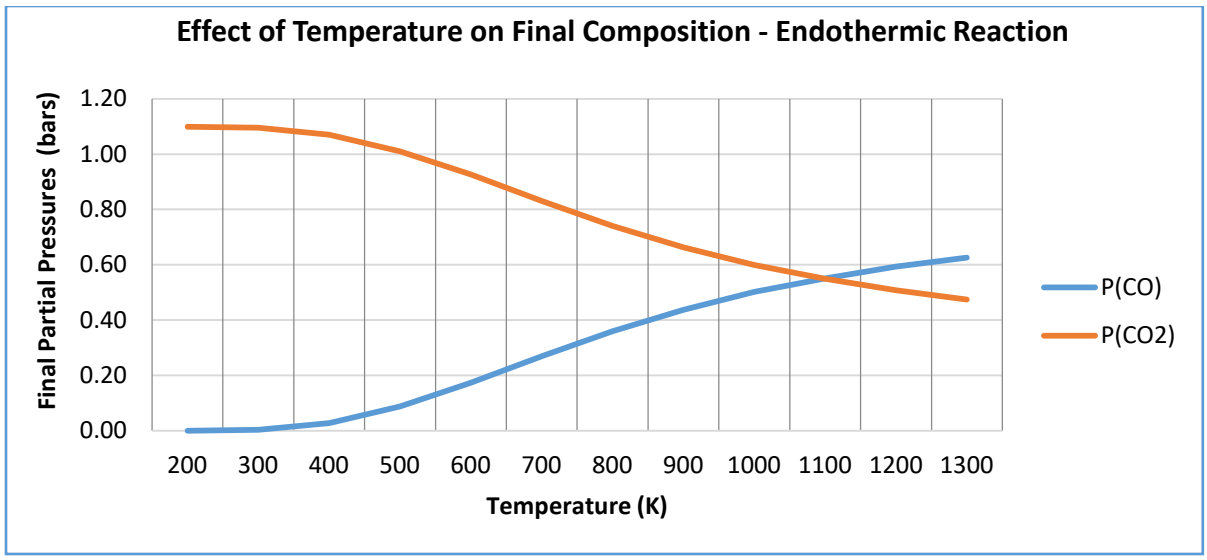
An endothermic reaction

Consider this example of an endothermic reaction:

H_2 (g) + CO_2 (g) ⇌ H_2O (g) + CO (g)

Setting up the simulations as shown in the dashboard below and running multiple simulations with temperature variation as before, we can see that the free-energy in fact decreases as the temperature rises and the final compositions clearly show the equilibrium for this endothermic reaction moving to the right. The crossover in this case occurs at a temperature of just over 1100K when the total entropy becomes positive and the standard free-energy change becomes negative – essentially making this endothermic reaction spontaneous in the forward direction towards the products. Our simulation results have shown again that the direction of spontaneity is directly related to the sign of the total standard-state entropy change. As before, the crossover point can be predicted by standard-state entropies without regard to the initial composition.





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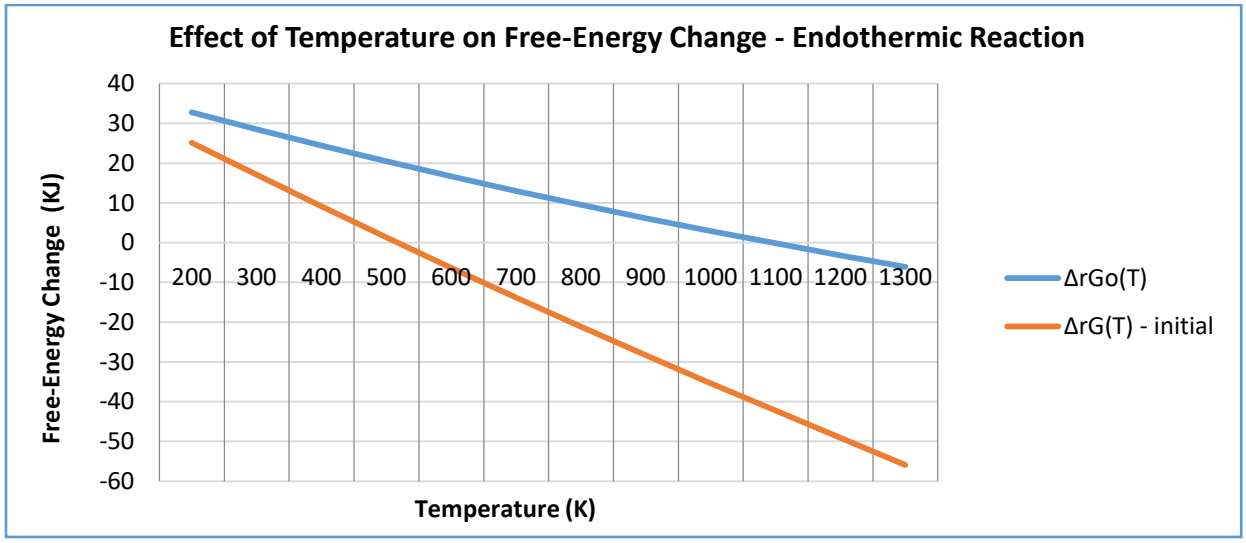

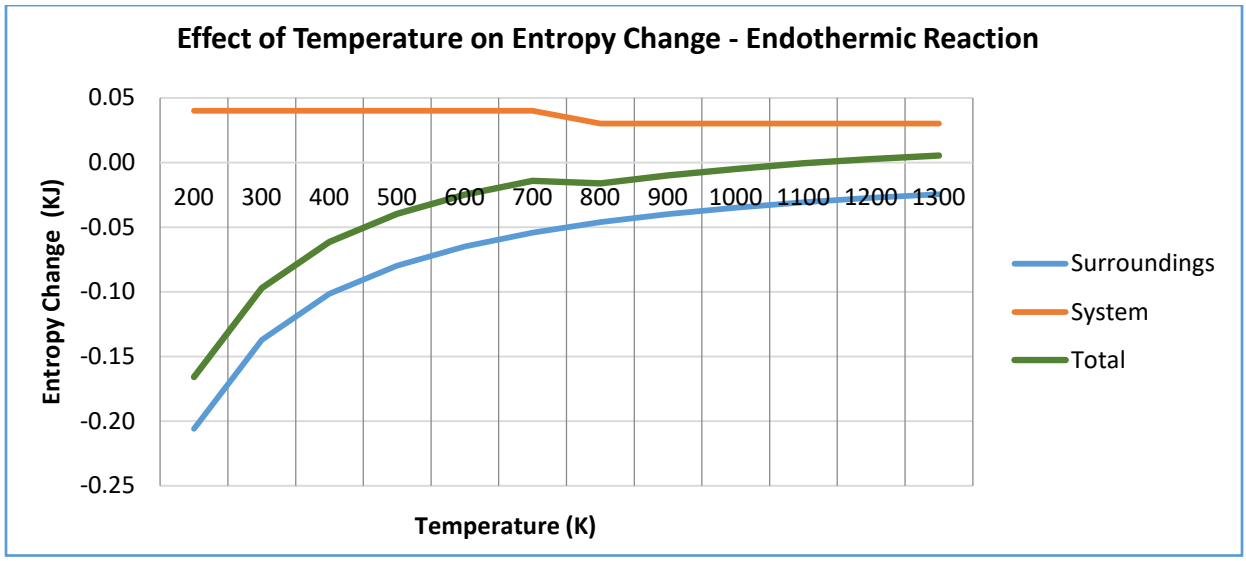

Effect of initial concentrations

We have seen that the sign of the total standard-state entropy change determines the direction of spontaneity of a reaction and we noted earlier that this is independent of the initial composition. To understand this better, let us re-run the endothermic reaction from the previous section with the initial reactant concentrations set 10 times higher than before as shown in the dashboard below. The graphs below show that the *crossover occurs at exactly the same temperature as before* – just over 1100K – even though the initial concentrations are much higher in the current simulations. Now we are ready to explain why.

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Temperature (T): 200 K

Pressure Factor (P): 1.0 X

Select Ionization Reaction

Buffer/Compound:

Formula Expansion:

Specify Reaction Rate Parameters

Rate Model: $R = k * [R1]^X * [R2]^Y * [R3]^Z$

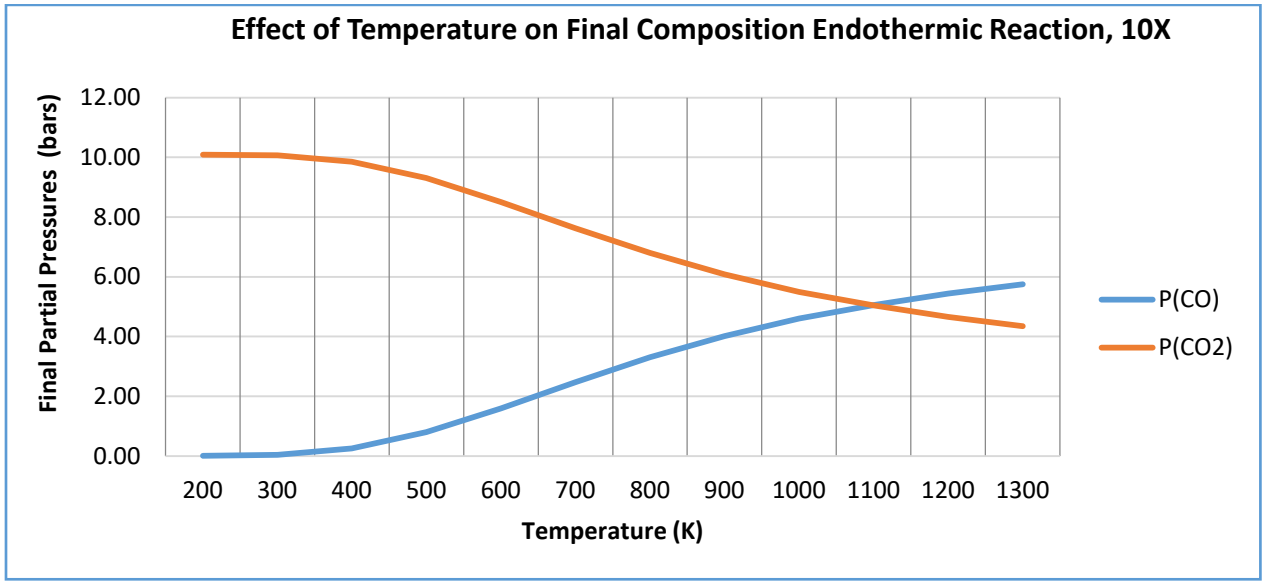
k 0 X 0 Y 0 Z 0

Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	H2 [gas]	1	10	bars (moles/L if used as solute)	
Reactant #2 (R2)	CO2 [gas]	1	10	bars (moles/L if used as solute)	
Reactant #3 (R3)	None	1	1		
Product #1 (P1)	H2O [gas]	1	0.1	bars	
Product #2 (P2)	CO [gas]	1	0.1	bars	
Product #3 (P3)	None	1	1		

Run the Reaction | Get Thermodynamic Properties Only | Check Equation Validity Only | Clear All

Equation:

H2 [gas] + CO2 [gas] + <---> H2O [gas] + CO [gas] +



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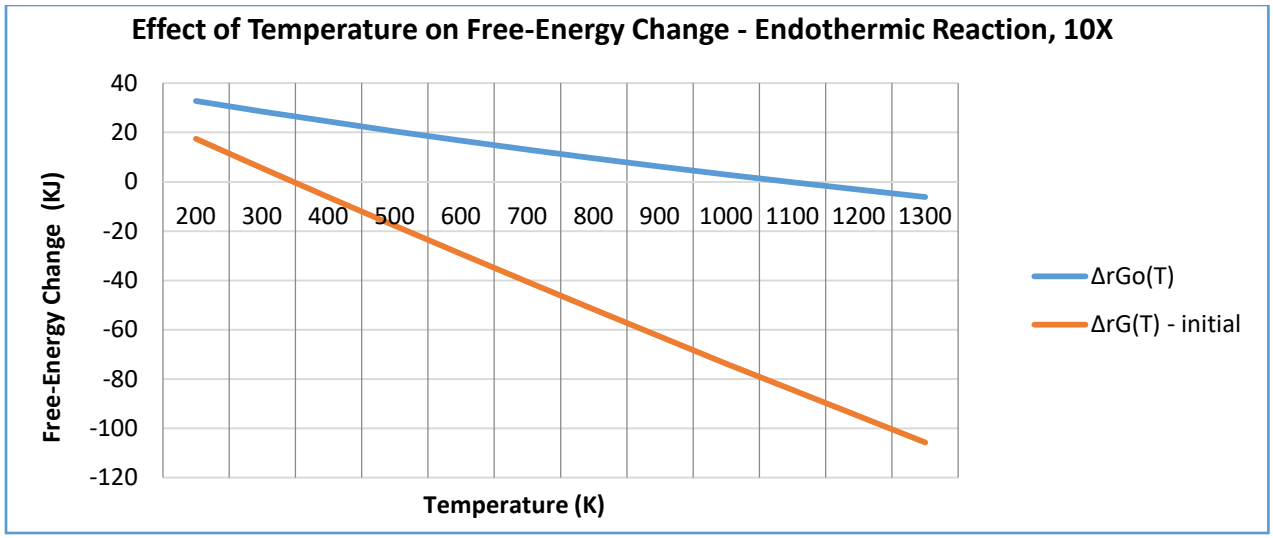

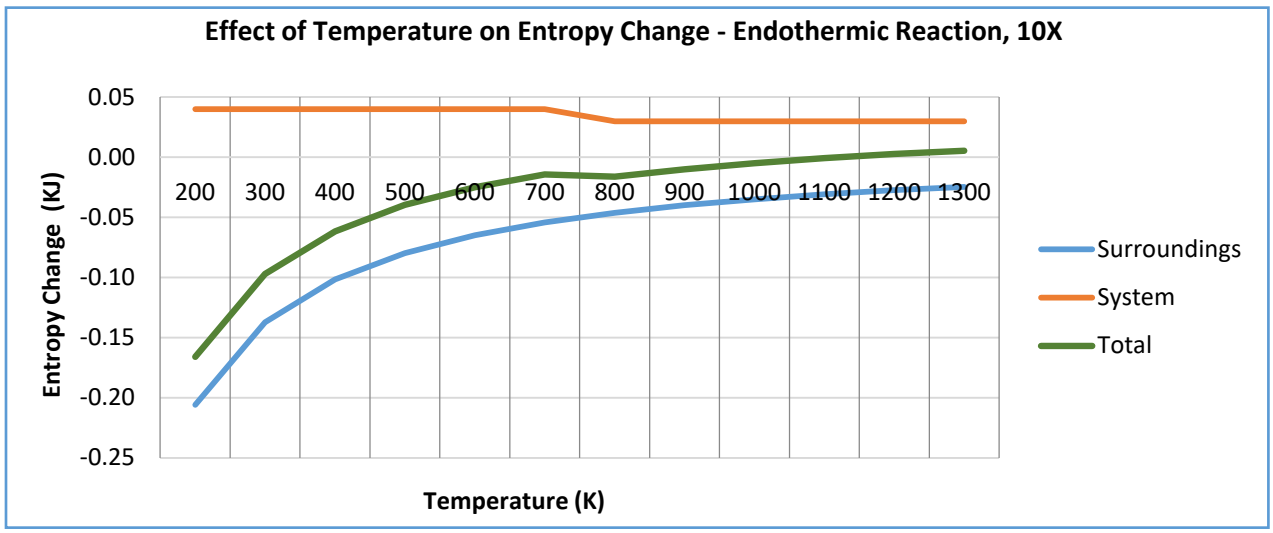

The reaction free-energy change ($\Delta_r G = = \Delta_r G^\circ + R\ T\ \ln Q$, where Q is the reaction quotient) differs from the standard free-energy change by the quantity RTlnQ. Since RTlnQ is initially negative for a large reactant concentration relative to product concentration, $\Delta_r G$ starts out by being more negative than $\Delta_r G^\circ$ as we can see in the chart above. As long as $\Delta_r G < 0$, the reaction proceeds to the right spontaneously – this is certainly the case initially when the starting reactant concentrations are large.

As reactant molecules are used up and product molecules are generated, lnQ increases (i.e., becomes less negative or more positive). Further rightward progress of the reaction can then be sustained only by a sufficiently negative $\Delta_r G^\circ$. The more negative $\Delta_r G^\circ$ is, the farther it can push the reaction to the right while counteracting the increasingly positive lnQ and keeping $\Delta_r G < 0$. The sign and magnitude of $\Delta_r G^\circ$ in turn depend on the temperature, which determines the total entropy change of the system and the surroundings as $\Delta S - \Delta_r H/T$ for an endothermic reaction.

This process is independent of the initial reactant concentrations because any excess reactants will have already produced excess products by the time lnQ is close to zero, and from there it is the total standard-

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state entropy change that drives additional conversion of reactants to products and makes the reaction spontaneous in the forward direction.

The temperature at which the crossover occurs – where in this case an endothermic reaction becomes spontaneous towards the products – is the point where the decrease in the entropy of the surroundings is in exact balance with the increase in system entropy and the total entropy change is zero. At this point, the system is on the verge of becoming spontaneous towards the products, but $\Delta_r G^o$ is zero at this temperature, so the reaction cannot progress further. Any temperature increase beyond this makes the total entropy change positive, turns $\Delta_r G^o$ negative, and pushes the system more towards the products as the charts above illustrate. Thus the crossover temperature can be predicted by calculating the total standard-state entropy alone.

Conclusion

We have used ChemReaX as a virtual lab to bring to life a complicated concept such as entropy in chemical reactions. Using a series of simulated exothermic and endothermic reactions, we have demonstrated the fundamental role of the total entropy of the universe (entropy of the system + the entropy of the surroundings) in determining the direction of spontaneity of any given chemical reaction. Additional investigations of entropy and other topics can be undertaken through ChemReaX simulations using the examples and approach in this tutorial article as templates.

References

ChemReaX - a chemical reaction modeling and simulation app from ScienceBySimulation - General Reactions. Retrieved from https://www.sciencebysimulation.com/chemreax

Atkins, P. W., & Paula, J. D. (2014). *Physical chemistry / Peter Atkins, Julio de Paula*. New York: W. H. Freeman and Co.

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