

Chapter 2 Supplemental Exercises

The first exercise uses the Excel spreadsheet “A&E from Tmax with random T error.xls”

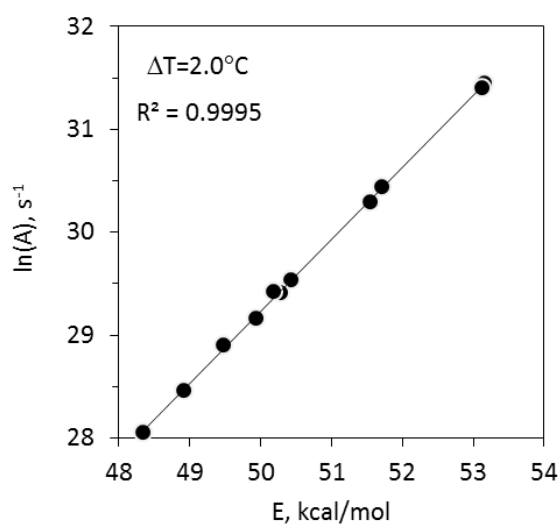
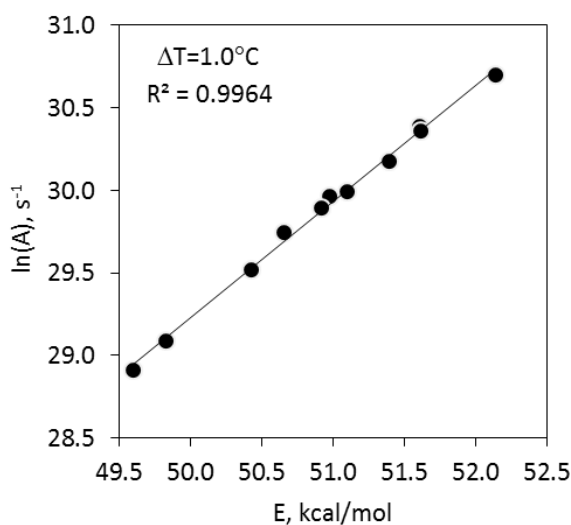
This spreadsheet uses Kissinger’s method to derive A and E from T_{\max} at 4 heating rates

1. In the A&E spreadsheet, change the default value of A to something within the range of 10^{12} to 10^{16} s^{-1} and the default value of E to something in the range of 45 to 60 kcal/mol.

(a) Construct three tables of A & E values derived for random temperature measurement errors (std. err.) of 0.3, 1.0, and 2.0 °C. Press F9 three times to ensure a new random sampling of the temperature errors for each std. dev. Record the predicted T_{\max} values for the reaction at heating rates of 3 °C/Myr and 10 °C/ms for each A-E pair. The following table and plot gives example results for $A=2 \times 10^{13} \text{ s}^{-1}$ and $E=52 \text{ kcal/mol}$ and a standard error of 1 °C.

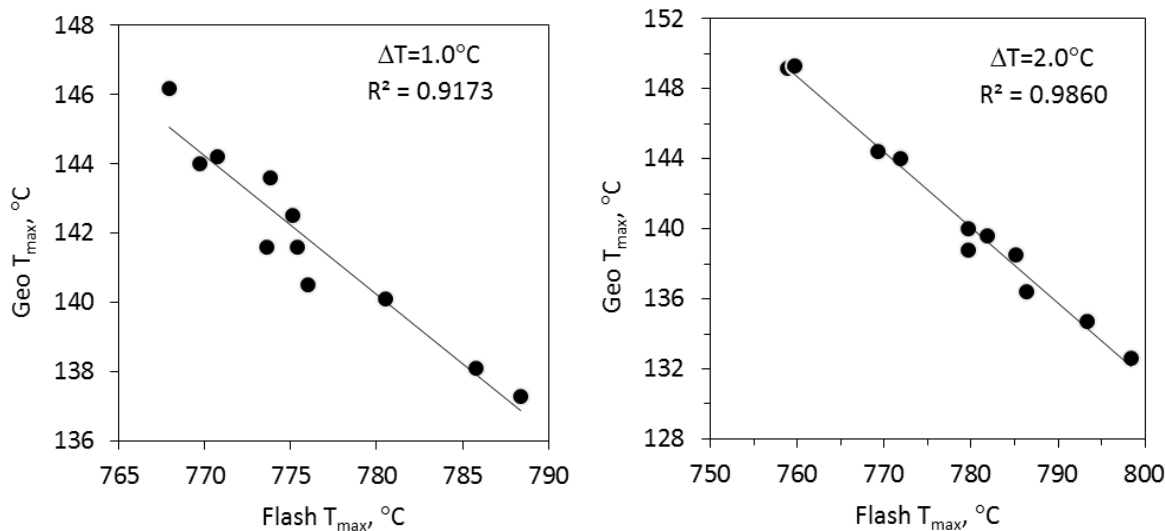
$A, \text{ s}^{-1}$	$E, \text{ cal/mol}$	Geo T_{\max}	Flash T_{\max}
1.57e13	51609	144.0	769.7
4.30e12	49828	138.1	785.8
1.53e13	51618	144.2	770.7
1.27e13	51393	143.6	773.8
6.58e12	50422	140.1	780.5
1.06e13	51103	142.5	775.1
1.03e13	50975	141.6	773.6
3.60e12	49595	137.3	788.4
9.58e12	50916	141.6	775.4
2.15e13	52142	146.2	767.9
8.29e12	50657	140.5	776.0

- (b) Plot the value of $\ln(A)$ or $\log(A)$ versus E and calculate the correlation coefficient. What does the correlation coefficient tell you about the relationship between A and E ?



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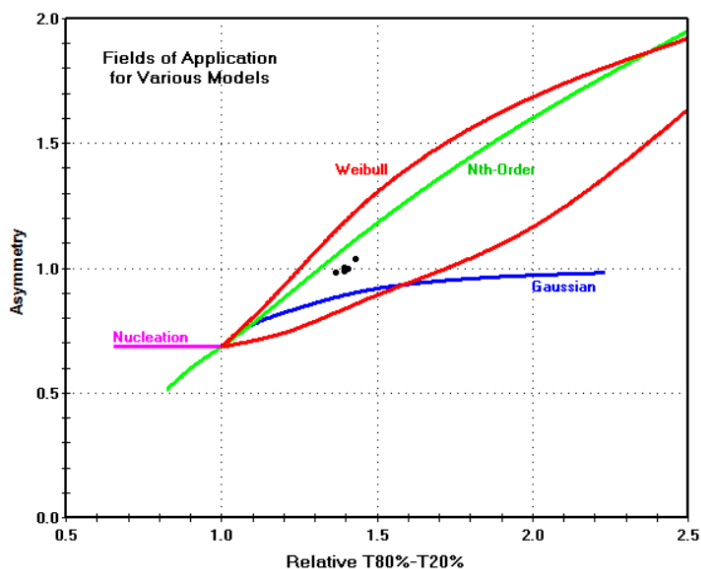
- (c) The 1-2-3 rule says that an error of 1 kcal/mol in E can be compensated by a twofold change in A and causes a shift in the calculated $\text{Geo } T_{\max}$ by 3 °C. Use the results in your tables to quantify the accuracy of that rule.
- (d) Plot the $\text{Geo } T_{\max}$ versus the Flash T_{\max} . Why does it have a negative slope? How does the slope vary with the standard error in measured T ?



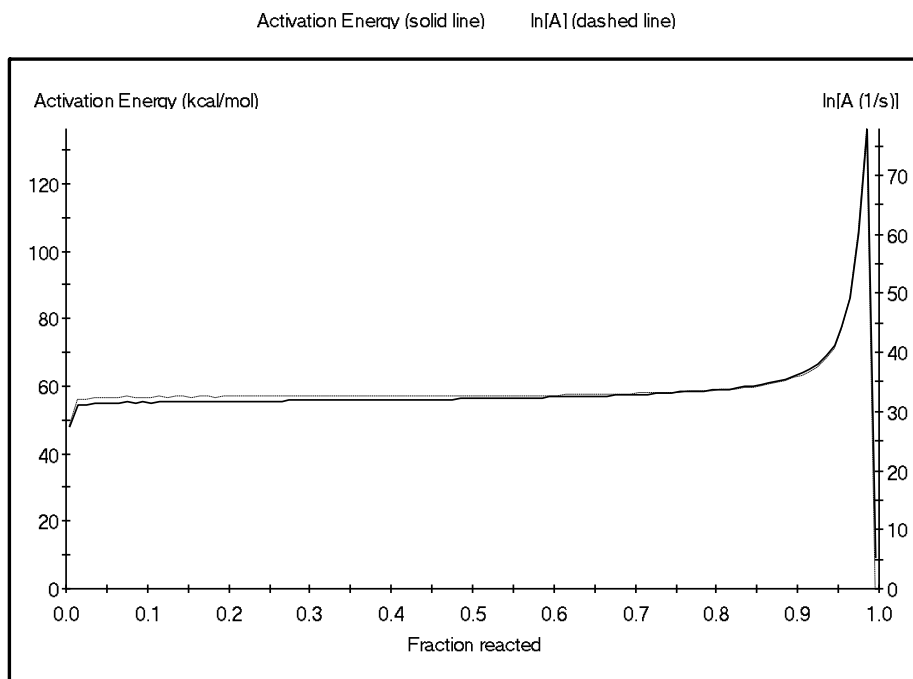
The following exercises use Kinetics2015 for kinetic analysis

2. The following questions relate to analysis of the Chapter 2 “Distributed reactivity syndata”.

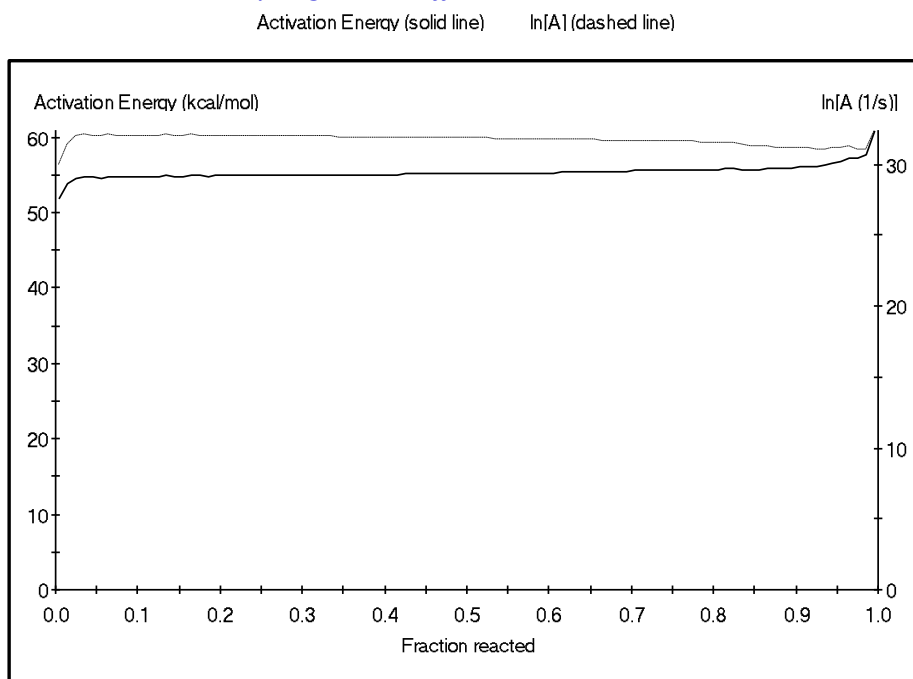
(a) Analyze the data without a baseline correction using the isoconversional method and fraction reacted per unit time. In the lower-left corner of the first step in the analysis, click the box labeled “Model Guide”. Where do the data points plot in terms of suggested models?



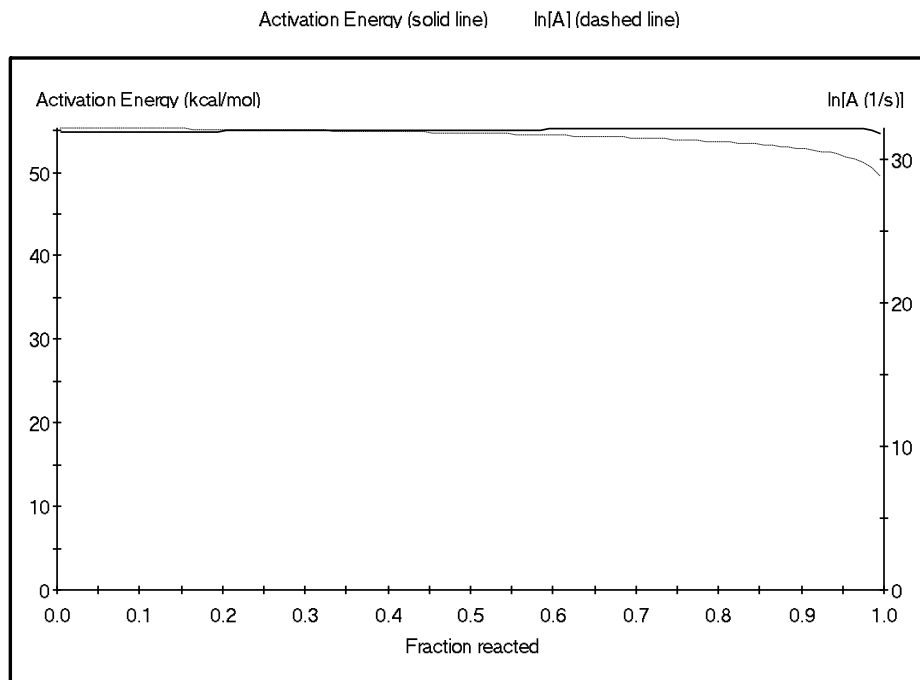
(b) After completing the analysis, plot A and E versus conversion. How would you interpret the A & E changes in the last 5% of conversion?



(c) Make a baseline correction to all the data and reanalyze. First look at the model guide plot. How have the dots shifted? Complete the isoconversional analysis. How does your plot of A and E compare to the one I did? Why might it be different?

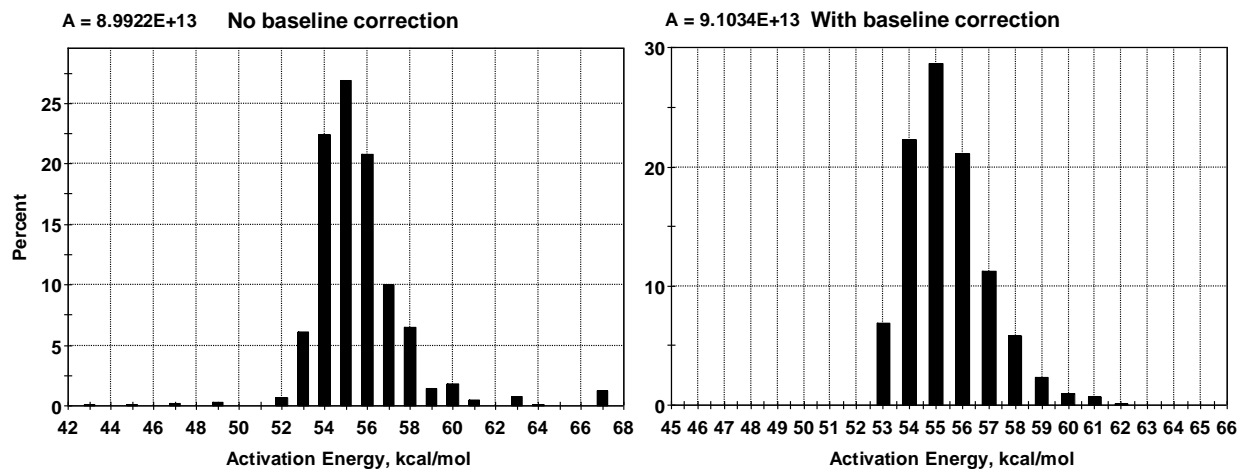


(d) The chemical reaction model used to make the syndata used $n=1.7$ and $\sigma=1.0\%$ of E_0 . Without added noise and baseline, the dots on the model guide plot are much closer to the n th-order line than the Gaussian line. The plot of A and E versus conversion is as follows:



Why does A drop significantly in this plot? (Hint: what mathematical distribution is related to a pseudo- n th-order reaction and what are the implications of having such a distribution?)

(e) Now analyze the data with and without baseline correction to the discrete activation energy model and compare the resulting histograms.

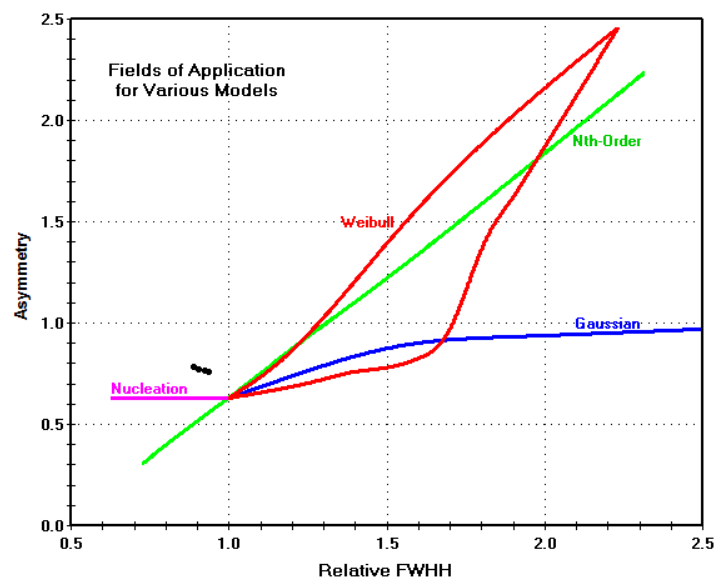


*What causes the activation energy contribution at 67 kcal/mol without a baseline correction?
 Given that 1% of 55 kcal/mol is 0.55 kcal/mol, what is the major contributor to the activation energy distribution after baseline correction?*

- The following exercise uses simulated data calculated from a sequential reaction model with added noise. Read the data files entitled "Sigmoidal syndata x cpm" one at a time into Kinetics2015 using the data command and trim the high and low temperature data, leaving at least 40 °C of near-baseline data above and below the reaction. Note that the rate data have been normalized, so they are properly considered as relative reaction rates.*

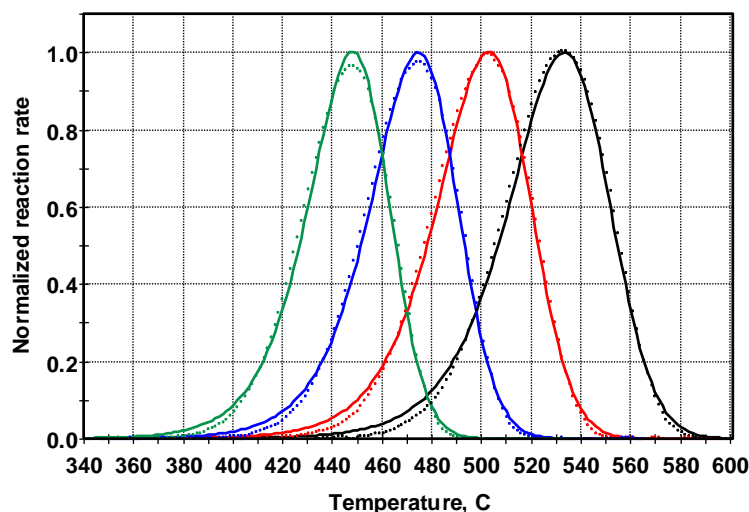
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- (a) Analyze the data with the parallel nucleation-growth Gaussian model, which has the most flexibility of the parallel reaction models. Base the kinetic analysis on reaction rates. In the first appearing screen after the analysis setup, check out how constant the activation energy and frequency factor are for the Friedman analysis. Then click on the “model selection” box. Do you see a graph similar to this one?

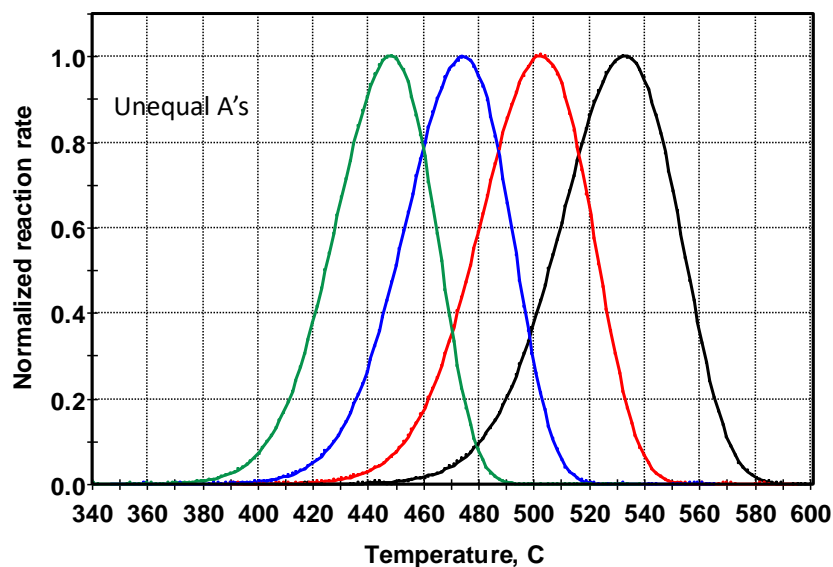


Is there any evidence for needing an activation energy distribution model?

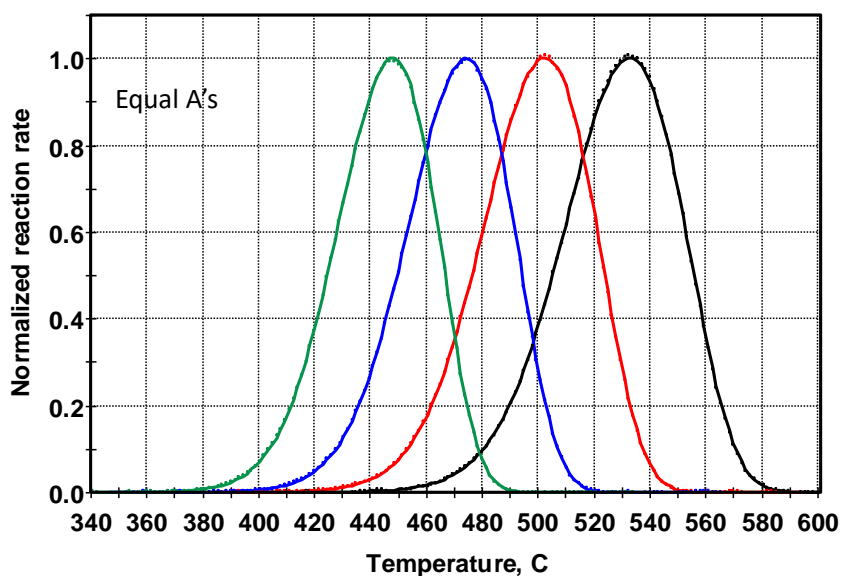
- (b) Fit the data with the nucleation-growth model, with $n=1$ and with n optimized, for $q = 0.99$ and 0.9999 . Create a table with the results from the four fits, including the residual sum of squares for both rates and cumulative reacted. Which parameters give the best fit? Does your best fit look something like this?



- (c) Fit the data to a sequential reaction model. Use the Alternate Pathway option with $A_1=1$ and $E_1=50$ (this makes k_1 negligible for A to C), and do not refine those parameters. Hint: $k_2 > k_3$, both A's are between 5×10^{12} and $5 \times 10^{13} \text{ s}^{-1}$, and both E's are between 48 and 55 kcal/mol. Your fit should look like this, with very small differences between the data and fit:



- (d) Use the A and E parameters from the fit in (c) to calculate the value of q at 450 °C using the relation immediately following eqn 2.38. How does it compare to the best fit parameters derived in (b)? What does that say about the physical interpretation of the fitted parameters?
- (e) Fit the data to a sequential reaction model entering the same initial value for A_2 and A_3 so that they are tied together during the regression analysis. How do the residuals compare to the model fitting separate A values for k_2 and k_3 . Your fit should look like this:



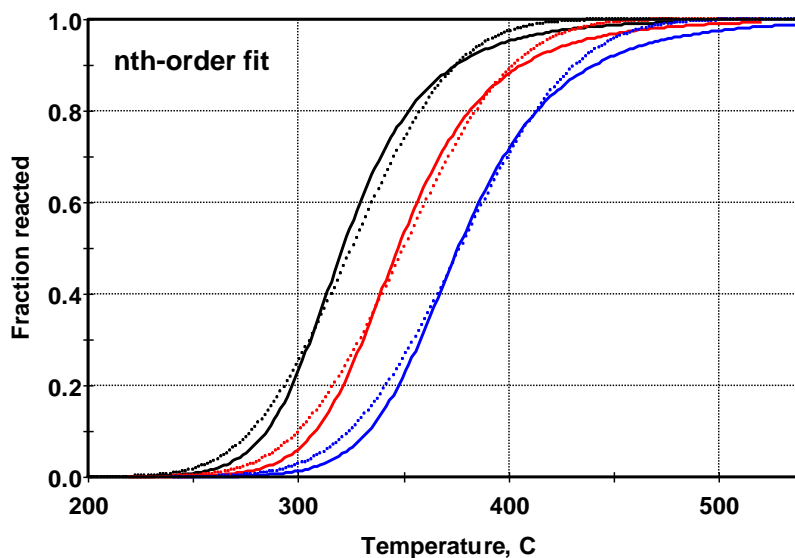
- (f) How do the fits for the sequential models compare to the fit to the nucleation-growth model? Given that real data is never a simple sequential model, that the nucleation-growth model is less likely to fall into a false minimum during non-linear regression, and that the nucleation-growth model can fit multiple peaks, be aware that what one learns from fitting simulated data must be used with caution for real systems.

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4. The Weibull distribution is a versatile distribution that is occasionally mentioned but rarely used for activation energy distributions. This exercise explores the relationships among the Weibull distribution, the Gaussian distribution, and a pseudo-nth-order reaction.

- (a) Using the `apply` command in *Kinetics2015*, create simulated cumulative (fraction reacted) data for $A=4 \times 10^{13} \text{ s}^{-1}$, $E=46 \text{ kcal/mol}$, $\eta=8 \text{ kcal/mol}$, and $\theta=3$. Use heating rates of 1, 5, and 25 °C/min for appropriate limits with 200 and 550 °C. Be sure to include enough significant figures in the input files.
- (b) Fit the constant heating rate data to nth-order, Gaussian, and nth-order-Gaussian models and complete the following Table. Show the fraction reacted plots for all three fits (the nth-order fit is shown as an example).

Model	A, s^{-1}	$E, \text{kcal/mol}$	n	$\sigma, \% \text{ of } E$	Cum r.s.s.
nth-order	6.06e12	42.48		---	0.356
Gaussian	4.13e13		---	5.75	0.054
nth-order Gaussian		45.99	1.56	5.24	0.025



- (c) Using the `Apply` command in *Kinetics2015*, create simulated cumulative (fraction reacted) data for $A=4 \times 10^{13} \text{ s}^{-1}$, $E=46 \text{ kcal/mol}$, $\eta=1 \text{ kcal/mol}$, and $\theta=1$. Use heating rates of 1, 5, and 25 °C/min for appropriate limits with 200 and 550 °C.
- (d) Fit the constant heating rate data to nth-order, Gaussian, and nth-order-Gaussian models and complete the following Table. Show the fraction reacted plots for all three fits.

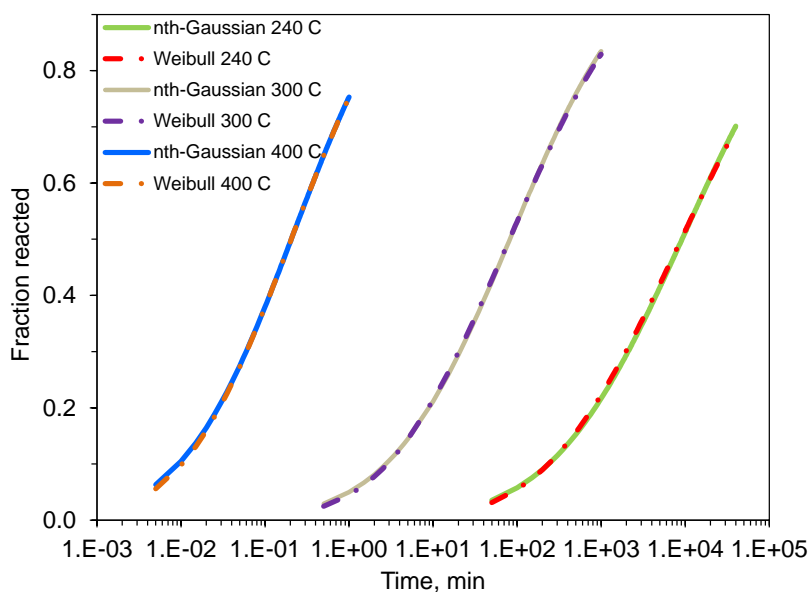
Model	A, s^{-1}	$E, \text{kcal/mol}$	n	$\sigma, \% \text{ of } E$	Cum r.s.s.
nth-order					
Gaussian	4.70e13		---	1.87	0.0241
nth-order Gaussian	5.95e13	45.73	1.44	0.10	0.0082

- (e) Explain the relative sensitivities of the residual sums of squares in the tables of parts (b) and (d) to n and σ in view of Figure 4 of Burnham and Braun, *Energy & Fuels* **13**, 1-22 (1999).

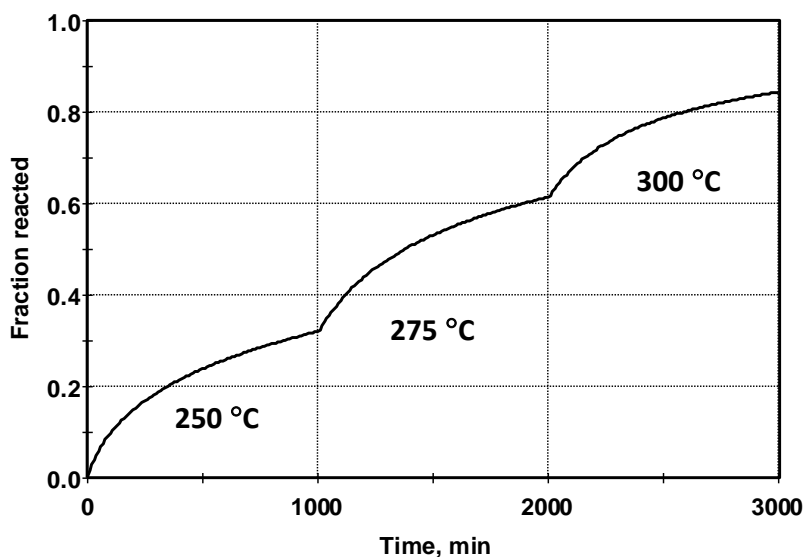
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5. The following exercise uses the Apply mode in Kinetics2015 to explore distributed reactivity models under isothermal conditions.

(a) Use the parameters in Supplemental Exercise 4(a) in the Kinetics2015 Apply mode to calculate the fraction reacted versus time for isothermal temperatures of 240, 300, and 400 °C for 4×10^4 min, 10^3 min, and 1 min, respectively. Next, use the parameters from the nth-order Gaussian model to calculate the fraction reacted at the same conditions. Create a plot comparing the two models, using logarithmic time on the abscissa. (Note: Kinetics2015 reports 100 points per simulation, so I created two overlapping simulations to get more resolution at short times.) What do you conclude from the close match of the two models?

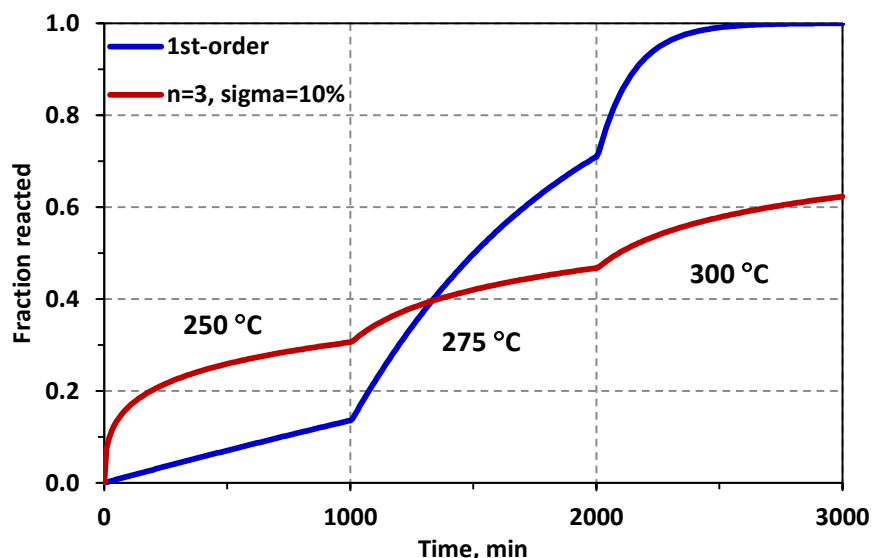


(b) Calculate the fraction reacted for the Weibull model for successive thermal segments of 1000 minutes at 250, 275, and 300 min. This can be accomplished in the Kinetics2015 Apply mode by reading in an arbitrary thermal history file.



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- (c) Repeat the successive thermal segment calculation with a first-order reaction having $A=4 \times 10^{13} \text{ s}^{-1}$ and $E=46 \text{ kcal/mol}$ and for an n th-order Gaussian reaction with the same A and E and $n=2$ and $\sigma=10$. Plot the fraction reacted as a function of time and compare to the figure from part (b). What is the primary characteristic that differentiates distributed reactivity models from a first-order model for successive isothermal treatments at increasing temperatures?

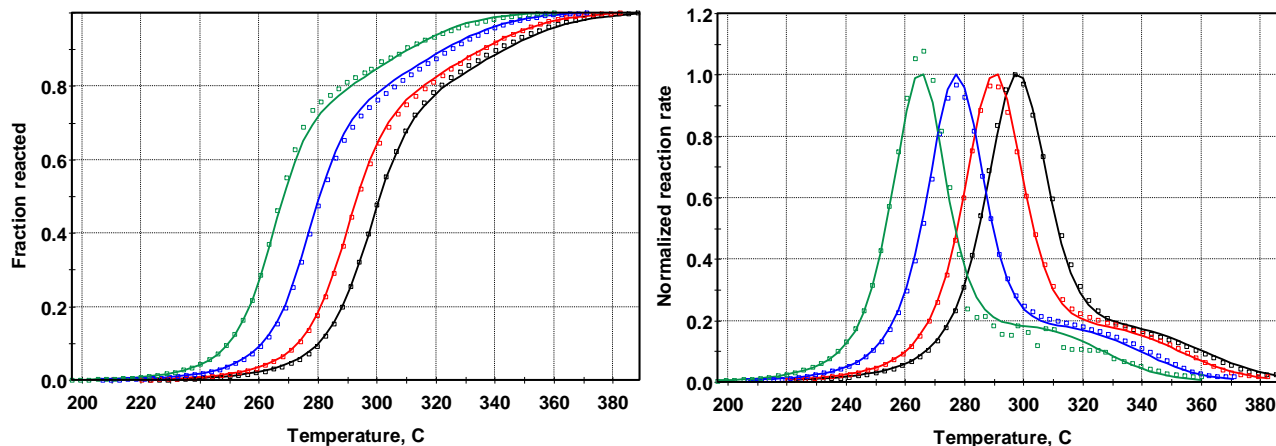


- (d) Look up Huang (*Org. Geochem.* 24, 233-241, 1999) and Burnham (*Chem. Eng. J.* 108, 47-50, 2005). Describe the implications of the plots in parts (b) and (c) for the type of models appropriate for these two reaction systems.

6. Polyvinyl Chloride (PVC) is a char-forming polymer that has both similarities to well-preserved algal kerogens. The following calculations show some of those reaction characteristics. The PVC data in the polyvinyl chloride folder of chapter 2 exercise data were kindly provided by Professor Luis Pérez-Maqueda of the Institute of Science and Materials of Seville, Spain.

- (a) Fit the data to an isoconversional reaction model. Plot E and the effective first-order A as a function of conversion. At what fraction reacted does T_{\max} occur and at what fraction reacted does the activation energy have a minimum? At what fraction of the reaction before the minimum does T_{\max} occur, and how does that compare to the value for a first-order reaction? Propose an explanation for why the activation energy declines over the first portion of the reaction.
- (b) Fit the data to two parallel reactions, one nucleation-growth reaction and an n th-order Gaussian distribution. Try a few different values for q , e.g., 0.99, 0.999, 0.9999. Don't try to minimize too many parameters at once, and gradually converge on a best fit. Try a few different values for q . Your best fit should have cum r.s.s ≤ 0.02 . Your fits should look something like:

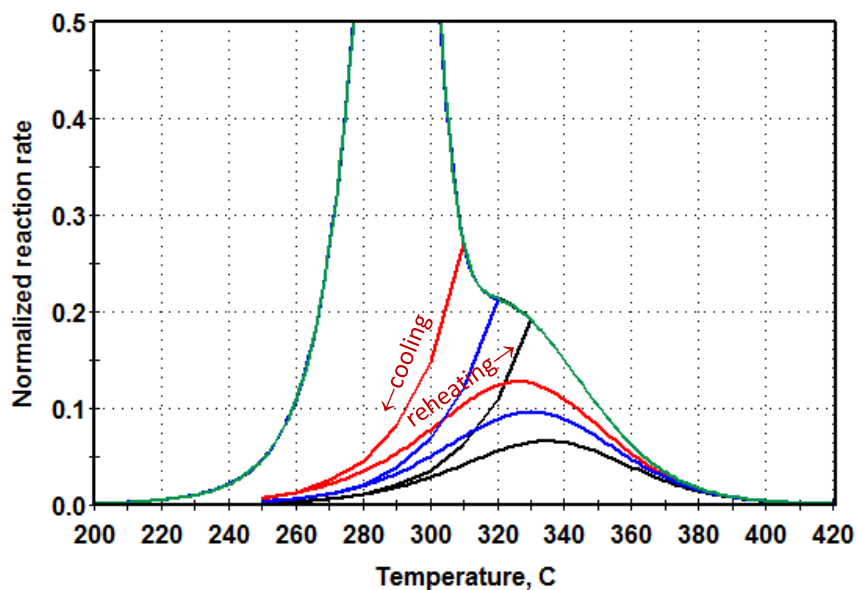
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Create a table of model parameters, including values for n constrained to one and σ constrained to zero for the char devolatilization.

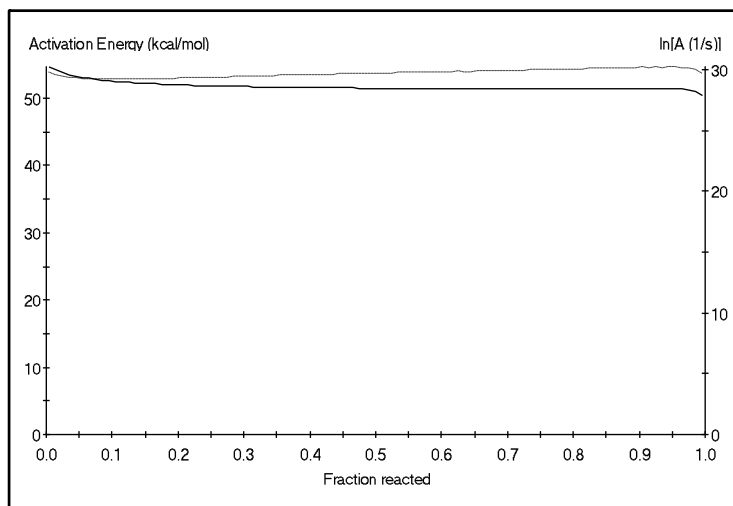
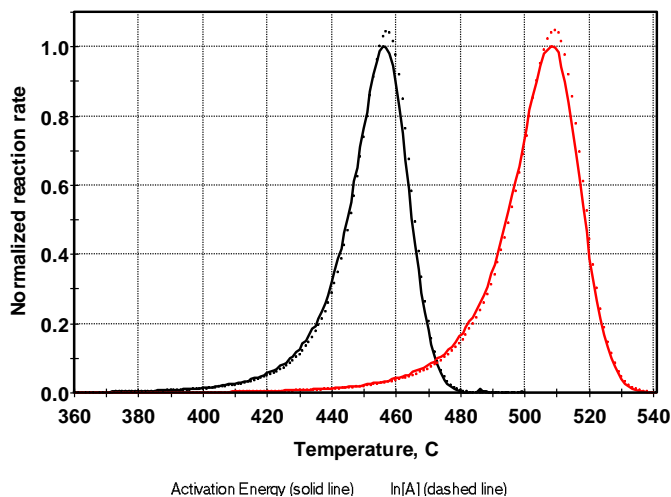
Char Model	$f1$	$A1, s^{-1}$	$E1, \text{kcal/mol}$	$m1$	$n1$	q	$A2, s^{-1}$	$E2, \text{kcal/mol}$	$n2$	$\sigma, \% \text{ of } E2$	Cum r.s.s.
n th-order											
Gaussian											
n th-Gauss											

(c) One of the characteristics of a distributed reactivity model is that T_{max} of the residual material increases if the sample is partially reacted, cooled, and then reheated at a constant heating rate. React the n th-order and Gaussian models from (b) using the Kinetics2015 Apply mode at the following heating schedules: Heat to 310, 320, 330, 340, 350, and 360 at 10 °C/min, cool to 250 °C at 100 °C/min, then heat again at 10 °C/min to 420 °C. You should get a series of six plots like the three shown below. Determine T_{max} for each of the reheating phases. Plot T_{max} versus the maximum temperature of the first heating for each of the three models. What similarities and differences do you see?



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7. Use the sequential Gaussian and Nucleation-Growth model in the Apply mode to create simulated data to explore the character of the traditional autocatalytic reaction, which is achieved using limit [3] of that model. Enter initial value of one for B and a fraction of one for C in the optimize line.
- (a) Create synthetic data from 340 to 550 °C at 2 and 25 °C/min using $A_2=A_3=1 \times 10^{13} \text{ s}^{-1}$, $E_2=55 \text{ kcal/mol}$, and $E_3=51 \text{ kcal/mol}$. Extract the time-temperature-rate data at each heating rate and analyze by the isoconversional method. You should get plots like this:



How does the derived A value correspond to the one used for the data creation? Why does E decrease as the fraction reacted increases?

- (b) Analyze the synthetic rate data with the nucleation-growth model for $q=0.99$, 0.999 , and 0.9999 . Complete the following table:

q	A, s^{-1}	$E, \text{kcal/mol}$	n	m	Rate r.s.s.
0.99					
0.999					
0.9999					

Which value of q has the lowest residuals? Calculate q from k_2 and k_3 and explain why the value of q in the table having the lowest residuals has the lowest residuals.

- (c) Change A_2 to $1 \times 10^{12} \text{ s}^{-1}$ and repeat (a) and (b).

Chapter 4 Supplemental Exercises

The following exercises use Kinetics2015 for kinetic analysis. Fit to rates. You can use either equal weighting of points or files as you choose—you will get a slightly different answer.

1. *Analyze the bituminous coal, type II organic matter, and type II-S organic matter data using nth-order, Gaussian E, and Discrete E distribution models. Fill in the following Table for each sample (3 tables; as a help, I have inserted some answers for the type II shale):*

Model	E parameter	kcal/mol	A, s ⁻¹	n	σ	r.s.s.
Friedman	E at 50% conv.		6.34e14	1	0	---
Kissinger	E for T _{max}			1	0	---
nth-order	E	51.89			0	0.127
Gaussian E	Mean E			1		0.147
Discrete E	Primary E	53.00		1	0	0.006

For the bituminous coal, add two lines for a fit to two parallel Gaussian models.

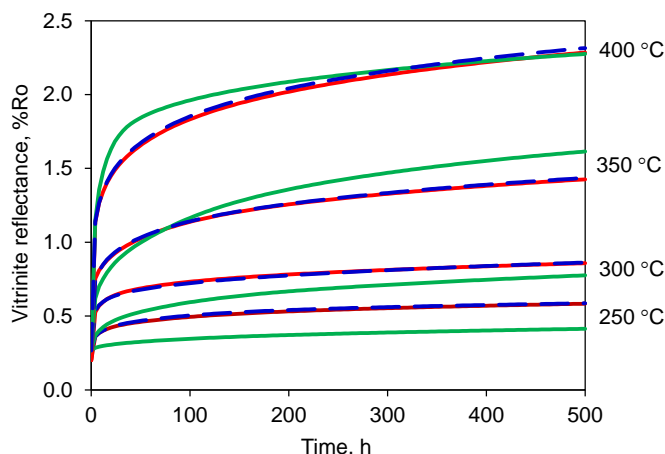
2. *Analyze the polyethylene and boghead coal data using serial (alternate pathway option) and nucleation-growth models. Constrain n to 1 and sigma to zero. Also for the latter, enter A=10 and E=50 for the A→C reaction and do not refine to eliminate that reaction from the fit. Enter the same initial A value derived from Kissinger's method for each of the two steps in the serial model so that they will be constrained to be equal on the first optimization attempt. Then let the two A values be different and enter the most plausible parameters. Fill out the following table for each sample (2 tables):*

Model	E parameter	kcal/mol	A, s ⁻¹	n	σ	m	Rate r.s.s.
Friedman	E at 50% conv.						
Kissinger	E for T _{max}						
Serial A→B	E ₂						
Serial B→C	E ₃						
Serial A→B	E ₂						
Serial B→C	E ₃						
Nucleation-growth	E						

Chapter 6 Supplemental Exercises

The following exercise uses the Easy%Ro 2016 and Vitrimat 2016 spreadsheets at extras.springer.com.

1. Three algorithms exist in the Easy%Ro and Vitrimat programs to calculate vitrinite reflectance.
 - (a) Calculate reflectance as a function of time for 0 to 576 h in 4 h increments with both programs for $T=250, 300, 320, 340, 360, 400$, and $450\text{ }^{\circ}\text{C}$. The algorithms require non-zero difference in temperature for successive points, so increment the temperature by $0.0001\text{ }^{\circ}\text{C}$ each time step. Plot the Easy%Ro and two Vitrimat values versus time for the various temperatures. A similar plot is given here:



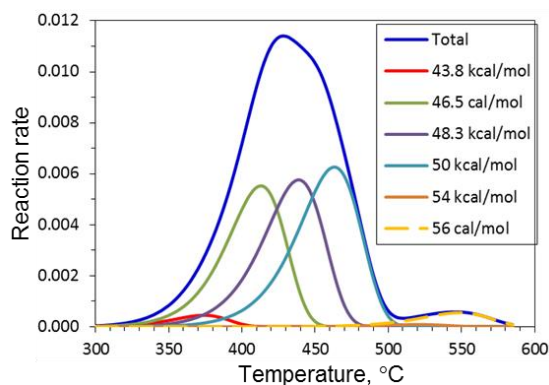
- What is the general form of all curves? How do the three algorithms compare in more detail?*
- (b) Plot the results from three algorithms as a function of temperature for $t=24, 72, 144$, and 288 h .
 - (c) Plot H/C versus O/C from Vitrimat for $50,000\text{ h}$ at $300\text{ }^{\circ}\text{C}$ and 125 h at $400\text{ }^{\circ}\text{C}$. Is there any significant difference?

The following two exercises use PMod2 for simulation and Excel for plotting.

2. Enter into PMod2 the full Behar mechanism for Type II kerogen in Tables 6.9 and 6.10. Run the calculation for a closed system heated at $2\text{ }^{\circ}\text{C/h}$. Show a plot of total kerogen, DCM-NSOs, C5-NSOs, HC1, HC2, and non-HC gas versus temperature and versus vitrinite reflectance. For the latter, you should get curves similar to those in Figure 7.9, although species have been grouped to show trends other than the individual species. There are two factors you must consider if you want to compare to Behar's data.
 - (1) You need to decide on whether you want to consider the insoluble product of kerogen decomposition as another kerogen or a coke. Either convention is OK as long as you remember what you did and make the proper interpretation of the species. However, an enhanced Pepper-Corvi expulsion model would allow you to choose different sorption coefficients for kerogen and coke, so expulsion using such a model could differ depending on which convention you use.
 - (2) The presence of pyrite means that the sample is not strictly kerogen and has other gas-producing reactions ($\text{FeS}_2 \rightarrow \text{FeS}$). Whether you choose to consider pyrite as unreactive kerogen or a mineral diluent will affect your plots a little. The most rigorous way would be to include it as a mineral species and include reaction parameters for its conversion. Explain how you decided to deal with pyrite.

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3. Run the same mechanism at 2 °C/h in an open system. Be sure to make DCM-NSO nonvolatile.
- (a) Show a graph of Rock-Eval parameters S1, S2, PI and T_{max} versus temperature.
- (b) Why is HC2 zero?
- (c) Show a graph of Rock-Eval parameters S1, S2, and T_{max} versus temperature.
- (d) Why does S1 have the value it has, and what is the corresponding value of PI?
- (e) Is the reported T_{max} on the Rock-Eval temperature scale?
- (f) Use Excel or some other program to create a plot similar to the following for the rate of decomposition for kerogen and each of its components, but at a heating rate of 25 °C/min. How do the T_{max} values of the individual components correspond to the jumps in T_{max} shown in the plot from (c)?



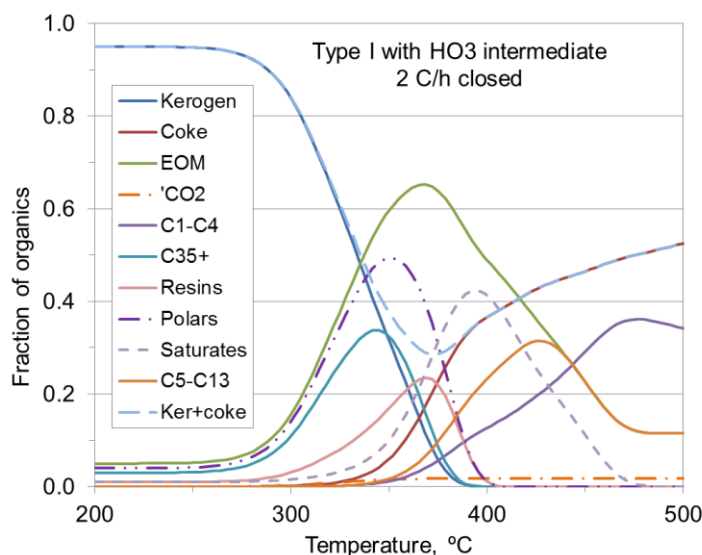
4. The following is a moderately complex compositional model for Green River oil shale. Enter the following mechanism into PMod2. Use an initial mass fraction of 0.05 for KER1, 0.35 each for KER2 and KER3, 0.03 for HO3, 0.01 each for MO3 and MO1.

Rxn	Reactant	fi	Ai	Ei	Products									
1	KER1				MO1	CO2	CH4	COKE1						
	k1	0.3	5.00E+13	48	0.5	0.35	0.03	0.12						
	k2	0.5	5.00E+13	50	0.5	0.35	0.03	0.12						
	k3	0.2	5.00E+13	52	0.5	0.35	0.03	0.12						
2	KER2				HO3	COKE1								
	k4	0.25	5.00E+13	47	0.8	0.2								
	k5	0.5	5.00E+13	49	0.8	0.2								
	k6	0.25	5.00E+13	51	0.8	0.2								
3	KER3				MO3	MO1	LO1	CHx	CH4	COKE1				
	k7	1	5.00E+13	53	0.4	0.25	0.06	0.02	0.02	0.25				
4	HO3				MO3	MO1	LO1	CHx	CH4	COKE1				
	k8	1	5.00E+13	53	0.4	0.25	0.06	0.02	0.02	0.25				
5	MO3				MO1	LO1	LO2	CHx	CH4	COKE1				
	k9	1	5.00E+13	54	0.25	0.2	0.1	0.1	0.05	0.3				
6	MO1				LO1	LO2	CHx	CH4	COKE1					
	k10	1	5.00E+13	57	0.35	0.2	0.1	0.05	0.3					
7	LO1				CHx	CH4	COKE1							
	k11	1	2.00E+13	58	0.5	0.2	0.3							
8	CHx				CH4	COKE1								
	k12	1	1.00E+13	61	0.7	0.3								
9	COKE1				CH4	COKE2								
	k13	0.4	5.00E+13	56	0.9	0.1								
	k14	0.3	5.00E+13	59	0.9	0.1								
	k15	0.2	5.00E+13	62	0.9	0.1								
	k16	0.1	5.00E+13	65	0.9	0.1								

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(a) Calculate the reaction in a closed system at 2 °C/h. Make a plot similar to that in Supplemental Exercise 2 using the formal variable names.

(b) In the following plot, I have regrouped some of the species in other ways that chemical analyses are performed. The following definitions apply: HO3=C35+, Resins=MO3, EOM=HO3+MO3+MO1+LO1+LO2, Polars=HO3+MO3, Saturates=MO1+LO1, C5-C13=LO1+LO2, and C1-C4=CH4+CHx.



Why does the sum of kerogen plus coke go through a minimum, and how does it compare to the various results in Figure 6.20?

(c) Make the corresponding plot using vitrinite reflectance as the abscissa. How does the kerogen plus coke yield compare to the various results in Figure 6.20? At what reflectance do polars and saturates have their maximum concentrations, and how do they compare with results in Figure 6.19? At what reflectance do EOM and C5-C13 have their maximum concentrations, and how do they compare to the results in Figure 6.15? What is the remaining oil species at 500 °C, and how does it relate to the results in Figure 5.13?

(d) Calculate the reaction at 2 °C/min in an open system. Assign HO3 as non-volatile. How does the temperature at 50% oil evolution from the reactor compare to the results in Figures 4.12 and 4.15?

4. Enter the lignite coal decomposition mechanism of Behar et al. (2008) shown in Tables 6.3 and 6.4 into PMod2. Calculate the reaction at 2 °C/h in a closed system, including Rock Eval parameters of the unextracted sample. Consider DCM-NSOs to be non-volatile.

(a) Plot the chemical species versus vitrinite reflectance

(b) Plot T_{max} versus vitrinite reflectance between 0.2 and 1.6 %Ro. What is the initial kinetic T_{max} value? What reaction channel dominates that T_{max} value? What are the kinetic T_{max} values at 0.7 and 1.4 %Ro. What reaction channel dominates the latter value?

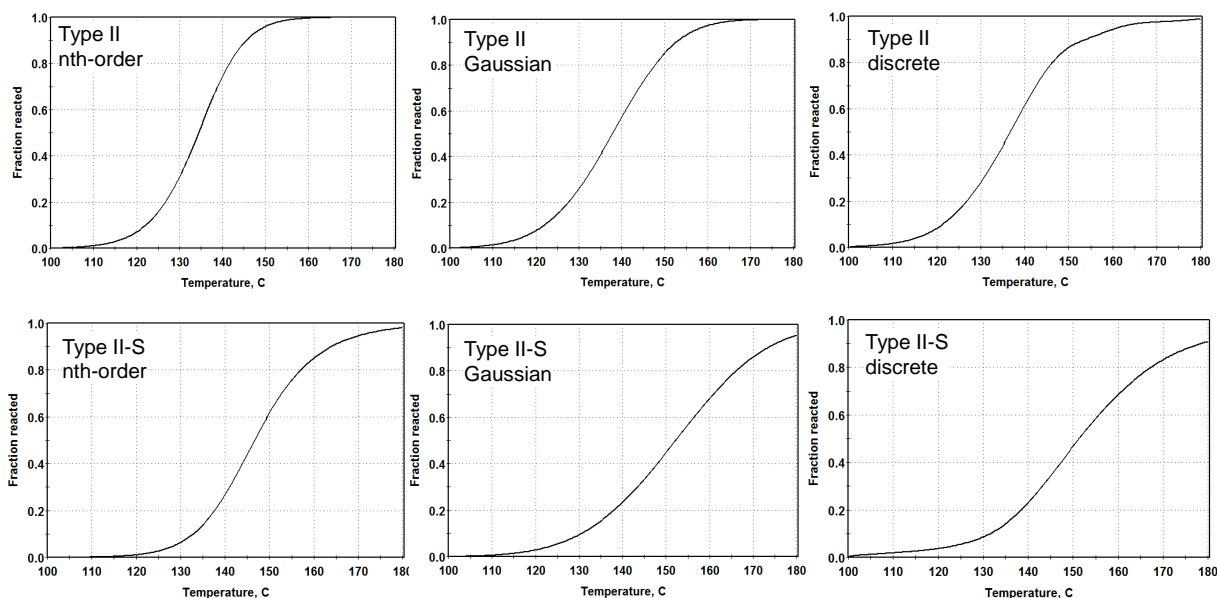
(c) Using the Tmax Calc spreadsheet, calculate the kinetic T_{max} at 4 °C/min for the 51.4, 53.7, and 56.2 kcal/mol reaction channels. Compare them to Figure 4.45 and draw a correlation to coal rank.

(d) Now compare the T_{max} versus %Ro trend with Figure 6.10. What is an obvious deficiency of the Behar Type III mechanism?

Chapter 7 Supplemental Exercises

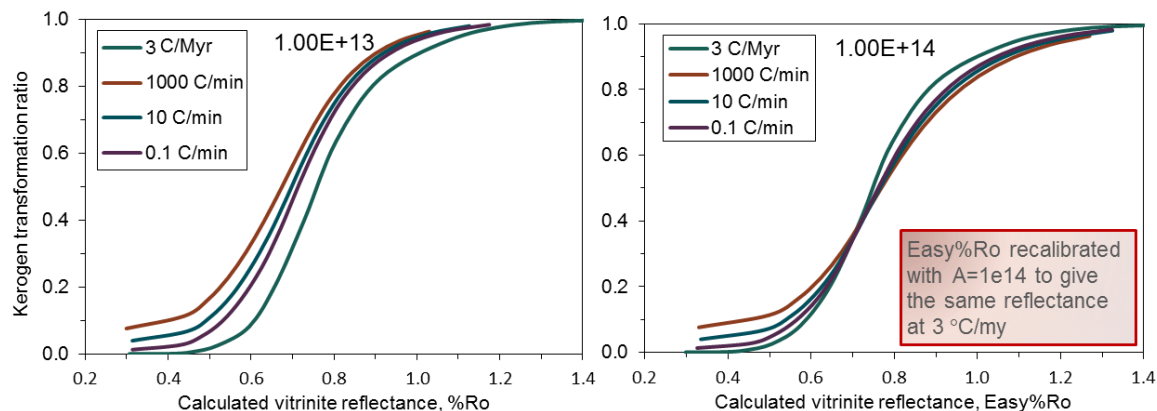
1. You want to estimate whether petroleum has been generated in a basin.

- Sediment undergoes a gradual burial of 100 m per million years. What is the average deposition thickness per year?
- The heat flow from the mantle is such that the geothermal gradient is 30 °C/km. What heating rate does the sediment experience?
- Using that heating rate and assuming that the bulk kinetics represent oil generation, create plots of oil generation versus temperature matter for Gaussian, nth-order, and discrete E models of the Type II and Type II-S organic using the parameters derived in Supplemental Exercise 1 of Chapter 4.



(d) How does the difference between the two kerogen types compare to the variations among the kinetic models for each kerogen type?

2. The Basin%Ro program uses essentially the same frequency factor as Easy%Ro. However, work on many kerogen samples indicates that the most probable frequency factor is $\sim 2 \times 10^{14} \text{ s}^{-1}$. This difference in A causes the most probable relationship between VR and TR to be different for geological and laboratory heating, as shown in the left panel of the following figure:



- (a) Using either the Easy%Ro spreadsheet or your own program, derive an activation energy distribution for $A=2 \times 10^{14} \text{ s}^{-1}$ that matches Basin%Ro for a heating rate of $3 \text{ }^{\circ}\text{C/Myr}$. Manual adjustment is adequate for this purpose. Give a table of activation energies and reactive fractions.
- (b) Create a figure similar to the right-hand panel. Is there any significant difference in the TR-VR relationship from what is shown here?

3. Run the same Behar Type II mechanism used in Chapter 6 at $2 \text{ }^{\circ}\text{C/h}$ using the Pepper-Corvi expulsion mechanism with an expulsion threshold of 100 mg/g for oil and zero for gas.

- (a) Show a plot S1, S2, PI and Tmax
- (b) Why is S1 different from the open system value?
- (c) What energy channels dominate T_{max} at %Ro=0.5 and 1.0, respectively?
- (d) What species are primarily generated from kerogen above %Ro=0.9?

The primary product from kerogen from this model is always DCM-NSOs. However, this question and answer highlights a definitional issue. Generation of methane, hydrogen, and some light hydrocarbons (per previous chapters) from mature kerogen is the reality. For real samples, all non-extractable organic matter is called kerogen, and mature kerogens generate those light gases as the aromatic rings condense into larger rings. Some lumped species models distinguish between kerogen and semi-coke, coke, or char with the latter three representing residual kerogen from which these secondary gases are generated.

4. Run the same mechanism at $2 \text{ }^{\circ}\text{C/Myr}$ using the Pepper-Corvi mechanisms with expulsion thresholds of 50, 100, and 200 mg/g for oil and 20 mg/g for gas.

- (a) Show graphs of total kerogen, Ker1, Ker2, oil, gas, DCM-NSOs, x-oil and x-gas as a function of temperature and vitrinite reflectance. Compare your results to Figure 7.10.
- (b) Now plot the various oil species as a function of vitrinite reflectance for the various expulsion thresholds. How does the composition of the expelled oil change with expulsion threshold?

5. Consider an in-situ process where the buildup of pressure within the formation increases as the heating rate increases. If the pressure builds up to 5 atm at $1 \text{ }^{\circ}\text{C/min}$ and 2 atm at $1 \text{ }^{\circ}\text{C/h}$ at 2 atm, what would the apparent activation energy be for oil evolution if the true A and E are $5 \times 10^{13} \text{ s}^{-1}$ and $E=53 \text{ kcal/mol}$? (Hint: use Eq. 5.3 to generate synthetic data at the two conditions and then fit the resulting data with Kinetics2015.)

6. You are designing a plug-flow surface reactor using the type II source rock as oil shale. The rock has a FA yield of 25 gal/ton. You want to produce 5,000 bbl/day of oil.

- (a) How many tons per day do you need to process if the reactor yields 90% of Fischer Assay? (assume the yield loss is due to incomplete kerogen conversion and oil coking and cracking)
- (b) If the process operates at $480 \text{ }^{\circ}\text{C}$ and you design for 97% kerogen conversion, what is the required residence time for the four kinetic models derived in the supplemental homework for Chapter 4? (Hint: use Kinetics2015 in the Apply mode.) Fill out the following table.

Model	Residence time (min)
first-order	
nth-order	
Gaussian E distribution	
discrete E distribution	

- (c) What is the best estimate for the reactor volume? Assume a shale density of 2200 kg/m^3 .
- (d) What are the implications of using the wrong kinetic model?
- (e) Compare your residence times to those for Type I oil shale in Exercise 9 of Chapter 7.
7. Chemical engineers usually consider continuous flow, perfectly stirred reactors in terms of simple reactions. However, for real systems, such as the coal liquefaction discussed in Section 5.1, one must consider the distribution of reactivity as well as the distribution of residence times for sequential reactors.
- (a) Consider a single continuous flow, perfectly stirred reactor with an average residence time of 10 min at 430°C . Use Kinetics2015, the IsoGauss Integral 2016.xlsx spreadsheet at extras.springer.com, or a program of your own writing to calculate the extent of reaction for both the first and the second reaction in Table 5.1. What is the fraction remaining of each and the total fraction reacted?
- (b) If you have two such reactors in series, why is the total fraction remaining not merely the square of the fraction remaining for a single reactor as in Exercise 12 of Chapter 7?
- (c) Using the IsoGauss Integral 2016 spreadsheet, calculate the fractions remaining and total fraction remaining after each of two continuous flow, perfectly stirred reactors with an average residence time of 5 min at 430°C .