Understanding Chemical Kinetics Using ChemReaX™

A tutorial from ScienceBySimulation

Kumar Venkat

Introduction

While thermodynamics can be used to predict whether a reaction will occur, an understanding of chemical kinetics is required in order to quantify how fast a reaction will proceed. In this article, we will run a set of virtual experiments using our free online chemistry simulation app, ChemReaX, to demonstrate the basic concepts related to reaction kinetics. The examples in this article can be used as a template for designing course-specific virtual lab activities and exercises to investigate chemical kinetics further in a classroom setting.

Brief Theory of Chemical Kinetics in a Virtual Lab Context

Chemical kinetics is the study of reaction rates and is complementary to the thermodynamic considerations of whether a reaction is spontaneous. The rate of a reaction (i.e., how fast it proceeds) at constant temperature depends on the concentrations or partial pressures of the reactants and products, and can be modeled by differential equations called rate laws. The rate also depends on catalysts which do not appear in the balanced equation. In practice, the reaction rates -- including the overall order -- can only be determined by experiment under specific conditions and then fitted to an appropriate model.

There are many different forms of integrated rate laws/models which express the rate of a reaction in terms of the reactant and product concentrations. A generalized integrated reaction rate model used in ChemReaX is: Rate $v = k * [R1]^X * [R2]^Y * [R3]^Z$, where R1, R2 and R3 are the reactants.

The square brackets in our notation denote either concentration (units: moles/L) or partial pressure (units: bars). The constants k, X, Y and Z must be experimentally determined for a given reaction at a given temperature, and are inputs to ChemReaX. The coefficient k is the rate constant for a reaction, and its units are chosen so as to convert the product of concentrations (each raised to some power) into a rate expressed as a change in concentration divided by time. A larger rate constant implies a faster reaction. The overall order of a reaction is X+Y+Z. Only the reactants are included in this particular rate model since the product concentrations do not vary independently and are dependent on the reactant concentrations at every point in time. For a reaction $aA + bB \rightleftharpoons cC + dD$, the rate of change of each concentration can be related to the overall reaction rate v as follows: $v = (-1/a)\,\Delta A/\Delta t = (-1b)\,\Delta B/\Delta t = (1/c)\,\Delta C/\Delta t = (1/d)\,\Delta D/\Delta t$.

The rate model is a differential equation that can be difficult to integrate analytically, especially as the reaction order increases. ChemReaX uses simulation to numerically integrate the differential equation and makes investigations of chemical kinetics easier.

The half-life of a reactant is the time taken for the concentration of that reactant to fall to half its initial value as the reaction progresses, and is independent of its initial concentration in a first-order reaction. The half-life does depend on the initial concentration of a reactant in second and higher-order reactions.

Copyright © 2017 by Science By Simulation. All rights reserved. **Contact: info@sciencebysimulation.com**

Reaction Order

We will use this exothermic reaction as an example to illustrate the kinetics of various reaction orders:

H2 (g) + I2 (g) ⇌ 2HI (g)

This reaction can be set up as shown in the ChemReaX 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 reaction rate is set in the top right corner of the dashboard.

Temperature (T): 721 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 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	0.5	bars (moles/L if used as solute)	
Reactant #2 (R2)	I2 [gas]	1	0.6	bars (moles/L if used as solute)	
Reactant #3 (R3)	None	1	1		
Product #1 (P1)	HI [gas]	2	0	bars	
Product #2 (P2)	None	1	1		
Product #3 (P3)	None	1	1		

The ChemReaX results panel below shows the simulation results after clicking “Run the Reaction”:

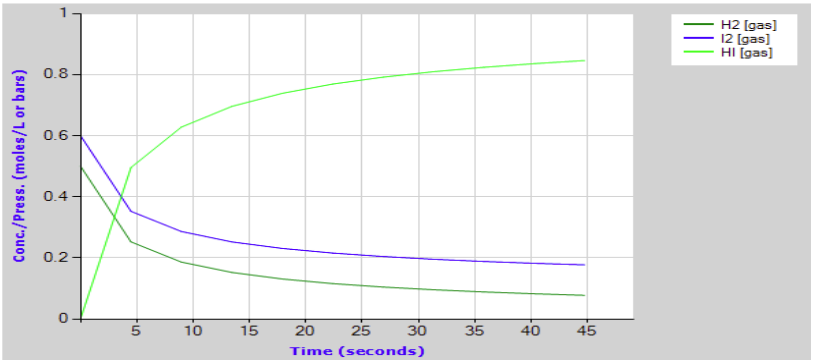
Thermodynamics: (@ T = 721.00 K)

Standard Enthalpy of Formation and Entropy	$\Delta_f H°(T)$ (KJ/mol)	$S°(T)$ (J/mol.K)	Reaction Thermodynamics & Equilibrium	Value	
H2 [gas]	12.37	156.49	Standard enthalpy change, $\Delta_r H°(T)$	-12.59	KJ
I2 [gas]	78.25	293.69	Standard entropy change, $\Delta S°(T)$	0.02	KJ
			Standard reaction free energy change, $\Delta_r G°(T)$	-23.83	KJ
HI [gas]	39.01	232.88	Reaction free energy change at initial composition, $\Delta_r G(T)$	-Infinity	KJ
			Equilibrium constant, K	5.322894e+001	

Data sources: NASA

Simulated Final State: (@ T = 721.00 K ; P = 1.00 X)

	Reactants, Products	Final Composition	Pressure-adjusted Composition	Units
R1	H2 [gas]	7.70668e-002	7.70668e-002	bars (moles/L if used as solute)
R2	I2 [gas]	1.77067e-001	1.77067e-001	bars (moles/L if used as solute)
R3				
P1	HI [gas]	8.45866e-001	8.45866e-001	bars
P2				
P3				



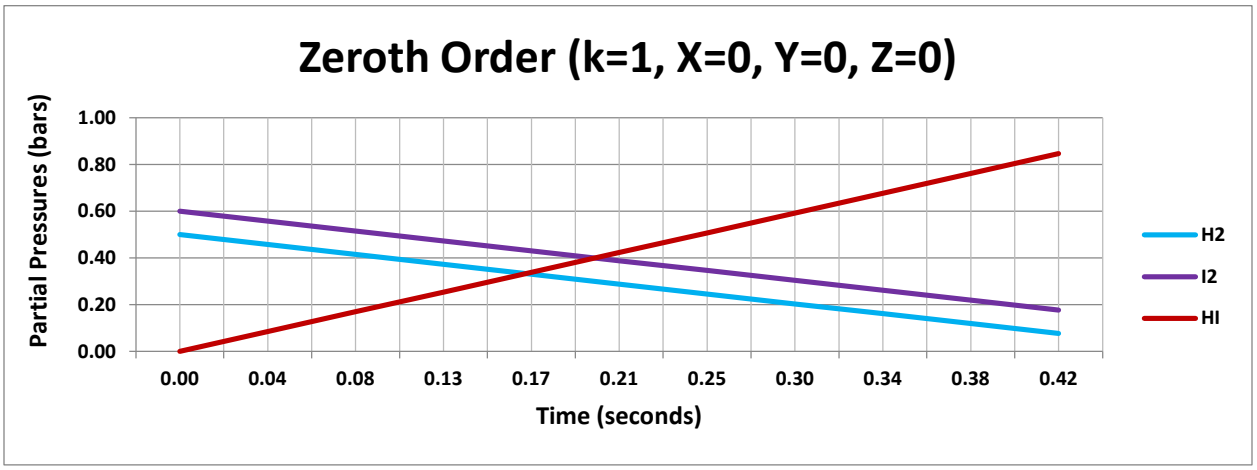
Copyright © 2017 by Science By Simulation. All rights reserved. Contact: info@sciencebysimulation.com

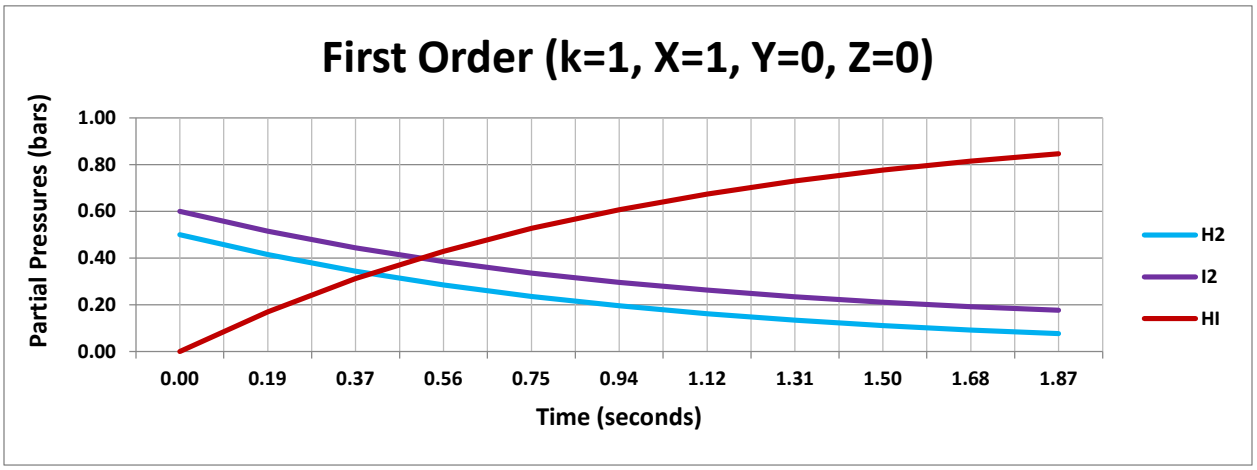
In addition to the final state and the kinetics chart above, ChemReaX also generates a detailed table of the simulated composition (partial pressures of the reactants and products in this case) over time as shown below. These tables can be copied and pasted into Excel spreadsheets for further manipulation and analysis. They are the sources of the data for all of the Excel graphing used in this article.

Simulated Kinetics (composition over time):

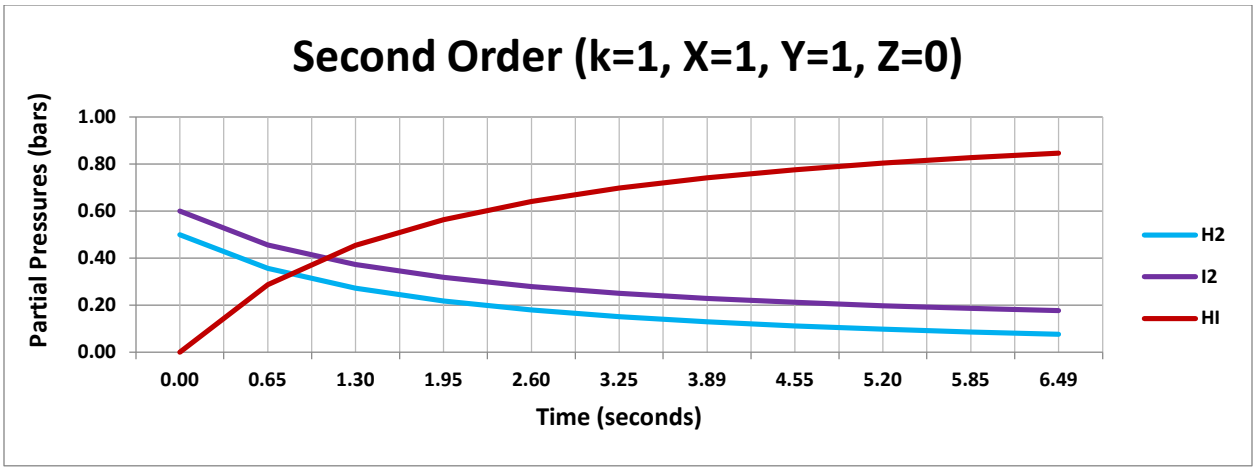
Time (seconds)	R1	R2	R3	P1	P2	P3
0.0000	5.00000E-001	6.00000E-001	0.00000E+000	0.00000E+000	0.00000E+000	0.00000E+000
4.4789	2.52211E-001	3.52211E-001	0.00000E+000	4.95578E-001	0.00000E+000	0.00000E+000
8.9520	1.86068E-001	2.86068E-001	0.00000E+000	6.27863E-001	0.00000E+000	0.00000E+000
13.4452	1.52020E-001	2.52020E-001	0.00000E+000	6.95960E-001	0.00000E+000	0.00000E+000
17.9301	1.30574E-001	2.30574E-001	0.00000E+000	7.38853E-001	0.00000E+000	0.00000E+000
22.3893	1.15570E-001	2.15570E-001	0.00000E+000	7.68860E-001	0.00000E+000	0.00000E+000
26.8634	1.04253E-001	2.04253E-001	0.00000E+000	7.91493E-001	0.00000E+000	0.00000E+000
31.3321	9.53715E-002	1.95371E-001	0.00000E+000	8.09257E-001	0.00000E+000	0.00000E+000
35.8268	8.81236E-002	1.88124E-001	0.00000E+000	8.23753E-001	0.00000E+000	0.00000E+000
40.3367	8.20808E-002	1.82081E-001	0.00000E+000	8.35838E-001	0.00000E+000	0.00000E+000
44.7469	7.70668E-002	1.77067E-001	0.00000E+000	8.45866E-001	0.00000E+000	0.00000E+000

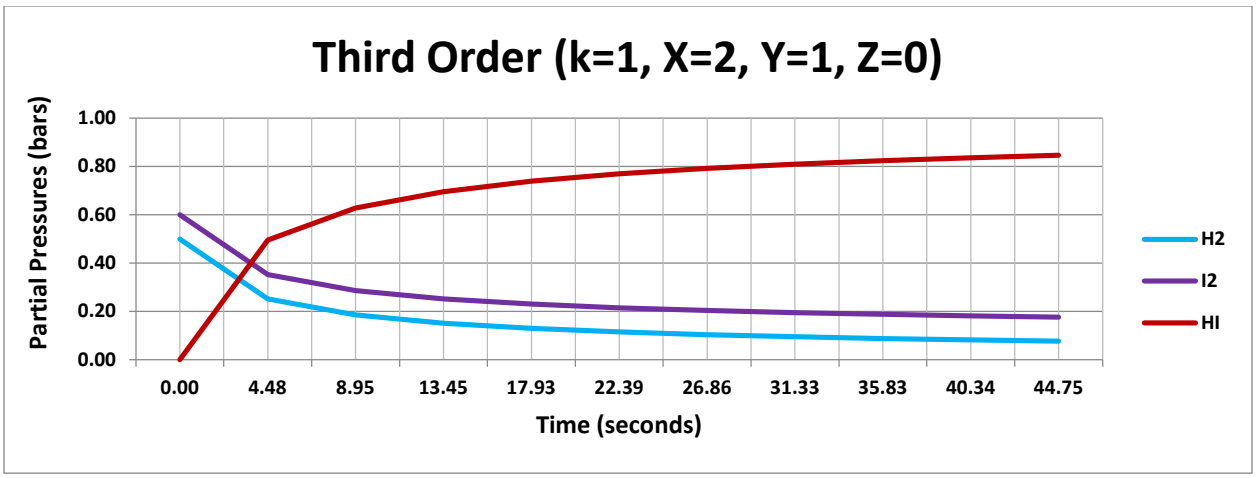
The reaction in the example above can be run with different values of X and Y to model various reaction orders (order = X + Y). The data from these runs have been graphed in Excel as follows to illustrate the same reaction simulated using reaction orders ranging from 0 to 3. As the reaction order increases, the shape of the curves change considerably. For higher orders, the slope of the concentration or partial pressure vs. time is sharper earlier on and then the rate of change slows down significantly leading to a long "tail". The time needed to reach the final state of the reaction increases with the reaction order.





Copyright © 2017 by Science By Simulation. All rights reserved. Contact: info@sciencebysimulation.com





Effect of the Rate Constant

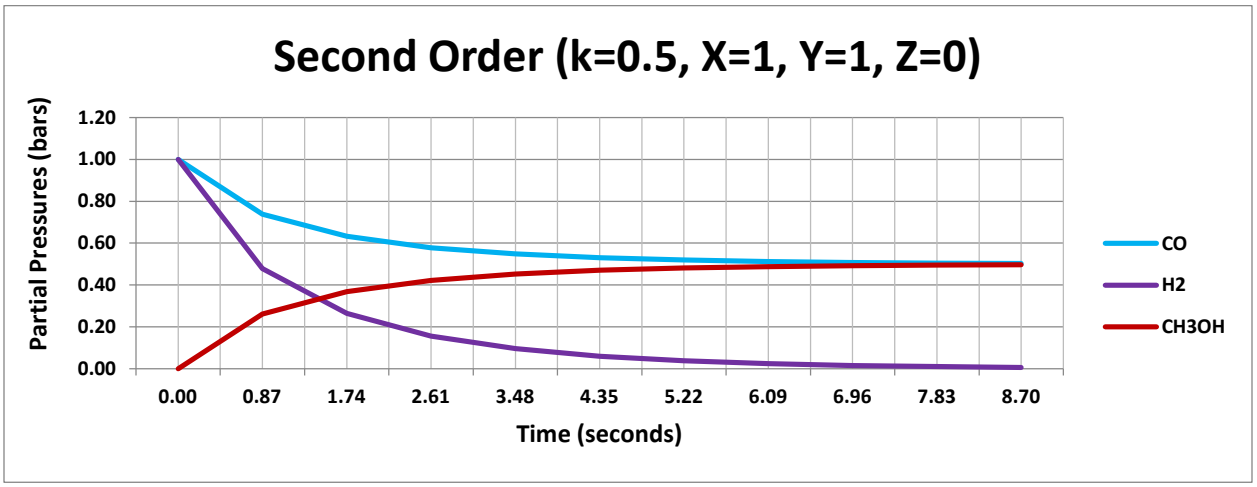
The rate constant k has a direct impact on how fast a reaction proceeds. Consider the exothermic synthesis of methanol from carbon monoxide and hydrogen, which has been set up in the ChemReaX dashboard below: **$CO\ (g) + 2H_2\ (g) \rightleftharpoons CH_3OH\ (g)$**

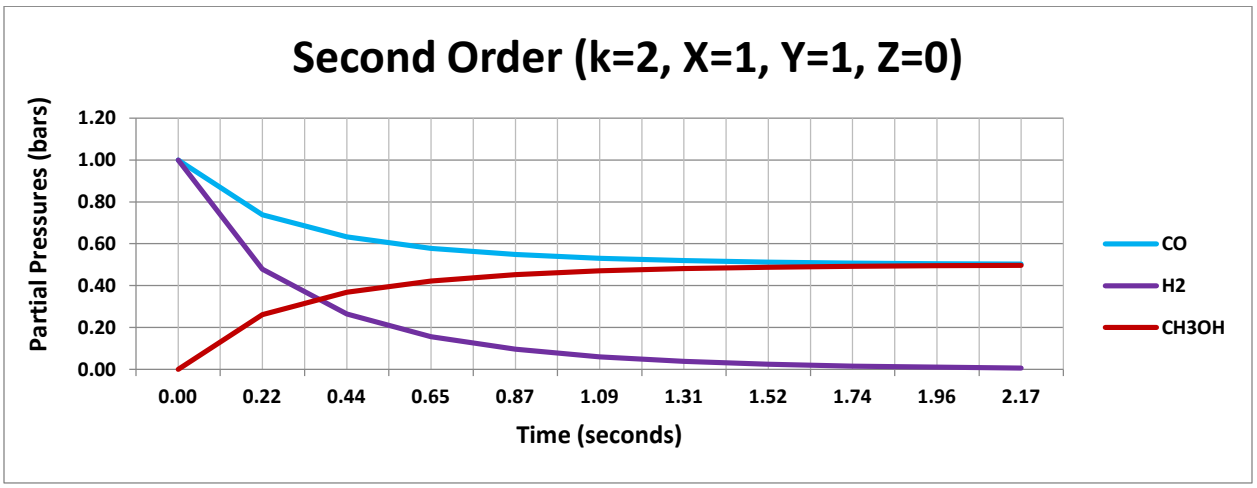
Temperature (T): 298.15 K
Pressure Factor (P): 1.0 X
Select Ionization Reaction
Buffer/Compound:
Formula Expansion:
Specify Reaction Rate Parameters
Rate Model: $R = k * [R1]^X * [R2]^Y * [R3]^Z$
k 1 X 1 Y 1 Z 0

Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	CO [gas]	1	1	bars (moles/L if used as solute)	
Reactant #2 (R2)	H2 [gas]	2	1	bars (moles/L if used as solute)	
Reactant #3 (R3)	None	1	1		
Product #1 (P1)	CH3OH [gas]	1	0	bars	
Product #2 (P2)	None	1	1		
Product #3 (P3)	None	1	1		

Copyright © 2017 by Science By Simulation. All rights reserved. Contact: info@sciencebysimulation.com

Based on data from running multiple simulations with values of the rate constant k, we can see from the graphs below that that the *reaction clearly speeds up as the rate constant increases*.





Copyright © 2017 by Science By Simulation. All rights reserved. **Contact: info@sciencebysimulation.com**

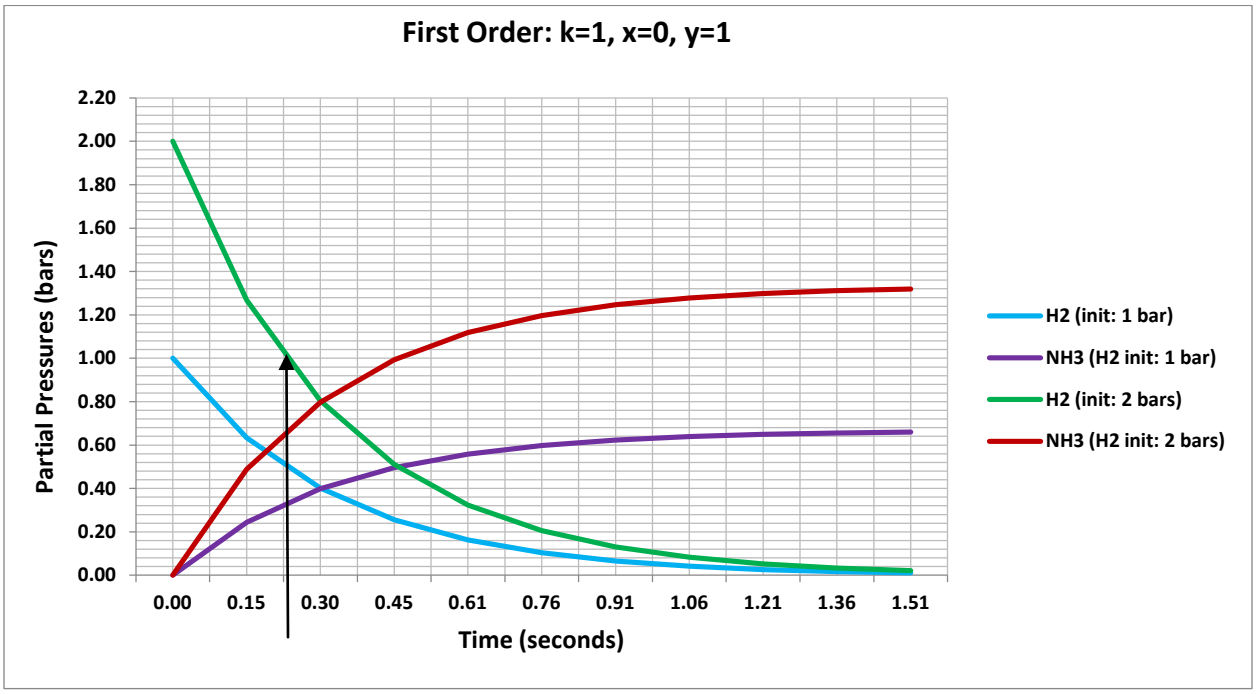
Half Lives of Reactants

We can now demonstrate the characteristics of the half-life of a reactant for first-order vs. higher-order reactions using the synthesis of ammonia as an example: **N2 (g) + 3H2 (g) ⇌ 2NH3 (g)**. This reaction has been set up in the ChemReaX dashboard below as a first-order reaction. H2 is the limiting reagent in this case, so we will use the partial pressure of H2 as one of the variables in our virtual experiment. The other variable is the order of the reaction (specifically the parameter Y in the rate model).

Temperature (T): 298.15 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 1 X 0 Y 1 Z 0

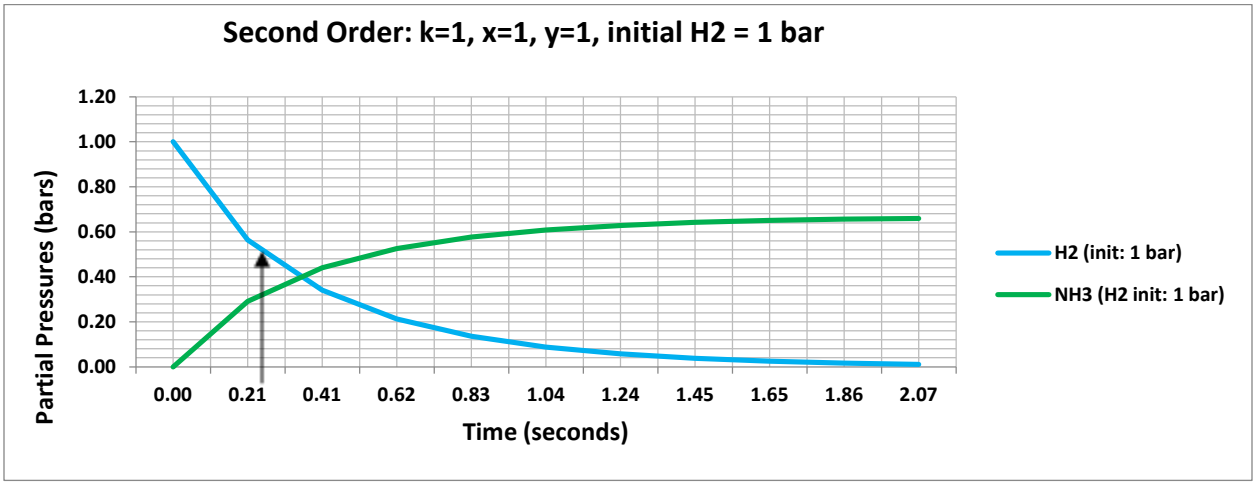
Select Reactants/Products	Species	Stoichiometric Coefficients	Initial Composition	Units	Exclude Pure Solids/Liquids from Reaction Quotient
Reactant #1 (R1)	N2 [gas]	1	1	bars (moles/L if used as solute)	
Reactant #2 (R2)	H2 [gas]	3	1	bars (moles/L if used as solute)	
Reactant #3 (R3)	None	1	1		
Product #1 (P1)	NH3 [gas]	2	0	bars	
Product #2 (P2)	None	1	1		
Product #3 (P3)	None	1	1		

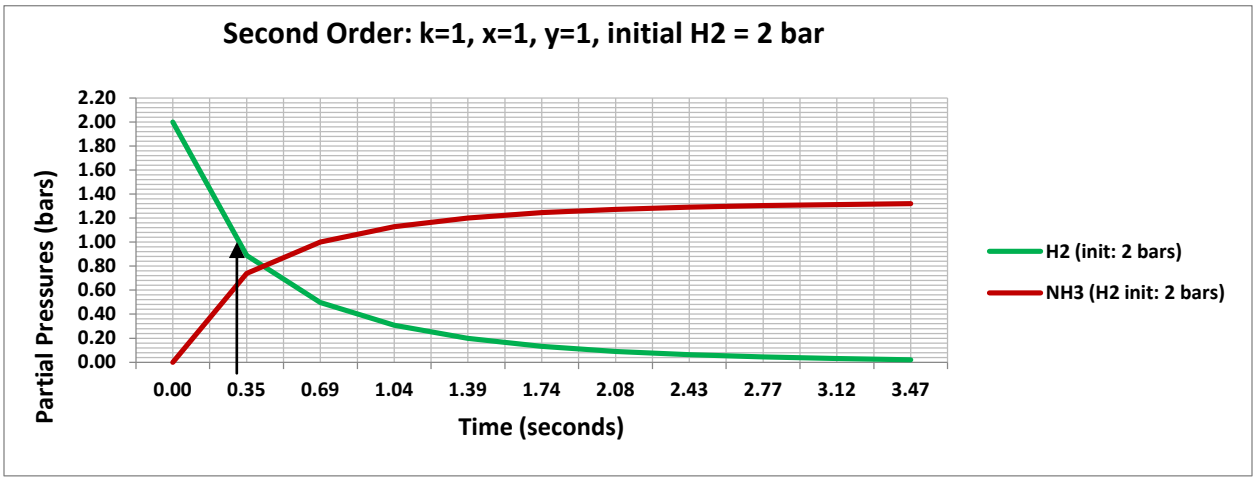
H2 is the limiting reagent in this case, so we will use the partial pressure of H2 as one of the variables in our virtual experiment. The chart below depicts the kinetics for a first-order reaction with the initial partial pressure of H2 at 1 bar and 2 bars. The half-life is the time taken for the partial pressure of H2 to reach half its initial value – it is clear from the curves that this occurs at about 0.225 second (indicated by the black arrow) *regardless* of the initial partial pressure of H2.



Copyright © 2017 by Science By Simulation. All rights reserved. Contact: info@sciencebysimulation.com

Now if we repeat the experiment as a second-order reaction, the results below show that the half-life of H2 *does* depend on the initial partial pressure of H2. By interpolation using the data table, it can be seem that the half lives are 0.266 second for an initial H2 partial pressure of 1 bar and 0.313 bar for an initial H2 partial pressure of 2 bars (both indicated approximately by black arrows in the charts below). The half life is larger for the case with a higher initial partial pressure.





Conclusion

We have used ChemReaX as a virtual lab to illustrate three specific concepts related to chemical kinetics: the reaction order, the rate constant, and the half lives of reactants. After running virtual experiments through simulation, we have used the data generated by the simulations to produce Excel charts for further analysis. This method of running multiple simulations and graphing the resulting data can provide students with significant additional insight into the subtleties of kinetics and other chemistry concepts that might otherwise remain highly theoretical. Additional investigations of kinetics and other topics can be undertaken through ChemReaX simulations using the examples and approach in this tutorial article as templates.

Copyright © 2017 by Science By Simulation. All rights reserved. **Contact: info@sciencebysimulation.com**

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.

Copyright © 2017 by Science By Simulation. All rights reserved.