

Exploring Reaction Equilibria Using ChemReaX™

A tutorial from [ScienceBySimulation](http://ScienceBySimulation.com)

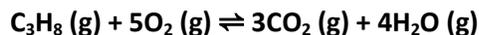
Kumar Venkat

Introduction

This article will demonstrate how our free online chemistry simulation app, [ChemReaX](http://ChemReaX.com), can be used as a virtual lab in general chemistry and physical chemistry courses in undergraduate and high-school AP programs. We will draw on a few selected topics related to general equilibrium and thermodynamics to illustrate how virtual lab activities can be designed around ChemReaX, enabling students to learn critical chemistry concepts through virtual experimentation, data collection and data analysis. We will start with a simulation study of a reaction with a limiting reagent, and then use simulation to examine the impacts of changes in temperature, pressure and reactant concentration on various reaction equilibria.

Limiting Reagent

A limiting reagent in a chemical reaction is completely consumed when the reaction completes, leaving some excess amounts of the other reactants. An example of this can be constructed using the combustion of propane, with oxygen as a limiting reagent:



This reaction can be set up easily in ChemReaX 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. We will use the default temperature of 298.15K in this demonstration.

Temperature (T):	298.15 K	<input type="checkbox"/> Select Ionization Reaction	Buffer/Compound:		<input checked="" type="checkbox"/> Specify Reaction Rate Parameters
Pressure Factor (P):	1.0 X	Formula Expansion:			Rate Model: $R = k * [R1]^X * [R2]^Y * [R3]^Z$
					k 1 X 2 Y 0 Z 0
Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	C3H8 [gas]	1	1	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #2 (R2)	O2 [gas]	5	1	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #3 (R3)	None	1	1		<input type="checkbox"/>
Product #1 (P1)	CO2 [gas]	3	0.25	bars	<input type="checkbox"/>
Product #2 (P2)	H2O [gas]	4	0.25	bars	<input type="checkbox"/>
Product #3 (P3)	None	1	1		<input type="checkbox"/>

When this reaction is run by clicking the “Run the Reaction” button, the final composition of the reactants and products are generated by the simulator. The results panel below includes details of the underlying thermodynamics and shows the final simulated state of the reaction in both tabular and graphical form.

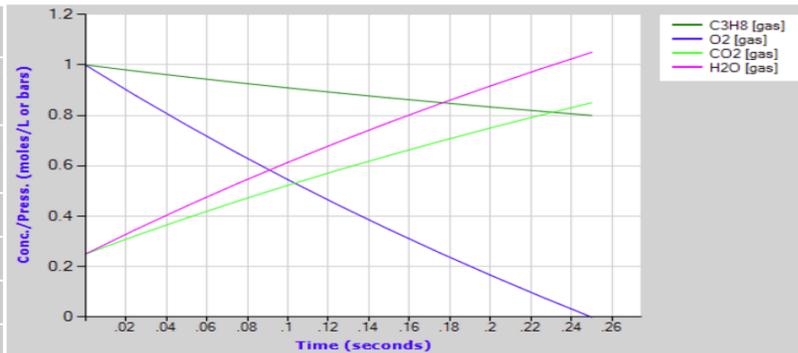
Thermodynamics: (@ T = 298.15 K)

Standard Enthalpy of Formation and Entropy	$\Delta_f H^\circ(T)$ (KJ/mol)	$S^\circ(T)$ (J/mol.K)	Reaction Thermodynamics & Equilibrium	Value
C3H8 [gas]	-104.68	270.32	Standard enthalpy change, $\Delta_r H^\circ(T)$	-2043.11 KJ
O2 [gas]	0.00	205.15	Standard entropy change, $\Delta_r S^\circ(T)$	0.10 KJ
			Standard reaction free energy change, $\Delta_r G^\circ(T)$	-2073.15 KJ
CO2 [gas]	-393.51	213.79	Reaction free energy change at initial composition, $\Delta_r G(T)$	-2097.21 KJ
H2O [gas]	-241.82	188.86	Equilibrium constant, K	Infinity

Data sources: NASA

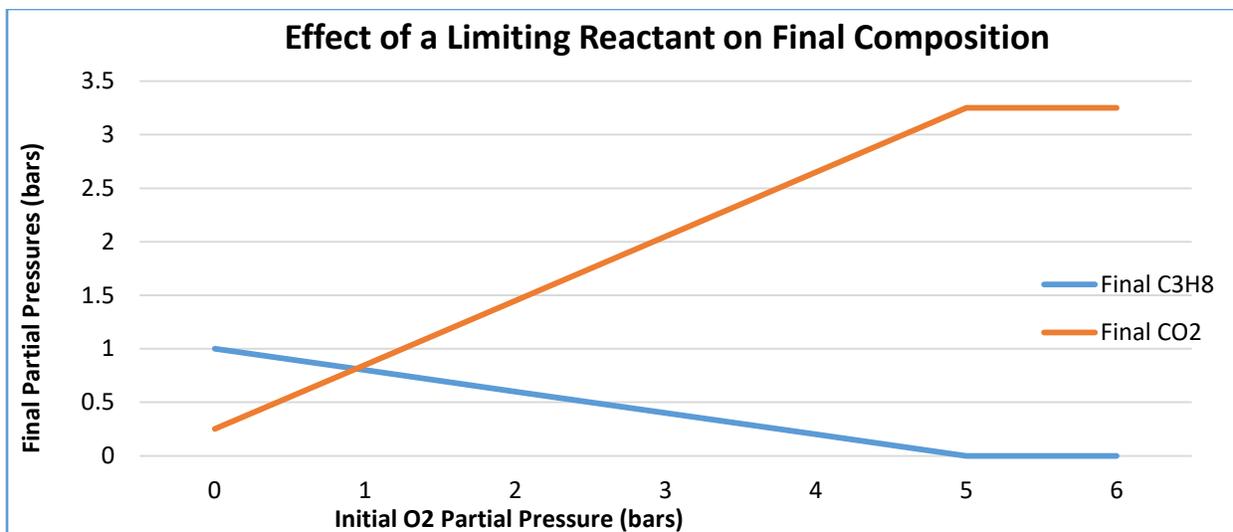
Simulated Final State: (@ T = 298.15 K ; P = 1.00 X)

	Reactants, Products	Final Composition	Pressure-adjusted Composition	Units
R1	C3H8 [gas]	8.00000e-001	8.00000e-001	bars (moles/L if used as solute)
R2	O2 [gas]	2.46045e-321	2.46045e-321	bars (moles/L if used as solute)
R3				
P1	CO2 [gas]	8.50000e-001	8.50000e-001	bars
P2	H2O [gas]	1.05000e+000	1.05000e+000	bars
P3				



The initial composition of O₂ specified in the dashboard makes it a limiting reactant since five molecules of O₂ are needed to combust one molecule of C₃H₈. The simulation result shows that all the O₂ is used up leaving a significant amount of unreacted C₃H₈.

Next, we can take this a step further by varying the initial partial pressure of O₂ over a range and collecting data on the final compositions. For example, if we vary the initial O₂ partial pressure from 0 to 6 bars, and run the simulation at increments of 1 bar, the resulting data from these runs can be graphed in Excel as shown below. O₂ is clearly the limiting reactant until its partial pressure is raised to exactly 5 bars – at this point, the C₃H₈ is completely used up and it becomes the limiting reactant as the O₂ partial pressure is increased further. CO₂, which is a product, reaches its maximum partial pressure when the C₃H₈ is fully used up.



Temperature Variation – Exothermic Reaction

Per Le Chatelier's principle, an increase in temperature will move the equilibrium of an exothermic chemical reaction towards the reactants in order to absorb the additional heat being supplied. A good example is the exothermic synthesis of methanol from carbon monoxide and hydrogen:



There are two basic thermodynamic equations to keep in mind while studying this. The standard free-energy change ($\Delta_r G^\circ = \Delta_r H^\circ - T \Delta S^\circ$) is negative and dominated by the negative enthalpy change ($\Delta_r H^\circ$) at lower temperatures. For the initial composition shown in the dashboard below, the initial reaction free-energy change ($\Delta_r G = \Delta_r G^\circ + R T \ln Q$, where Q is the reaction quotient) is negative as well, spontaneously pushing the reaction to the right towards the products.

Temperature (T): K

Pressure Factor (P): X

Select Ionization Reaction

Buffer/Compound:

Formula Expansion:

Specify Reaction Rate Parameters

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

k X Y Z

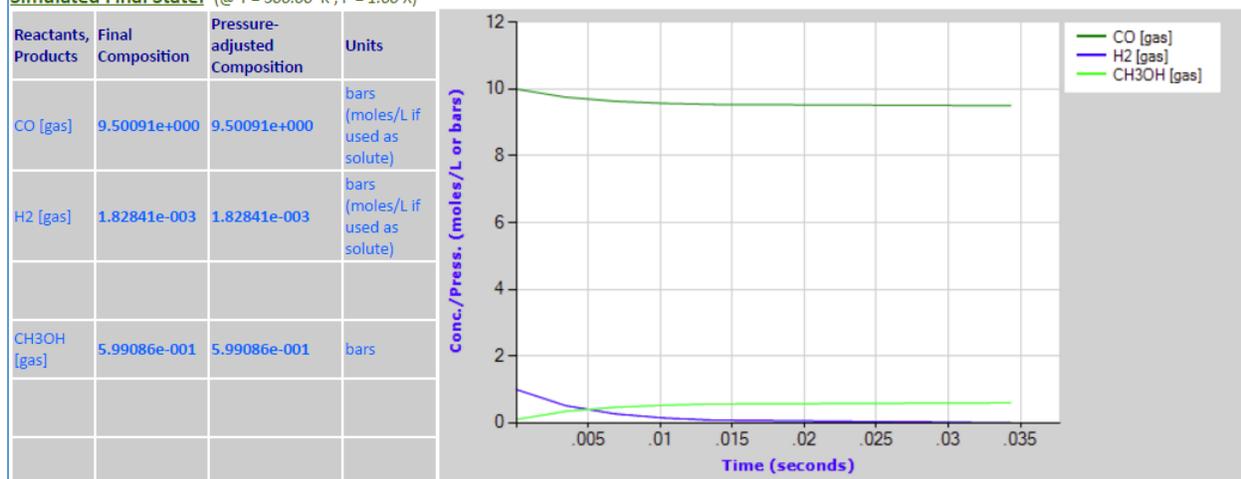
Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	CO [gas]	1	10	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #2 (R2)	H2 [gas]	2	1	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #3 (R3)	None	1	1		<input type="checkbox"/>
Product #1 (P1)	CH3OH [gas]	1	0.1	bars	<input type="checkbox"/>
Product #2 (P2)	None	1	1		<input type="checkbox"/>
Product #3 (P3)	None	1	1		<input type="checkbox"/>

Thermodynamics: (@ T = 300.00 K)

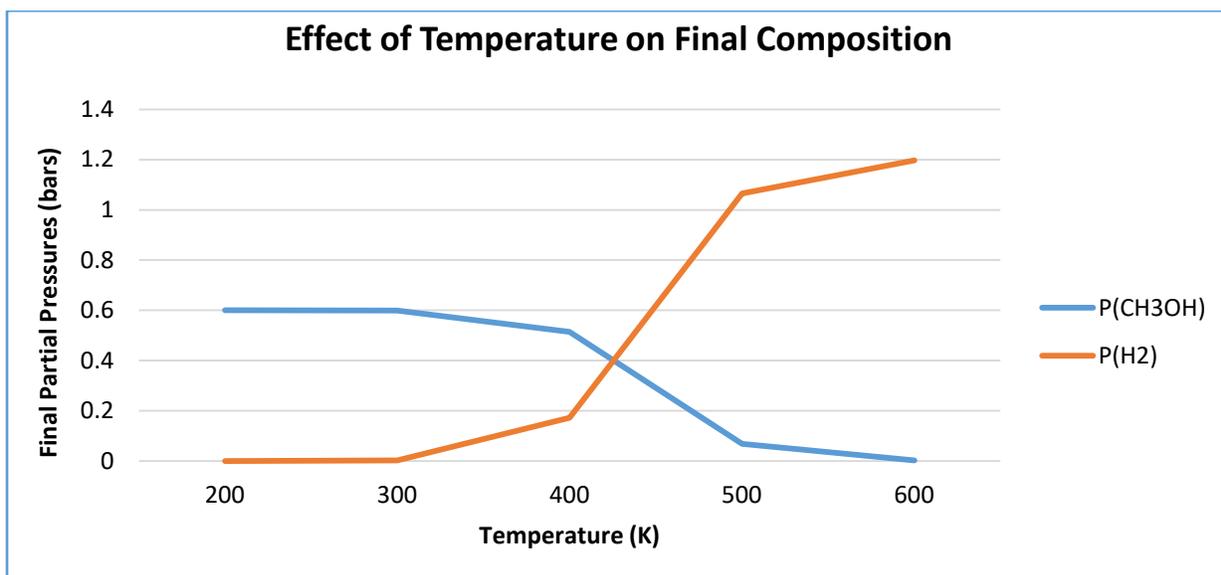
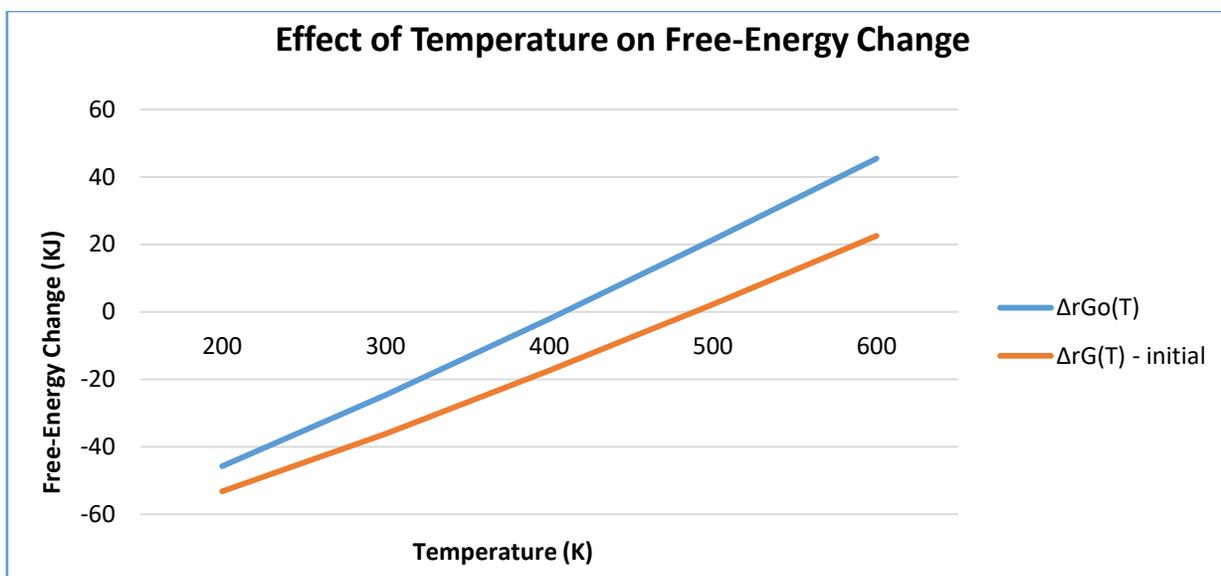
Standard Enthalpy of Formation and Entropy	$\Delta_f H^\circ(T)$ (KJ/mol)	$S^\circ(T)$ (J/mol.K)	Reaction Thermodynamics & Equilibrium	Value
CO [gas]	-110.48	197.84	Standard enthalpy change, $\Delta_r H^\circ(T)$	-90.49 KJ
H2 [gas]	0.05	130.86	Standard entropy change, $\Delta_r S^\circ(T)$	-0.22 KJ
			Standard reaction free energy change, $\Delta_r G^\circ(T)$	-24.65 KJ
CH3OH [gas]	-200.86	240.08	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)

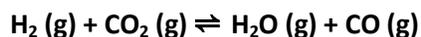


As temperature rises, however, the small negative entropy change (ΔS°) seen in the results panel above becomes more important and the sign of the free-energy change flips, spontaneously pushing the reaction in the opposite direction towards the reactants. The Excel charts below show the data collected from five simulation runs, with H₂ as the controlling reactant (with an excess of the other reactant, CO) and the temperature varying from 200K to 600K. The free-energy changes become gradually more positive as the temperature rises. The final composition follows the free-energy change, consisting of only the product at low temperatures and only the reactants at high temperatures. The equilibrium constant K decreases with increasing temperature in this case.



Temperature Variation – Endothermic Reaction

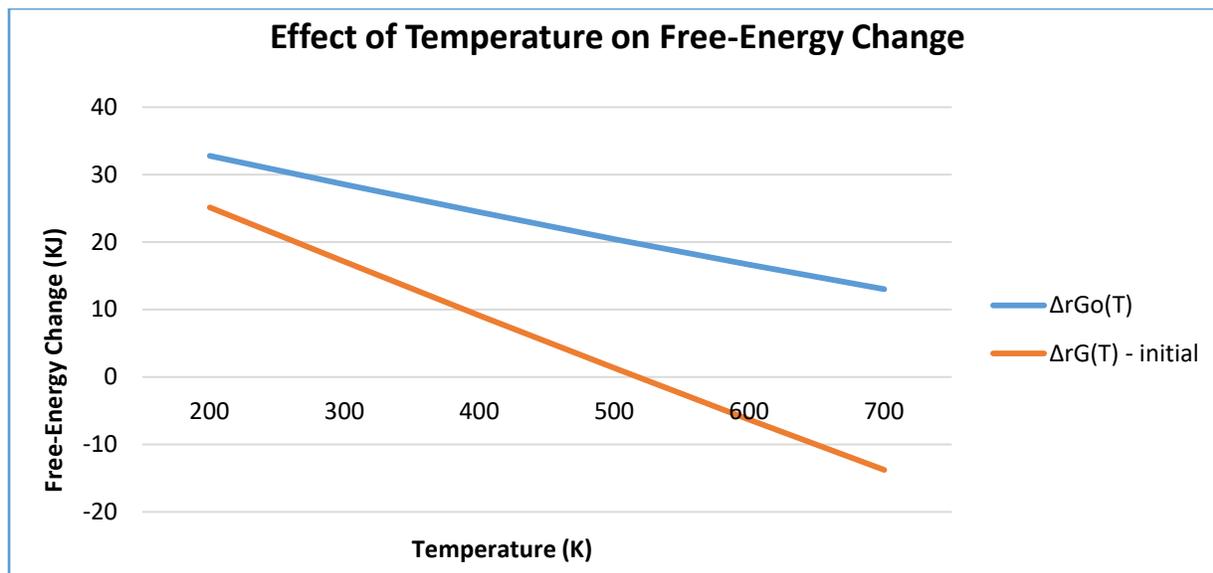
Le Chatelier's principle also implies the complement of the previous case, which is that the equilibrium will shift towards the products at higher temperatures for endothermic reactions in order to absorb the extra heat. Let us use the following example of an endothermic reaction:

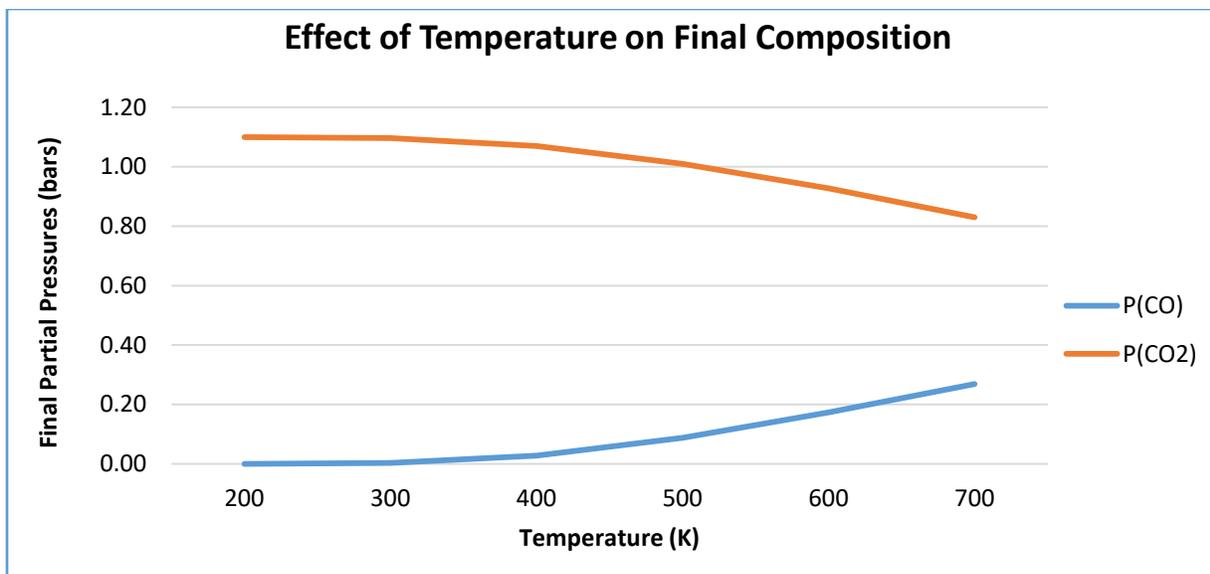


Setting up the simulations as shown in the dashboard below and running multiple simulations with temperature variation, we can see that the free-energy in fact decreases as the temperature rises and the final compositions clearly show the equilibrium moving to the right towards products. The equilibrium constant K increases with increasing temperature in this case.

Temperature (T): 300 K Select Ionization Reaction
 Pressure Factor (P): 1.0 X Buffer/Compound: Formula Expansion: Specify Reaction Rate Parameters
 Rate Model: $R = k * [R1]^X * [R2]^Y * [R3]^Z$
 k 1 X 2 Y 1 Z 0

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





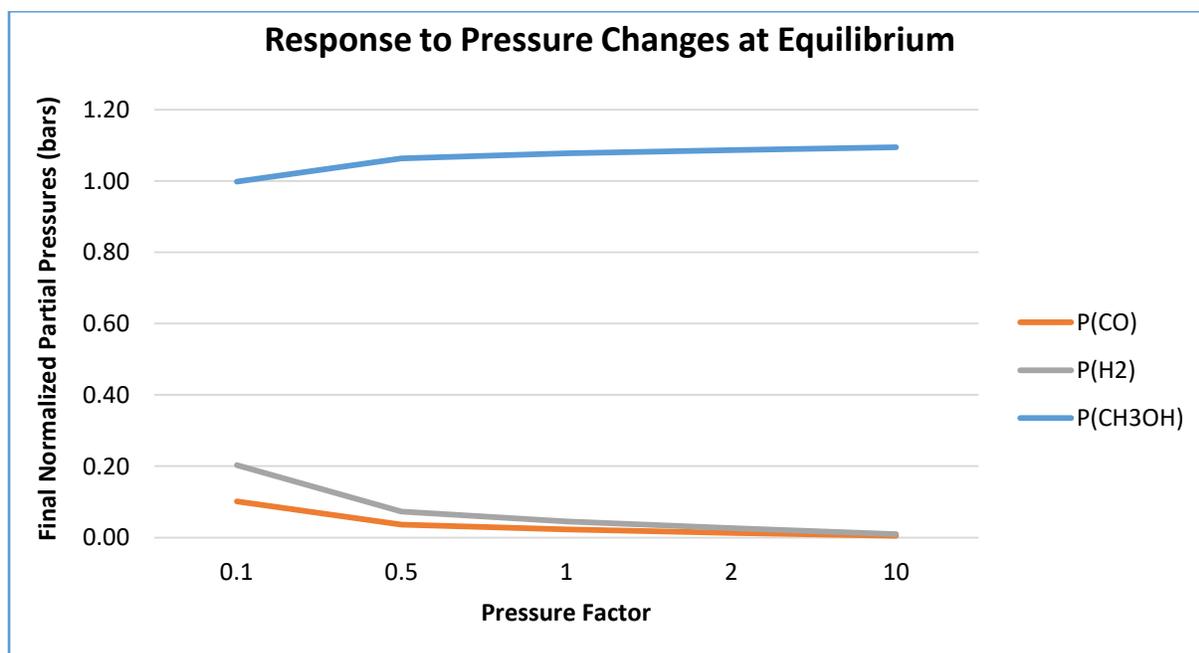
Pressure Variation

Continuing with the theme of applying stresses to a reaction at equilibrium, let us consider pressure changes next. According to Le Chatelier's principle, if the pressure within a reaction vessel is increased or decreased by confining the gas species to a smaller or larger volume (when a reaction is at equilibrium otherwise), then the equilibrium composition of the gases will change such that the total number of gas molecules are decreased or increased. The equilibrium composition will shift in a direction that can neutralize the pressure change. This only applies when there are unequal numbers of gas molecules on the two sides of a reaction. The equilibrium constant K is independent of pressure and does not change in this scenario.

To experiment with this, we can change the pressure factor for the methanol synthesis reaction as shown in the dashboard below, where a factor of 2 means that pressure is now twice as much as the baseline pressure under which an original equilibrium was reached. The Excel chart shows the results of five simulations with the pressure factor varying from 0.1 to 10. As the pressure increases, the equilibrium shifts to the right and more methanol is produced, and the reverse is true as the pressure decreases.

Temperature (T): 298.15 K Select Ionization Reaction
 Buffer/Compound:
 Pressure Factor (P): 2 X Formula Expansion: Specify Reaction Rate Parameters
 Rate Model: $R = k * [R1]^X * [R2]^Y * [R3]^Z$
 k 1 X 2 Y 1 Z 1

Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	CO [gas]	1	1	bars (mole/L if used as solute)	<input type="checkbox"/>
Reactant #2 (R2)	H2 [gas]	2	2	bars (mole/L if used as solute)	<input type="checkbox"/>
Reactant #3 (R3)	None	1	1		<input type="checkbox"/>
Product #1 (P1)	CH3OH [gas]	1	0.1	bars	<input type="checkbox"/>
Product #2 (P2)	None	1	1		<input type="checkbox"/>
Product #3 (P3)	None	1	1		<input type="checkbox"/>

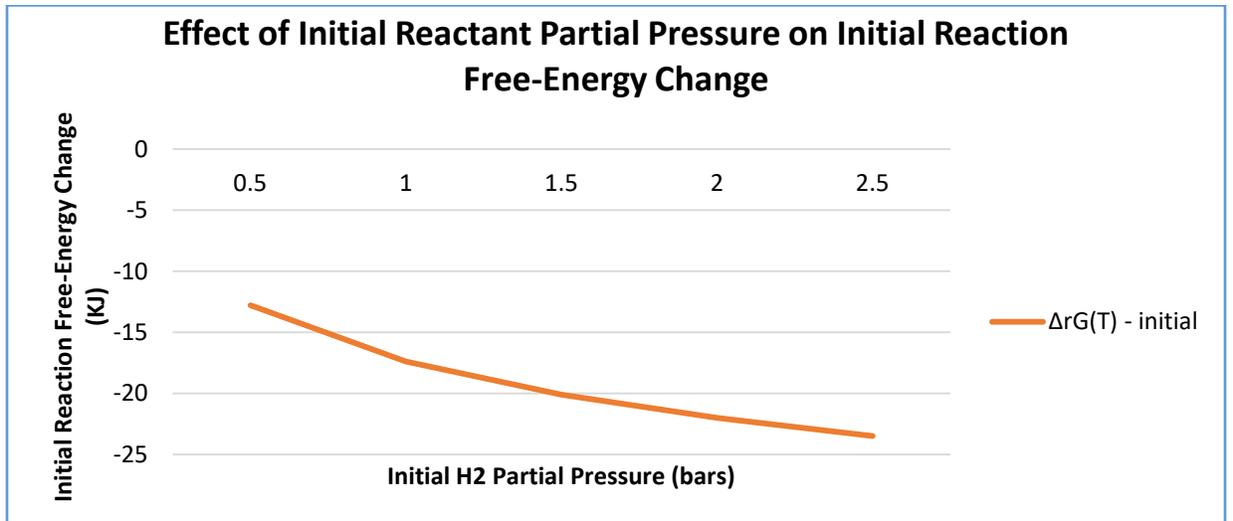


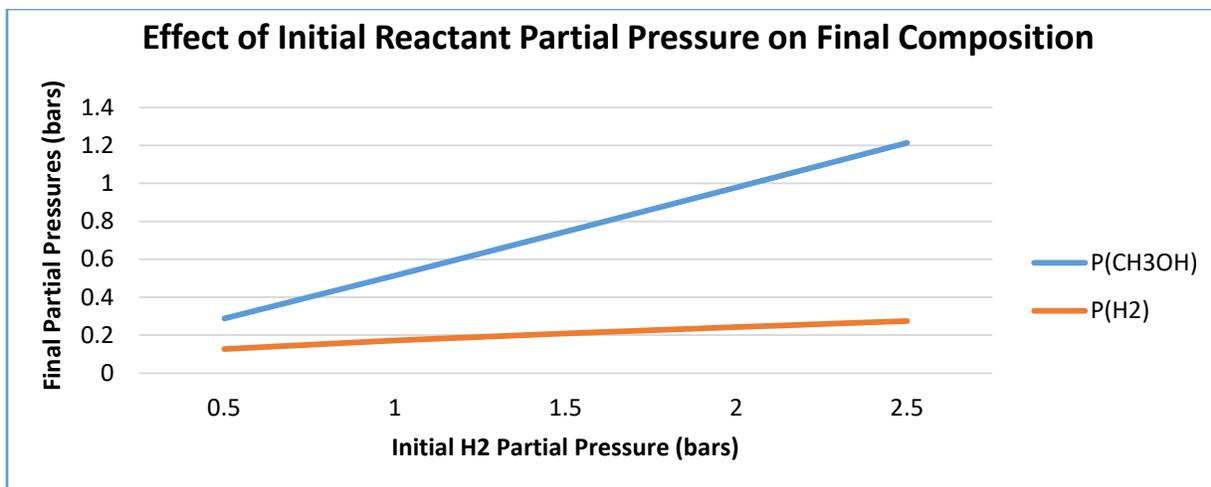
Concentration Variation

Finally, increasing the concentration or partial pressure of any reaction component will cause a shift in the equilibrium composition such that some of the added substance is used up. To see this clearly, we can go back to the methanol synthesis example and hold one of the reactants at a high initial partial pressure and then vary the partial pressure of the other reactant (H₂). The Excel charts based on these multiple simulation results show that the initial reaction free-energy change becomes more negative as the initial H₂ partial pressure increases, suggesting a stronger initial tendency to convert the additional

reactant to product. The final composition indicates that most of the increase in the H₂ partial pressure is consumed by the reaction and is converted to an increase in the CH₃OH partial pressure. The equilibrium constant K is independent of the initial composition and does not change in this scenario.

Temperature (T):	400 K	<input type="checkbox"/> Select Ionization Reaction	Buffer/Compound:		<input type="checkbox"/> Specify Reaction Rate Parameters
Pressure Factor (P):	1.0 X	Formula Expansion:			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)	CO [gas]	1	10	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #2 (R2)	H2 [gas]	2	1	bars (moles/L if used as solute)	<input type="checkbox"/>
Reactant #3 (R3)	None	1	1		<input type="checkbox"/>
Product #1 (P1)	CH3OH [gas]	1	0.1	bars	<input type="checkbox"/>
Product #2 (P2)	None	1	1		<input type="checkbox"/>
Product #3 (P3)	None	1	1		<input type="checkbox"/>
<input type="button" value="Run the Reaction"/> <input type="button" value="Get Thermodynamic Properties Only"/> <input type="button" value="Check Equation Validity Only"/> <input type="button" value="Clear All"/>					





Conclusion

We have used topics in general equilibrium and thermodynamics to demonstrate how virtual lab assignments and activities can be built around ChemReaX and used as learning tools in undergraduate and high-school AP chemistry courses. ChemReaX includes thermodynamic data for a large number of chemical species, so students have the flexibility to construct and simulate a broad range of reactions. Data collected from multiple simulations can be graphed in Excel and analyzed to understand the impacts of varying one or more variables. Such virtual lab exercises make it possible for students to adopt an investigative and experimental approach to learning chemistry, driven by asking and answering interesting scientific questions and running “what-if” experiments to gain insights.

Reference

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