

# Principles of Kinetic Analysis for Condensed-Phase Thermal Decomposition

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# Outline of Presentation



- General background on kinetics (pp. 3-15)
- Approaches to kinetic analysis (p.16)
  - How not to do kinetic analysis (pp. 17-22)
  - Simple kinetic analyses and how to pick a reaction model (pp. 23-34)
  - Model fitting by non-linear regression (pp. 35-45)
- Examples of Kinetics by Model Fitting (pp. 46-62)

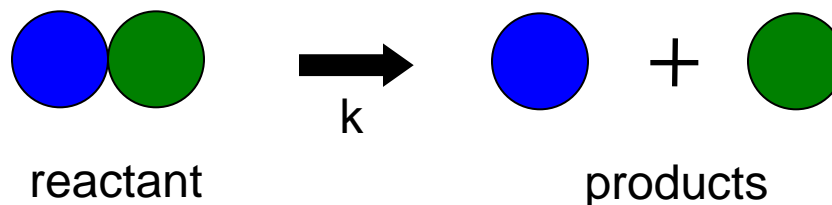
- All life and many manufacturing processes involve chemical reactions
  - Reactants  $\rightarrow$  Products
- Chemical reactions proceed at a finite rate
- The rate of virtually all chemical reactions varies with time and temperature
- Chemical kinetics describe how chemical reaction rates vary with time and temperature

# Why Study Chemical Kinetics?



- Understanding reaction characteristics
  - Acceleratory
  - Deceleratory
- Interpolation within the range of experience
  - Optimization of chemical and material processes
- Extrapolation outside the range of experience
  - Lifetime predictions
  - Petroleum formation
  - Explosions

# Unimolecular Decomposition



$k$  is the reaction rate constant

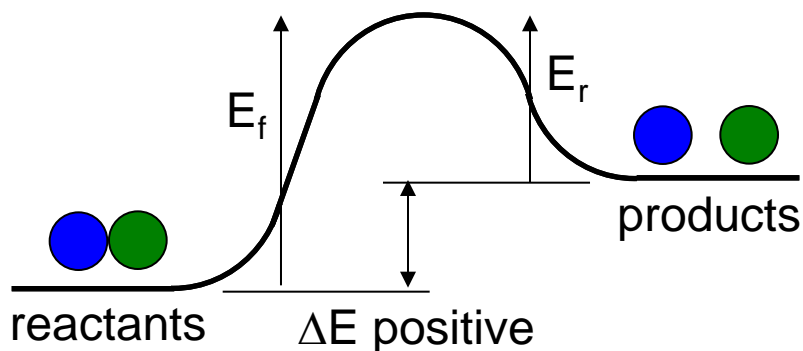
$k$  has units of reciprocal time

The reaction rate has units of quantity per unit time

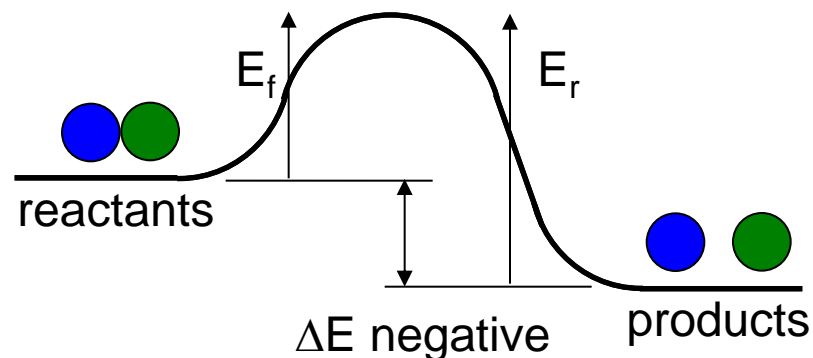
- The products can be either more stable or less stable than the reactants
- If the products are more stable, heat is given off
- If the products are less stable, heat is absorbed

# The Energy Barrier

Endothermic reactions



Exothermic reactions



- $E_f$  is the activation energy for the forward reaction
- $E_r$  is the activation energy for the reverse reaction
- $E_f - E_r$  is the energy change of the reaction,  $\Delta E$

# Unimolecular Reactions

- The reaction rate is proportional to how much reactant is present

$$\frac{dx}{dt} = -kx$$

where  $dx/dt$  is the limit when  $\Delta t$  becomes infinitesimally small (from differential calculus)

$x$  is the amount of the reactant

$t$  is time

$k$  is the rate constant

- $k$  has units of reciprocal time for unimolecular reactions
- The negative sign means that  $x$  decreases with time

# The Arrhenius Law

- Empirical relationship from 1889 describing the temperature dependence of chemical reactions

$$k = Ae^{-E/RT}$$

$k$  is the rate constant

$A$  is the pre-exponential factor or frequency factor

(units are reciprocal time for unimolecular reactions)

$E$  is the activation energy

$R$  is the universal gas constant (1.987 cal/mol·K)

$T$  is the absolute temperature (Kelvins)



# The Arrhenius Law is Approximate

- Gas phase reactions typically have a power temperature dependence in addition to the exponential dependence to account for collision frequency
  - $k = AT^b e^{-E/RT}$ , where b is ranges from  $1/2$  to  $3/2$
- Transition state theory provides a linear temperature term
  - $k = (k_B T/h) e^{-E/RT}$
  - $k_B$  is Boltzmann's constant and h is Planck's constant
- The power temperature dependence can be absorbed into the apparent activation energy with negligible error

[See Burnham and Braun, Energy & Fuels **13**, p. 3,1999, for specific examples]

# Transition State Theory

- A hypothetical transition state exists at the maximum energy in the reaction trajectory
- The pre-exponential factor is related to the molecular vibration frequency of the dissociating bond  $\sim 10^{14}$  Hz
- Transition state theory is often invoked under conditions far beyond its legitimate applicability
- Transition state theory has been only marginally useful for most reactions of practical interest
  - An exception is gas phase combustion modeling
  - Advances in computation methods are making it useful for probing mechanisms of complex reactions

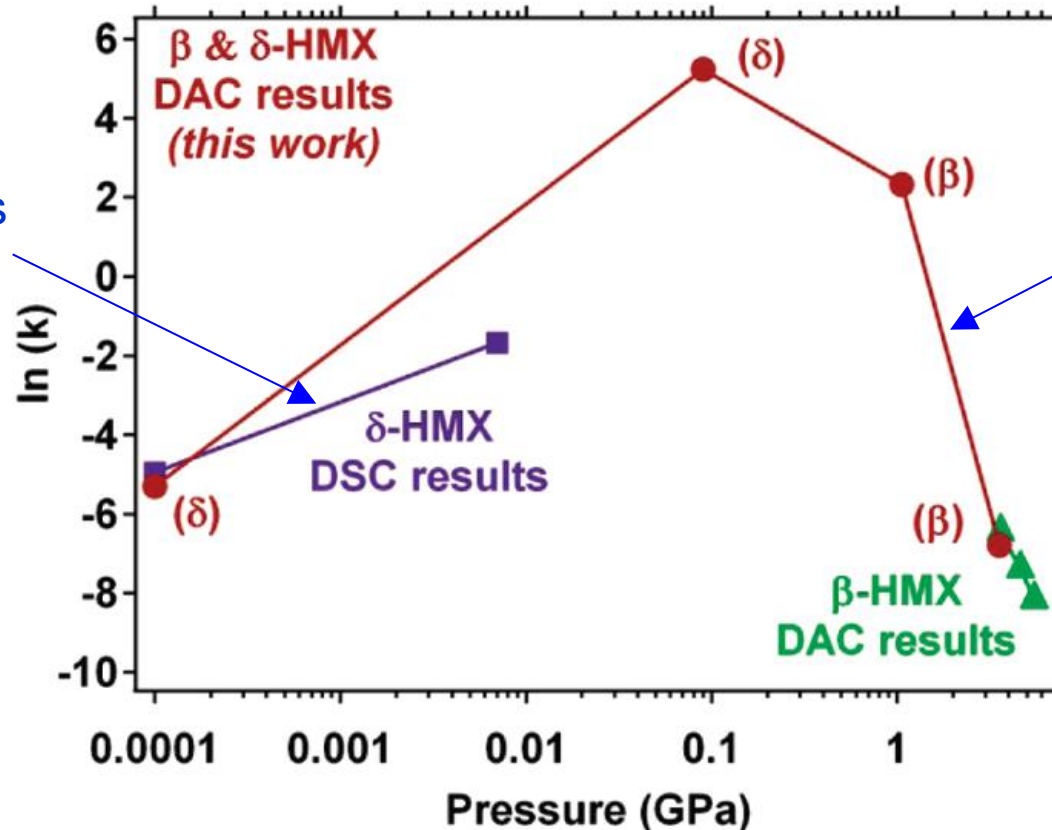
# The Effect of Pressure is Variable

- Pressure can either increase or decrease reaction rates, depending upon circumstances
- Increasing pressure for unimolecular decomposition
  - can increase rate for simple molecules by increasing energy redistribution
  - can decrease rate for complex molecules by inhibiting dissociation
- Increasing pressure for bimolecular reactions
  - can increase rate by increasing collision frequency at low densities
  - can decrease rate by increasing viscosity and decreasing freedom to move around at high densities
- Reversible reactions in which a gaseous product is formed from solid decomposition depend upon product pressure

# The Effect of Pressure Can Reverse

- The decomposition of energetic material HMX is one example of pressure reversal

Increase at lower pressures probably due to autocatalysis



Decrease at higher pressures due to some type of hindrance

Pressure-dependent decomposition kinetics of the energetic material HMX up to 3.6 GPa, E. Glascoe, et al., J. Phys. Chem. A, **113**, 13548-55, 2009.

# Separation of Functional Dependences

- It is commonly assumed that the dependences on conversion, temperature, and pressure can be separated

$$\frac{dx}{dt} = -k(T) f(1-x) h(P) \quad \text{where } x \text{ is the fraction remaining}$$

$$\frac{d\alpha}{dt} = k(T) f(\alpha) h(P) \quad \text{where } \alpha \text{ is the fraction reacted}$$

- Functions for  $f(\alpha)$  are commonly tabulated in the thermal analysis literature
- For solid  $\leftrightarrow$  solid + gas,  $h(P) = 1 - P/P_{eq}$ , where  $P$  is the gaseous product partial pressure and  $P_{eq}$  is the equilibrium vapor pressure

# Reaction Models Can Be Integrated

$$g(\alpha) = \int_0^{\alpha} d\alpha / f(\alpha)$$

- Many models can be integrated exactly for isothermal conditions
- Models can be integrated approximately for a constant heating rate
  - Depends on the well-known temperature integral:

$$\int_x^{\infty} [\exp(-x) / x^2] dx$$

where  $x = E/RT$

- Several hundred papers have addressed the temperature integral and its solution by various approximations  
[see, for example, J. H. Flynn, *Thermochimica Acta* **300**, 83-92, 1997]

# Tabulations Exist For Isothermal Models

**Table 1** Set of alternate reaction models applied to describe the reaction kinetics in heterogeneous solid state systems<sup>a</sup>

	Reaction model	$f(\alpha)$	$g(\alpha)$
1	Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	$1/2\alpha^{-1}$	$\alpha^2$
6	Mampel (first order)	$1 - \alpha$	$-\ln(1 - \alpha)$
7	Avrami-Erofeev	$4(1 - \alpha)[- \ln(1 - \alpha)]^{3/4}$	$[- \ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	$3(1 - \alpha)[- \ln(1 - \alpha)]^{2/3}$	$[- \ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	$2(1 - \alpha)[- \ln(1 - \alpha)]^{1/2}$	$[- \ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	$2(1 - \alpha)^{2/3} (1 - (1 - \alpha)^{1/3})^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
11	Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Second order	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$

# Two basic approaches to kinetic analysis



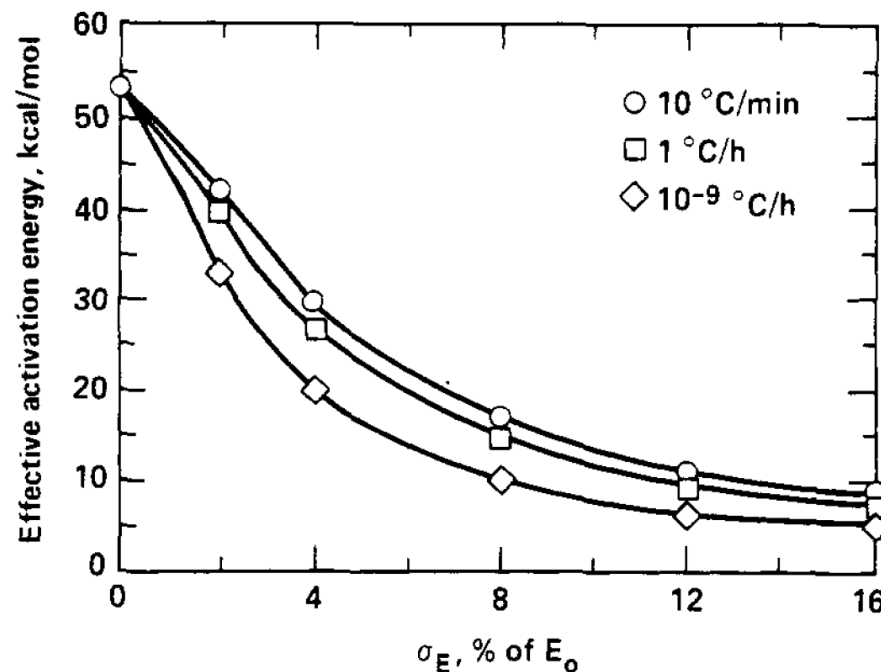
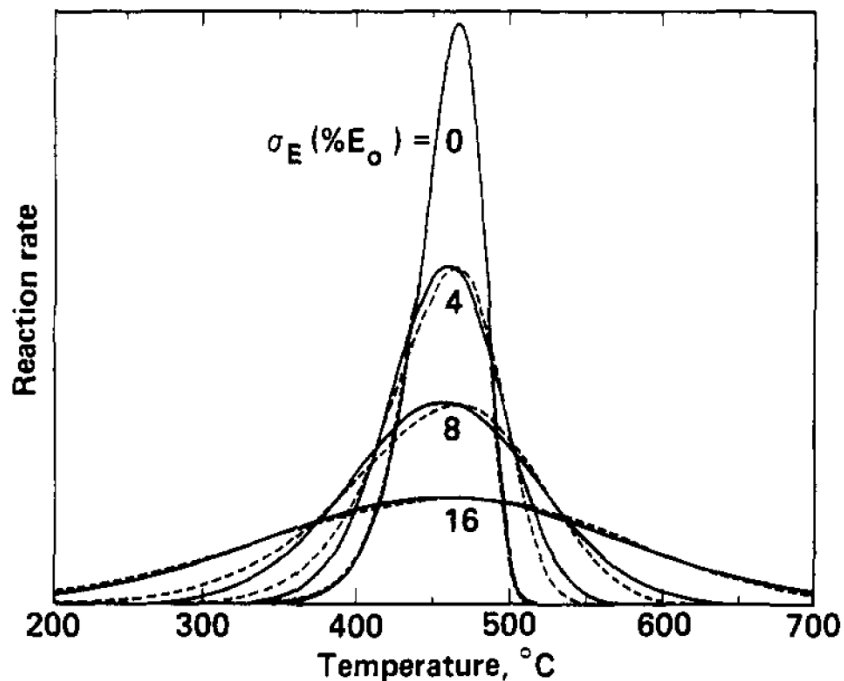
- Model fitting
  - Do some type of numerical comparison of selected models to determine the best model
- Isoconversional fitting
  - Assume that the reaction is infinitely sequential, i.e., that the same reactions occur at a given extent of conversion independent of temperature
- Both approaches can be used to make predictions for other thermal histories, including with Kinetics05



# Model Fitting is Often Done Poorly

- Many people have derived kinetics from a single heating rate experiment
  - Most common is to assume a first-order reaction
  - Others fitted all the reactions in the previous table with some approximation to the temperature integral and assumed that the fit with the lowest regression residuals was the correct model
- These approaches usually give the wrong kinetic parameters, and sometimes absurdly wrong, so predictions with the parameters are unreliable

# One Example of Why Fitting to a Single Heating Rate Doesn't Work



- Nonlinear regression fits of a first-order reaction to simulated data at a constant heating rate for a Gaussian distribution of activation energies
- Apparent activation energy as a function of the magnitude of the reactivity distribution—it can be qualitatively wrong!

R. L. Braun and A. K. Burnham, Energy & Fuels 1, 153-161, 1987

# Another Example of Why Fitting to a Single Heating Rate Doesn't Work

- Derived using a generalized Coats-Redfern Equation:

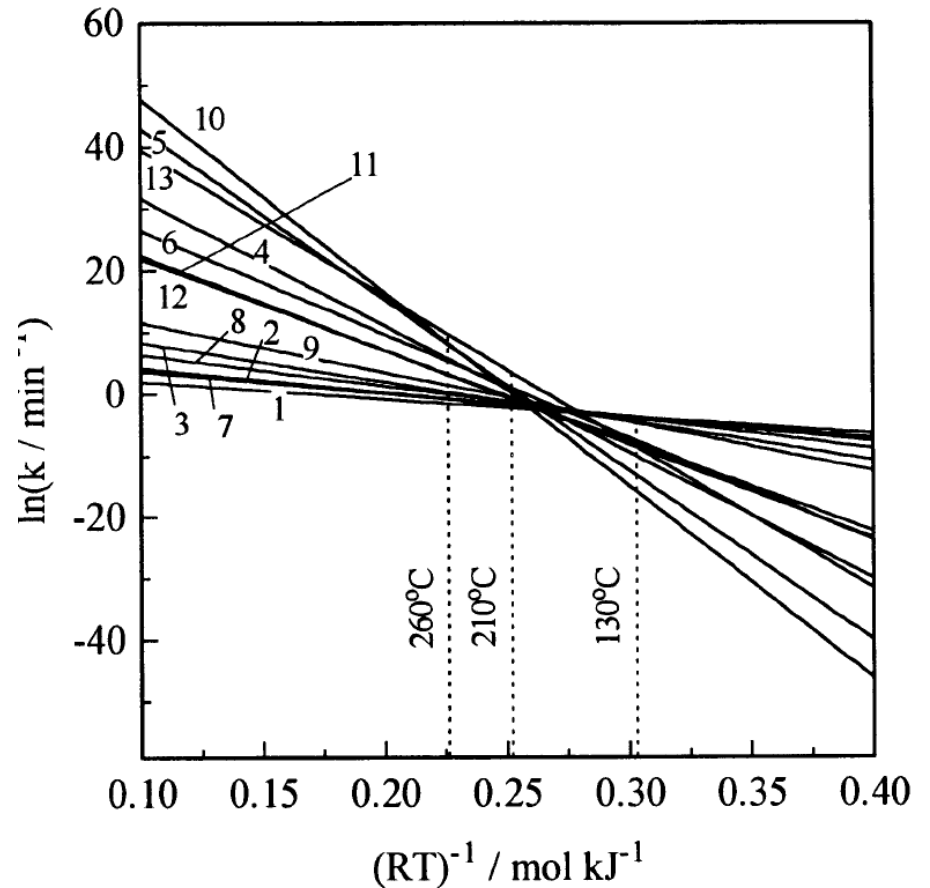
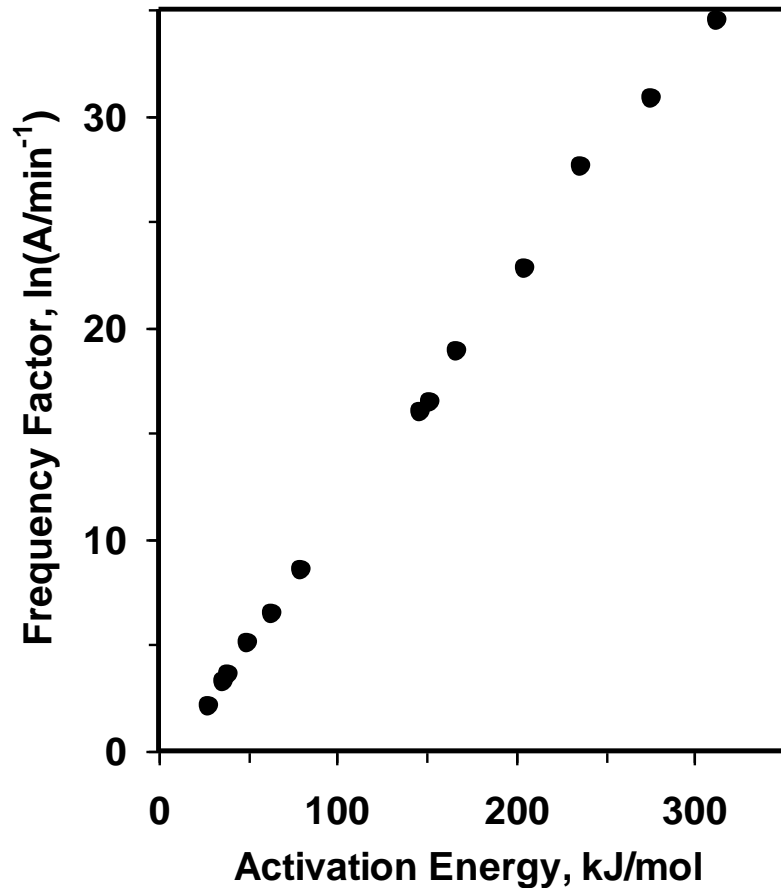
$$\ln[g(\alpha)/T^2] = \ln[(AR/\beta E)(1 - 2RT/E)] - E/RT$$

- The correlation coefficient is absolutely useless for model discernment

		$E/\text{kJ mol}^{-1}$	$\log(A/\text{min}^{-1})$	$-r^a$
Power law	1	$28.2 \pm 0.9$	$2.1 \pm 0.1$	0.9478
Power law	2	$40.0 \pm 1.1$	$3.6 \pm 0.1$	0.9539
Power law	3	$63.7 \pm 1.7$	$6.4 \pm 0.2$	0.9590
Power law	4	$205.8 \pm 5.1$	$22.7 \pm 0.6$	0.9647
One-dimensional diffusion	5	$276.9 \pm 6.8$	$30.7 \pm 0.8$	0.9653
Mampel (first order)	6 <sup>b</sup>	$167.8 \pm 2.2$	$18.8 \pm 0.3$	0.9894
Avrami-Erofeev	7	$36.4 \pm 0.6$	$3.2 \pm 0.1$	0.9858
Avrami-Erofeev	8 <sup>b</sup>	$51.0 \pm 0.7$	$5.0 \pm 0.1$	0.9872
Avrami-Erofeev	9 <sup>b</sup>	$80.2 \pm 1.1$	$8.5 \pm 0.1$	0.9884
Three-dimensional diffusion	10	$313.7 \pm 5.3$	$34.4 \pm 0.6$	0.9832
Contracting sphere	11	$153.2 \pm 2.6$	$16.4 \pm 0.3$	0.9824
Contracting cylinder	12	$147.5 \pm 2.9$	$15.9 \pm 0.3$	0.9776
Second order	13	$237.3 \pm 6.9$	$27.5 \pm 0.8$	0.9523

**Table 2** Arrhenius parameters computed for the thermal decomposition of ADN at  $5^\circ\text{C min}^{-1}$

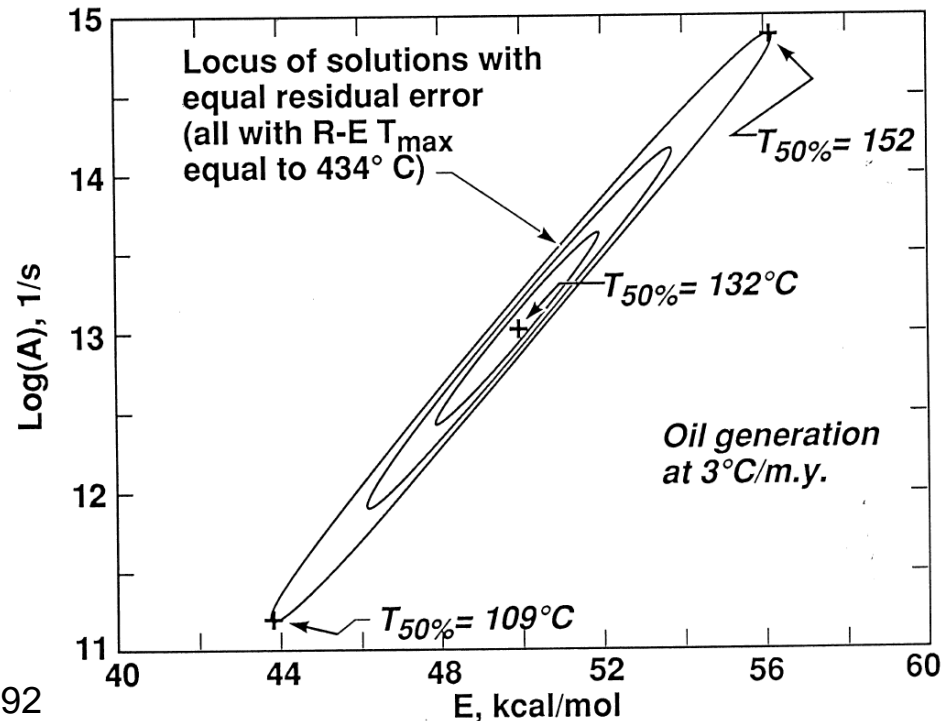
# A and E are Correlated for Various Models



A and  $E_a$  compensate for each other at the measurement temperature, but predictions diverge outside the measurement range

# Data at Different Temperatures Constrain Possible A-E Pairs and Extrapolations

- For a single rate measurement, possible A-E pairs are defined by a line of infinite length
- For measurements at 3 or more temperatures, the range of possible A-E pairs is defined by an error ellipsoid (narrow in shape)
- A-E pairs at the extremes of the error ellipsoid define the plausible range of the extrapolation
- The example at the right shows the range of kinetic extrapolations for natural petroleum formation based on a data set measuring the rate over a time-scale of up to a few hours



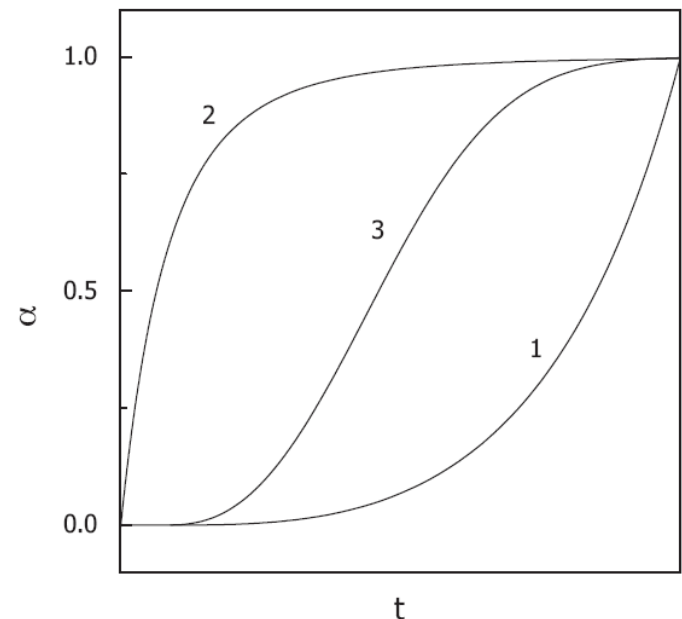
From A. Burnham, presentation at the AAPG annual meeting, Calgary, June 1992

# What have we learned?

- Single heating-rate kinetic methods don't work except by luck—**don't do it!**
- Improperly derived activation energies can be high or low from the true value by as much as a factor of five
- Even with the wrong model, A and E compensate for each other to get the average rate constant approximately right at the measurement temperature
- Most compensation law observations are due to imprecision and bad methodology, and most mechanistic interpretations are nonsense

# Back to basics to get it right

- First, get accurate data over a range of thermal histories
- Next, look at the reaction profile to understand its characteristics—you can narrow the choices considerably
- Reactions can be (1) accelerating, (2) decelerating, or (3) sigmoidal
- Decelerating reactions are the most common type for fossil fuel kinetics
- Sigmoidal reactions are the most common type for decomposition of energetic materials and crystalline solids



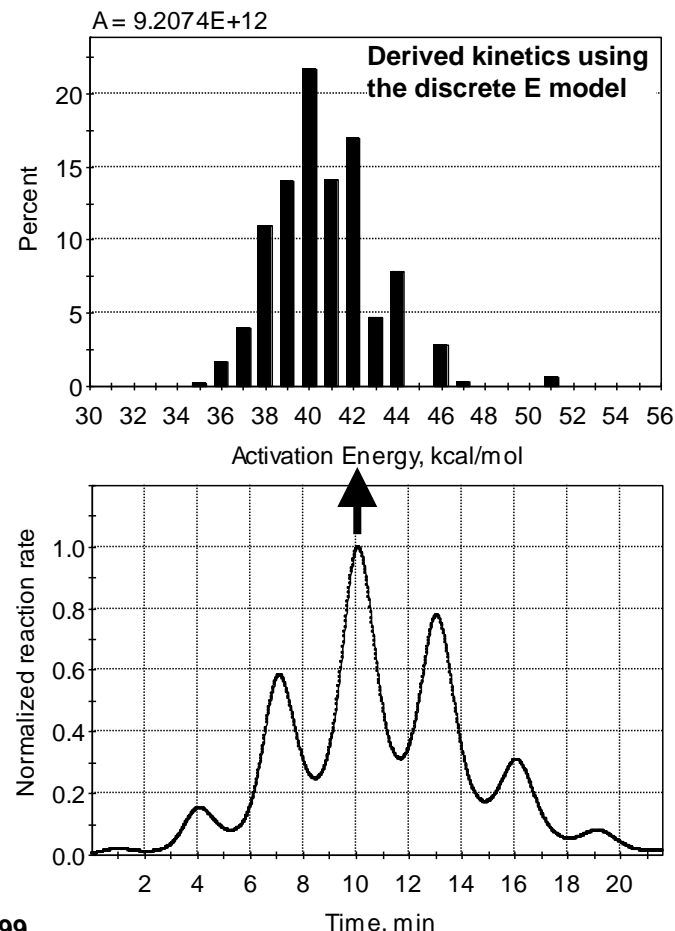
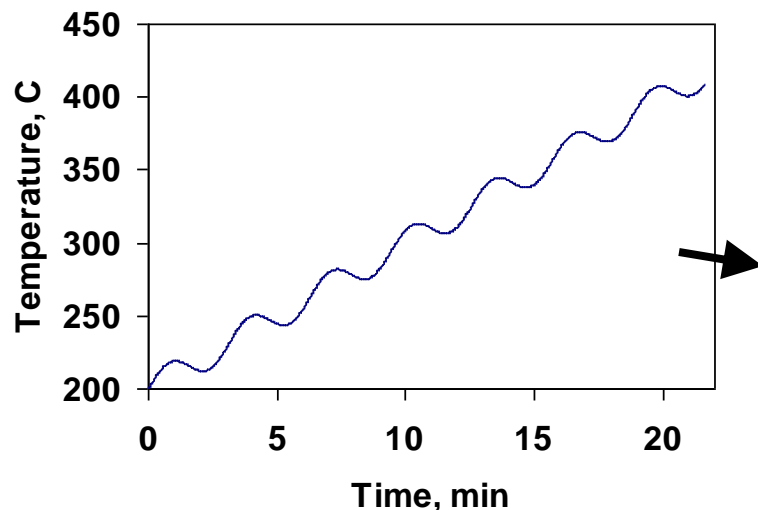
# Data requirements

- The data should cover as wide a temperature range as possible, as that helps constrain the model parameters
  - Enough temperature change to cause a tenfold change in reaction rate for isothermal experiments ( $\sim 40$  °C)
  - At least a factor of 10 change for constant heating rates
- Multiple heating schedules can include constant heating rate, isothermal, and arbitrary thermal histories
  - Having both nonisothermal and isothermal histories is advantageous, because they are sensitive to different aspects of the reaction
  - Having methods that can analyze arbitrary heating rates are advantageous, because ideal limits are hard to achieve in practice
  - Using sinusoidal ramped thermal histories is a promising but untapped approach



# Sidebar: Example of using a single sinusoidal ramped heating rate

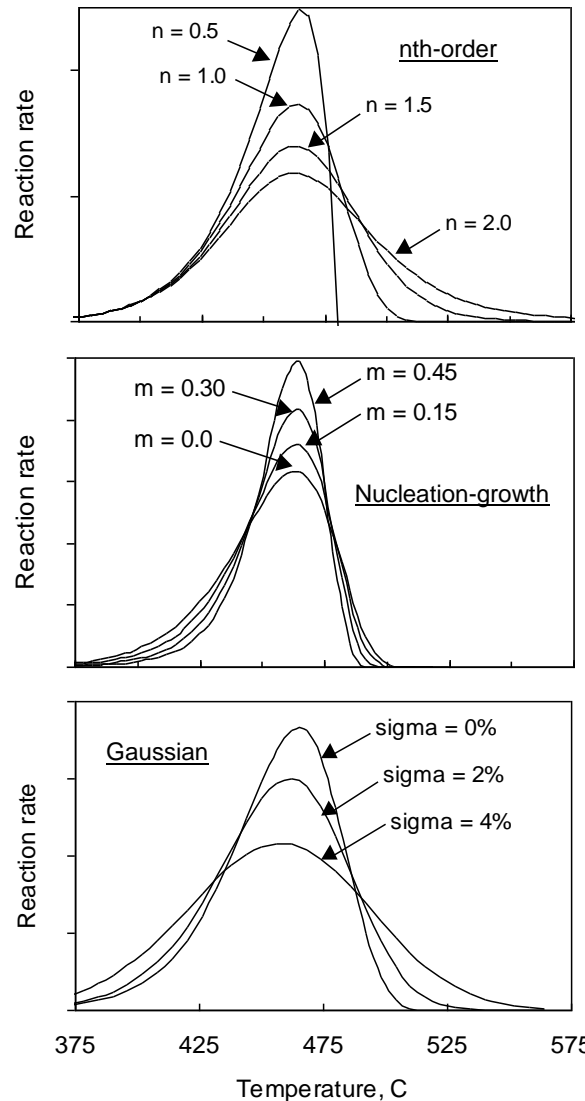
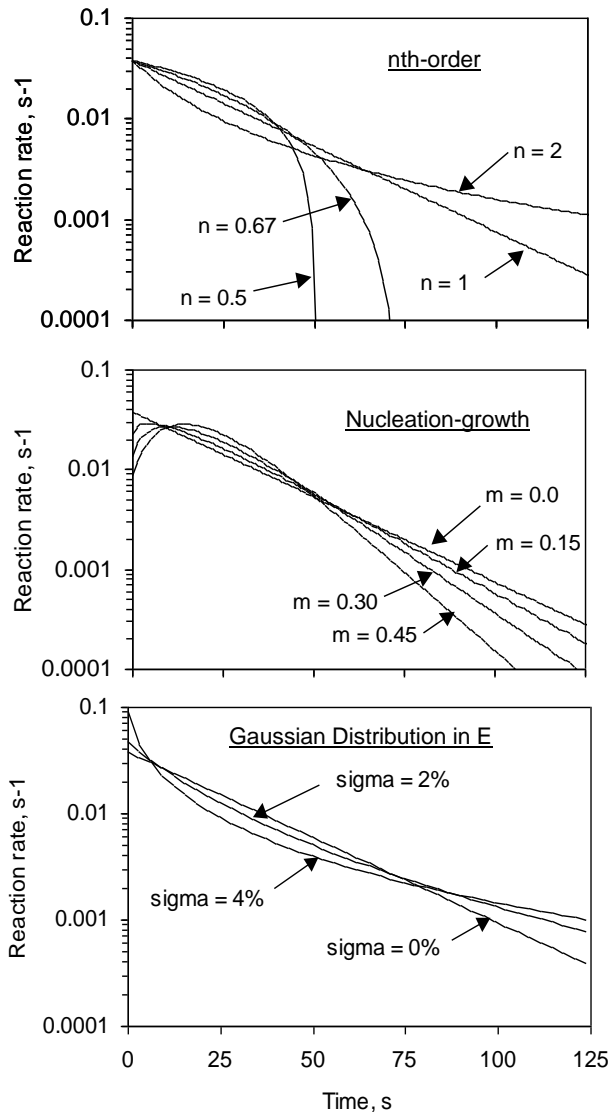
Create synthetic data for a reaction with  
 $A = 1e13 \text{ s}^{-1}$   
 $E = 40 \text{ kcal/mol}$   
Gaussian  $\sigma = 4\%$   
reaction order = 2  
reacting over this thermal history



AKB 8/99 Presented by A. Burnham at UC Davis, Oct 11, 1999

- This approach was mentioned by J. Flynn, *Thermochimica Acta* **300**, 83-92, 1997
- It is different from modulated DSC, which is designed to separate reversible and non-reversible contributions to the heat flow in DSC

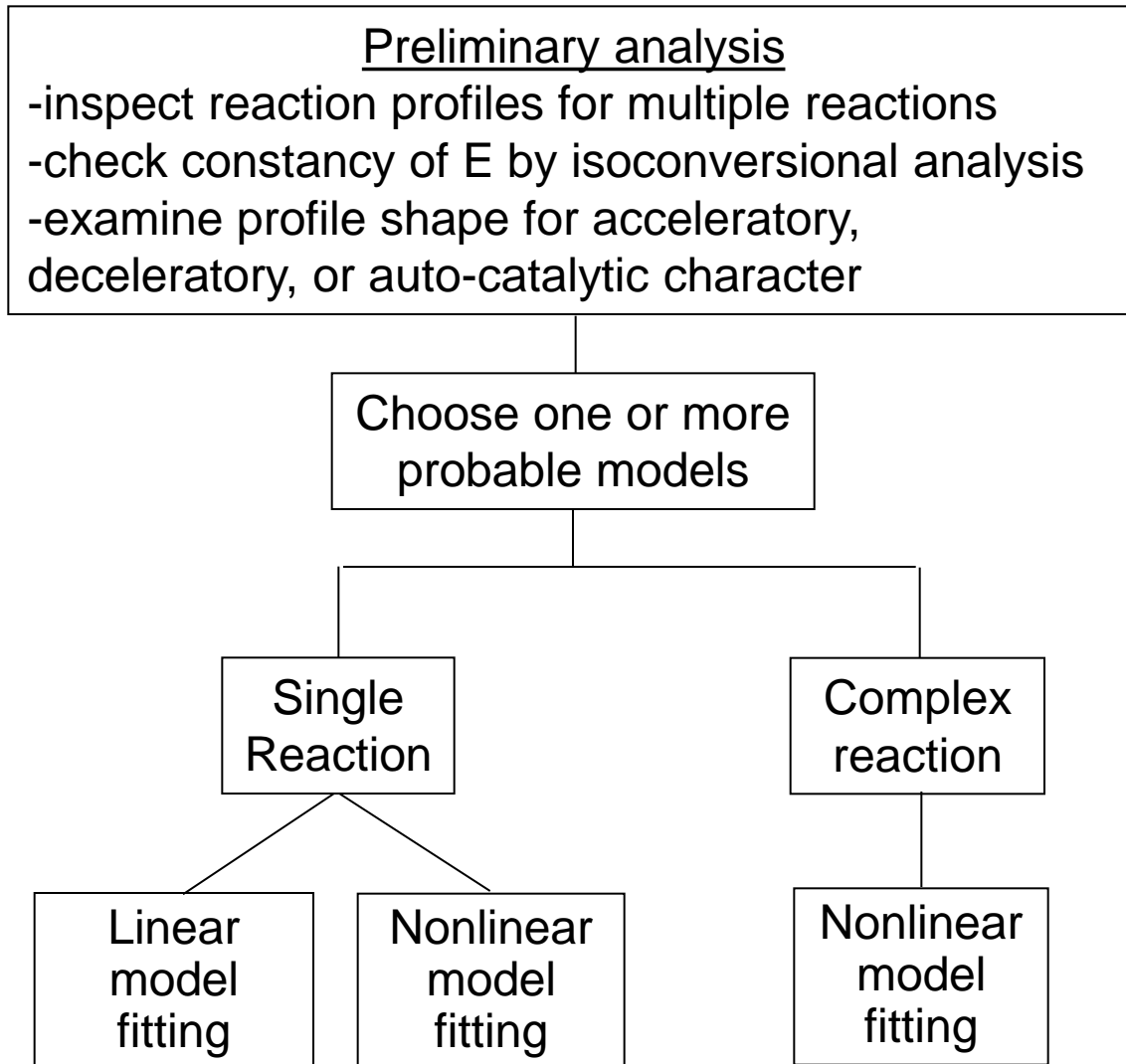
# Comparing Reaction Profiles to First-Order Behavior is Instructive



- nth-order and distributed reactivity models are both deceleratory
  - Is the rate of deceleration greater or less than a first-order reaction?
- Nucleation-growth models are sigmoidal
  - $m$  is a model growth parameter, which is zero for a first-order reaction

A. K. Burnham and R. L. Braun, Energy & Fuels **13**, 1-39, 1999

# The Model Selection Process Can Be Formalized

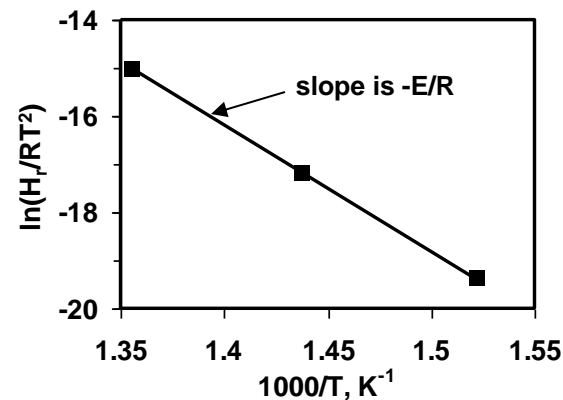
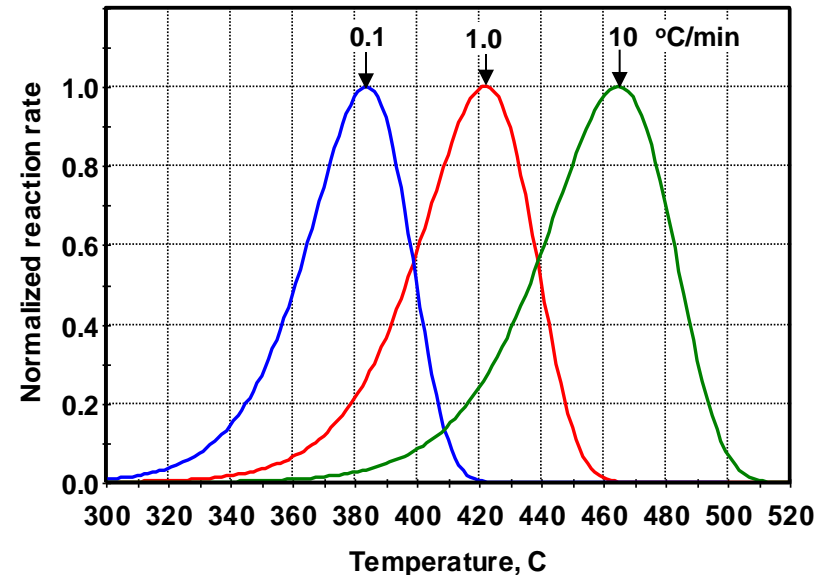


- Friedman's method is used to check the variation of  $E_a$  as a function of conversion
- Kissinger's method is used to estimate the mean values of  $A$  and  $E$  for multiple constant heating rate experiments
- The nonisothermal profile width and asymmetry are used to select a model and initial guesses for nonlinear regression analysis
- Nonlinear regression refines the program-supplied or user-supplied model parameters

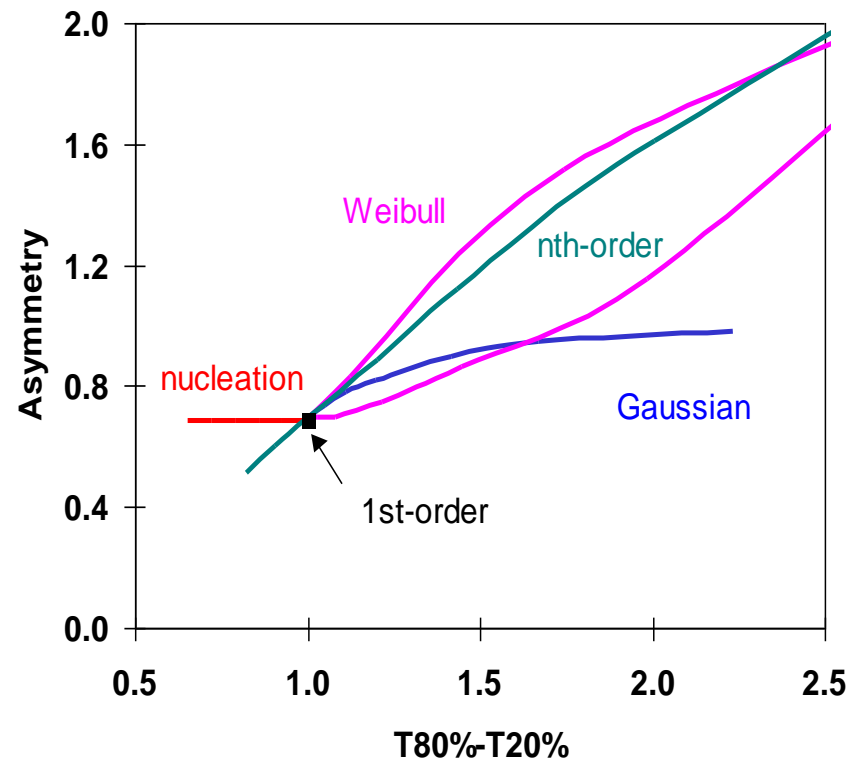
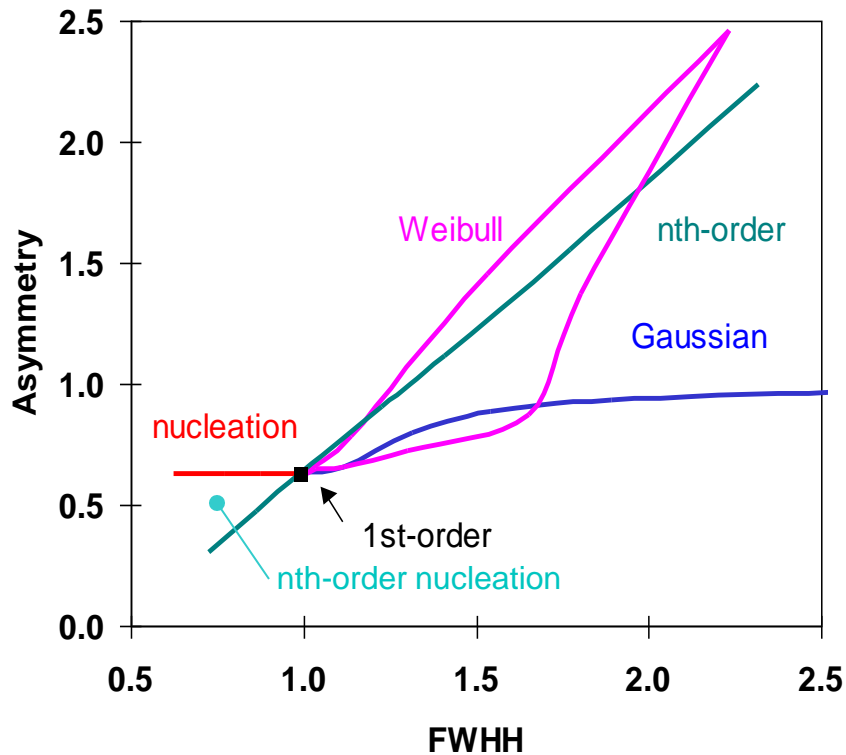
# Kissinger's method

$$\ln(H_r / RT_{max}^2) = -E / RT_{max} + \ln(A / E)$$

- $H_r$  is the heating rate
- A plot of  $H_r / RT_{max}^2$  versus  $1/T_{max}$  gives a slope of  $E/R$ , and the value of  $E$  can then extract  $A$  from the intercept
- As written, it is rigorously correct for first-order reactions
- A more complete formulation has a term  $f'(\alpha)$  in the “intercept” term—if it is not constant, the value of  $E$  is shifted
- As a practical matter, the shift is negligible for nth-order, nucleation-growth, and distributed reactivity models



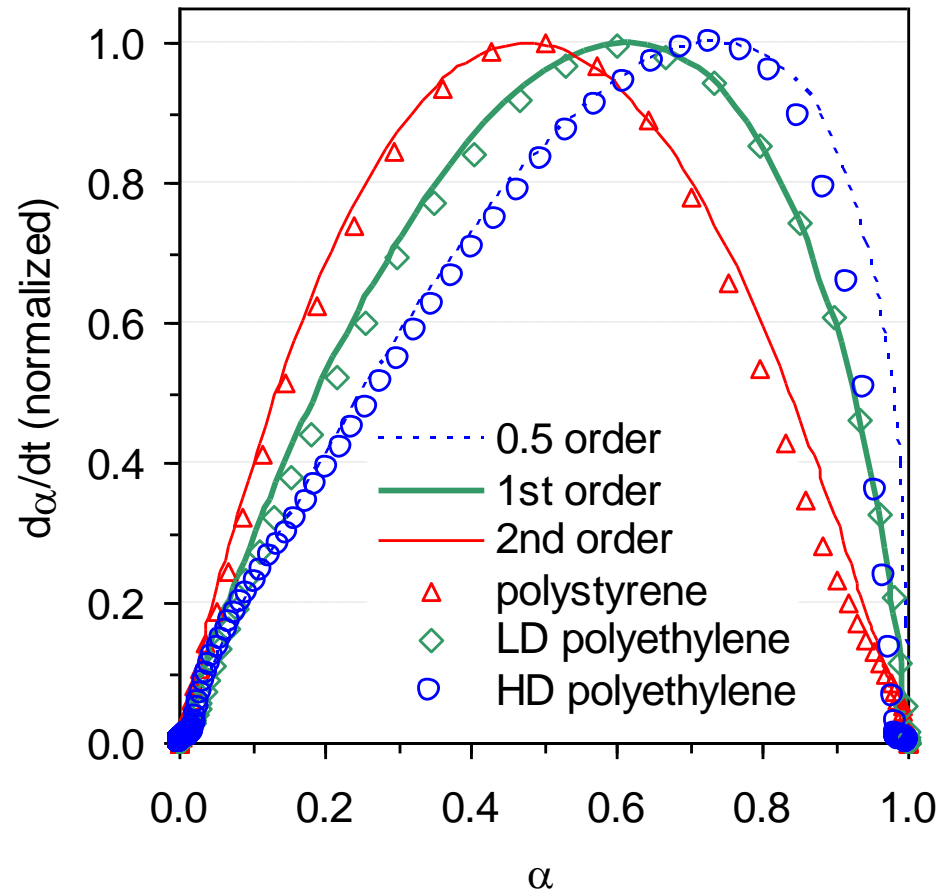
# Shapes of nonisothermal reaction profiles



- The left-hand plot is for rate data, and the right-hand plot is for fraction-reacted data
- Finding where the sample in question is located on one of these plots helps define the correct model

# Another Way to Estimate Reaction Order is to Plot Rate Versus Conversion

- Fractional order reactions are skewed to high conversion
- Higher order reactions are skewed to low conversion
- The three linear polymers shown all have profiles narrower than a first-order reaction
- Consequently, an  $n$ th-order nucleation-growth model is appropriate (Avrami-Erofeev or Prout-Tompkins—more on that later)



Vyazovkin et al., *Thermochim. Acta* **520**, 1-19 (2011)

# Isoconversional Kinetics are Instructive and Useful for Predictions, Also

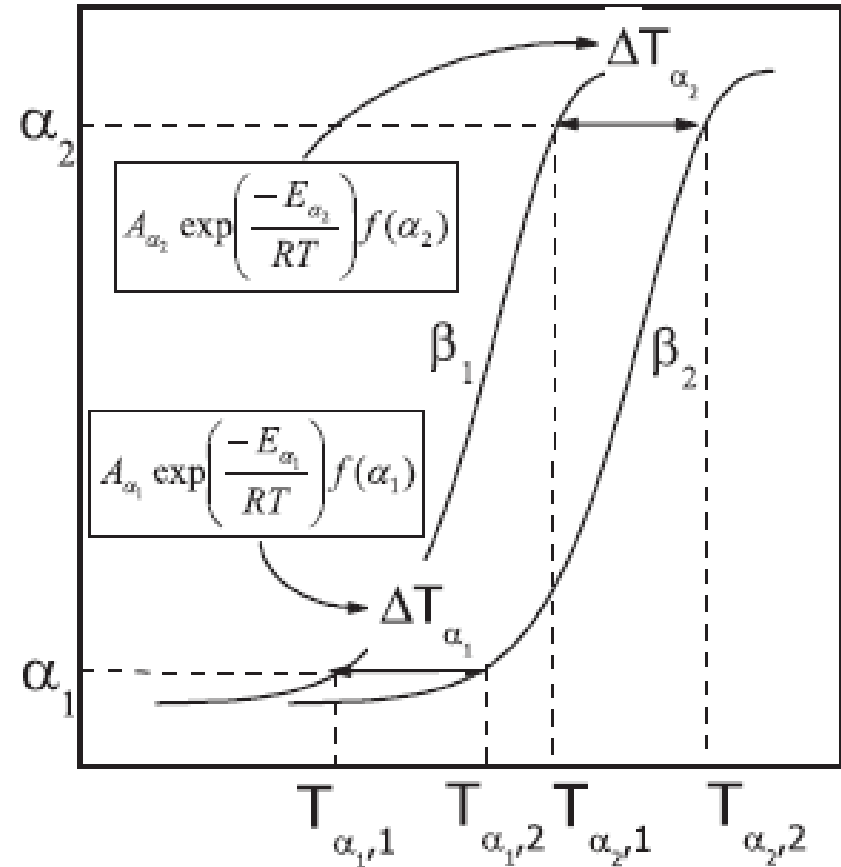
- Assumes simply that an Arrhenius plot of the  $i^{th}$  extent of conversion gives a true value of  $E$  and  $Af(\alpha)$  at that extent of conversion
- Many formalisms exist, but the two simplest, accurate methods are due to Friedman and Starink
- Friedman differential method

$$\ln(d\alpha / dt)_{\alpha,i} = -E_{\alpha} / RT_{\alpha,i} + \ln[A_{\alpha}f(\alpha)]$$

- Starink integral method

$$\ln(H_r / T_{\alpha,i}^{1.92})_{\alpha,i} = -1.0008E_{\alpha} / RT_{\alpha,i} + const$$

- Friedman's method works for any thermal history, while Starink's works only for constant heating rates





- Multi-heating-rate Coats-Redfern integral method

$$\ln[H_r / (T_{\alpha,i}^2 (1 - 2RT_{\alpha,i} / E))] = -E_{\alpha} / RT_{\alpha,i} + \ln[-AR / E \ln(1 - \alpha)]$$

- Iterative solution required because  $E$  is on both sides
- Although no quantitative comparison has been done to Starink's formula, this method recovers simple model parameters accurately

- Miura's formula

- Designed to take activation energy distributions into account to derive more fundamental A and E pairs

- For Friedman-like analysis:

$$A_{Miura} = \ln(0.58) H_r E / (RT^2 e^{-E/RT})$$

- For integral isoconversional analysis:

$$A_{Miura} = A \ln(0.58) / \ln(1 - \alpha)$$

# Review:

## Things to look for when picking a model



- Is the reaction deceleratory or sigmoidal for isothermal conditions?
  - If sigmoidal, use a nucleation-growth model
- Do  $A$  and  $E$  change with conversion for isoconversional analysis?
  - If an increase, use an  $E$  distribution model
  - If a decrease, the reaction is probably autocatalytic
- For constant heating rates, are there multiple peaks or inflection points that suggest multiple reactions?
  - If so, use parallel reactions or independent analyses
- For constant heating rates, is the reaction
  - Narrower or broader than a first order reaction? (see p.30)
  - Is it skewed more to high or low temperature compared to a first-order reaction? (see p.30)

# Model fitting by nonlinear regression

- Involves minimizing the residuals between measured and calculated curves
  - The minimization can be accomplished by a variety of mathematical methods
- The function to be minimized, hence the answer, will be slightly different for analyzing rate or fraction-reacted data
  - Minimizing to the actual function (rate for EGA and DSC and fraction reacted for TGA) has some advantages
  - It is possible and even desirable to minimize both simultaneously
- Minimizing to measured values is preferable to mathematically linearizing  $f(\alpha)$  or  $g(\alpha)$  and using linear regression, which usually weights the error-prone small values too heavily

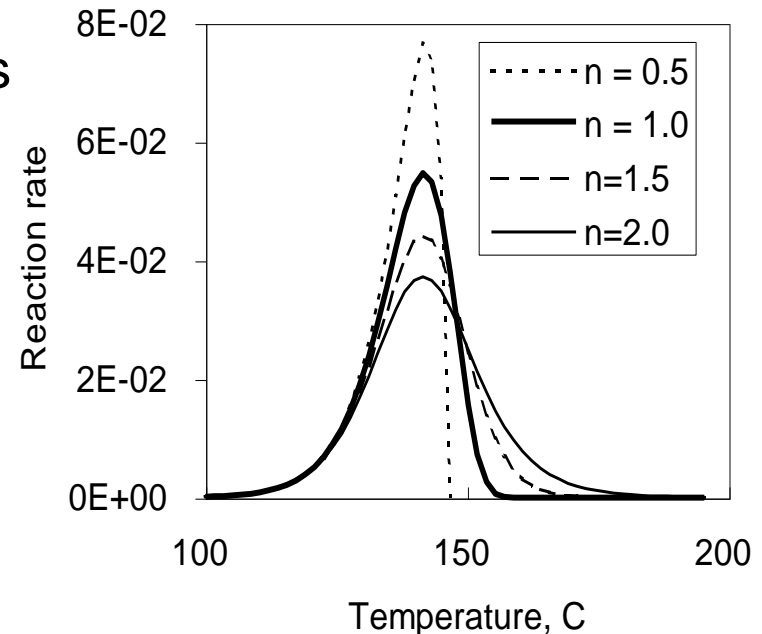
- Nth-order (up to 3 parallel reactions)
- Alternate pathway (including sequential reactions)
- Gaussian and Weibull  $E$  Distributions
- Discrete  $E$  Distributions (constant and variable  $A$ )
- Nucleation-growth (up to 3 parallel extended Prout-Tompkins reactions)
- Equilibrium-limited nucleation-growth
- Sequential Gaussian and nucleation-growth model
  - Contains numerous limits of above models

All these models are either deceleratory or sigmoidal in nature

# Nth-order models

$$\frac{dx}{dt} = -kx^n \qquad \frac{d\alpha}{dt} = k(1-\alpha)^n$$

- Reaction order has a completely different interpretation for decomposition of materials than in solution and gas kinetics
- Reaction orders of  $2/3$  and  $1/2$  apply to shrinking spheres and cylinders, respectfully
- Zero-order kinetics have been observed for a moving planar interface
- Reaction orders greater than 1 generally reflect a reactivity distribution, as a gamma distribution in frequency factor is equivalent to an nth-order reaction



# nth-order Gaussian distribution

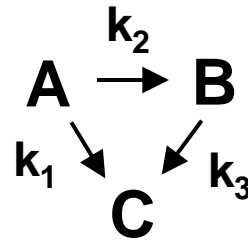
$$D(E) = (2\pi)^{-1/2} \sigma_E^{-1} \exp[-(E - E_0)^2 / 2\sigma_E^2]$$

- The model originated in the coal literature in the 1970s
- Although the model is often described in continuous mathematical distributions, the implementation is actually as a discrete distribution with weighting factors approximating a Gaussian distribution

$$dx / dt = -\sum_i w_i k_i x_i^n$$

- $w_i$  are Gaussian distribution weighting factors for reaction channels having evenly spaced energies, and  $\sum_i w_i = 1$
- $n$  is the reaction order, which can be 1 if desired
  - Having  $n$  greater than one enables one to fit a reaction profile skewed to high temperature, which is common for distributed reactivity reactions
- Up to three parallel nth-order Gaussian reactions are allowed to fit multiple peaks

# Alternate pathway reactions



- The primary motivation of this model was to enable oil to be formed directly from kerogen or via a bitumen intermediate
- One limit ( $k_1=0$ ) is the serial reaction model, which is useful as an alternative to a nucleation-growth model for narrow reaction profiles
- The three reactions all have independent reaction orders and Gaussian energy distributions, but the A values can be tied together if desired

# Weibull distribution of $E$

$$D(E) = (\beta / \eta)[(E - \gamma) / \eta]^{\beta-1} \exp \{ -[(E - \gamma) / \eta]^{\beta} \}$$

- $\eta$  is a width parameter,  $\beta$  is a shape parameter, and  $\gamma$  is the activation energy threshold
- The Weibull distribution is very flexible and can approximate Gaussian and nth-order distributions
- Up to three parallel Weibull reactions are allowed
- A Weibull distribution in  $E$  is completely different from a Weibull distribution in temperature advocated by some
  - the later is useful only for smoothing data, not deriving kinetics
- Although the model is described as a continuous mathematical distribution, the implementation is actually as a discrete distribution with weighting factors approximating a Weibull distribution



# Discrete $E$ distribution

- This is the most powerful model for materials having reactivity distributions without distinct multiple reactions
  - It has its roots in the German coal literature in 1967
- It assumes a set of equally spaced reaction channels separated by a constant  $E$  spacing selected by the user
- $A$  and the weighting factors for each energy channel are optimized by iterative linear and nonlinear regression
- The frequency factor can depend on activation energy in the form  $A = a + bE$  if desired
- It can be used to calculate the shift in Rock-Eval  $T_{\max}$  as a function of maturity for petroleum source rocks

# Nucleation-Growth Models

- These were developed for solid-state reactions and linear polymer decomposition more than 50 years ago
  - Don't be a Luddite and ignore them
- Different variations emerged from the Prout-Tompkins and Avrami-Erofeev (or JMA) approaches for solid-state reactions
- They are equally applicable to organic pyrolysis reactions
  - Initiation is analogous to nucleation
  - Propagation is analogous to growth
  - It is an approximation to the autocatalytic reaction  $A \rightarrow B$ ;  $B + A \rightarrow 2B$
- We use the extended Prout-Tompkins formalism

$$dx / dt = -kx^n (1 - qx)^m$$

- $x (=1-\alpha)$  is the fraction remaining
- $q$  is a user selectable initiation parameter (default in Kinetics05 is 0.99)
- $m$  is a growth parameter
- $n$  is still the reaction order

# Equilibrium-Limited Nucleation-Growth



- This is an extension of the nucleation-growth model to account for equilibrium inhibition
- Examples are
  - the distance away from a phase transition in solid-state transformations
  - The effect of a product gas inhibition in solid-state decomposition (e.g., CO<sub>2</sub> for calcite decomposition)

$$dx / dt = -kx^n (1 - qx)^m (1 - 1 / K_{eq})$$

where  $K_{eq}$  is the equilibrium constant

For an example ( $\beta \rightarrow \delta$  phase transformation of HMX), see Burnham et al., J. Phys. Chem. B **108**, 19432-19441, 2004

# Sequential Gaussian and Nucleation-Growth Model

- This model incorporates concepts from several models described in preceding slides

$$dA/dt = -\sum k_1 A^{n1} B^{m1} \quad (1)$$

$$dB/dt = \sum k_1 A^{n1} B^{m1} - \sum k_2 B^{n2} - k_3 B^{n3} C^{m3} \quad (2)$$

$$dC/dt = \sum k_2 B^{n2} + k_3 B^{n3} C^{m3} \quad (3)$$

- Reaction 1 is a sum over a Gaussian distribution of sigmoidal reactions intended to explicitly model initiation reactions
- Various familiar limits exist for this reaction network
  - If  $k_3$  and  $m_1$  are zero, it reduces to a serial reaction
  - If  $k_2$  and  $m_1$  are zero, it reduces to an autocatalytic reaction with a distinct reaction intermediate
  - If  $A=0$  and  $B=1$  at initial at initial time, it reduces to the traditional autocatalytic reaction

# 10-parameter Radical Reaction Model



<u>Reaction</u>	<u>Rate Law</u>	<u>Mass Balance</u>
(1) Initiation	$P \rightarrow 2R$	$\Delta P \rightarrow \Delta R$
(2) Recombination/disproportionation	$R + R \rightarrow P + 2E$	$\Delta R \rightarrow \Delta P + \Delta E$
(3) Hydrogen transfer/scission	$R + P \rightarrow 2E + R$	$\Delta P \rightarrow \Delta E$
(4) Volatile product formation	$R + E \rightarrow V + R$	$\Delta E \rightarrow \Delta V$

P = crosslinked polymer, R = radical, E = non-radical end group, V = volatile product

- This model was intended to do more rigorous modeling of organic decomposition, but it has not been explored much
- It is available only in the DOS emulation mode

# Examples of Model Fitting

- Nucleation-Growth (autocatalytic) Reactions
  - Cellulose
  - PEEK
  - Frejus Boghead Coal
- Surface Desorption
- Distributed Reactivity Reactions
  - Pittsburgh #8 coal
  - Farsund Formation Marine Shale
  - Hydroxyapatite Sintering
- Multiple Reactions
  - Estane
  - Poly (vinyl acetate)
  - Ammonium Perchlorate

# Cellulose has a narrow pyrolysis profile characteristic of an autocatalytic reaction

## Kinetic parameters

### Isoconversional analysis:

$E \sim 42$  kcal/mol;  $A \sim 10^{12}$  s<sup>-1</sup>  
approximately independent of conversion

### Extended Kissinger analysis:

$E$ , kcal/mol 43.3

$A$ , s<sup>-1</sup>  $4.0 \times 10^{12}$

rel. width 0.71

asym. 0.64

approx.  $m$  0.48

### Nonlinear regression analysis

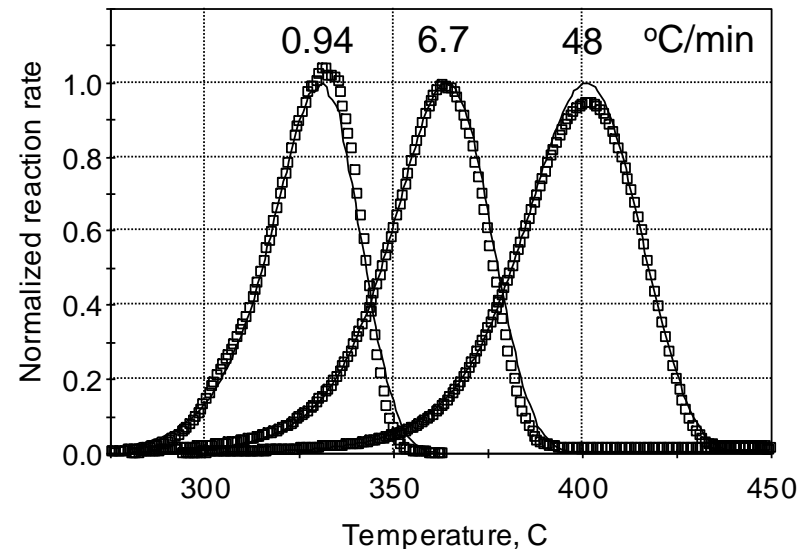
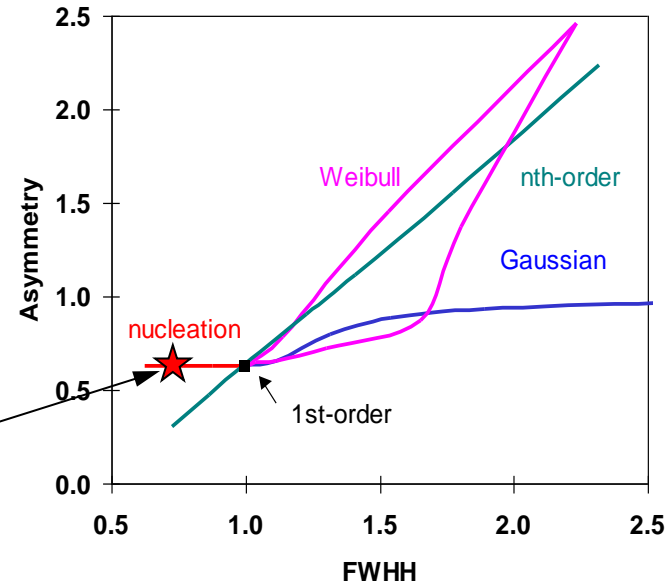
$E$ , kcal/mol 42.27

$A$ , s<sup>-1</sup>  $1.36 \times 10^7$

$m$  0.41

$$dx/dt = -kx(1-x)^m$$

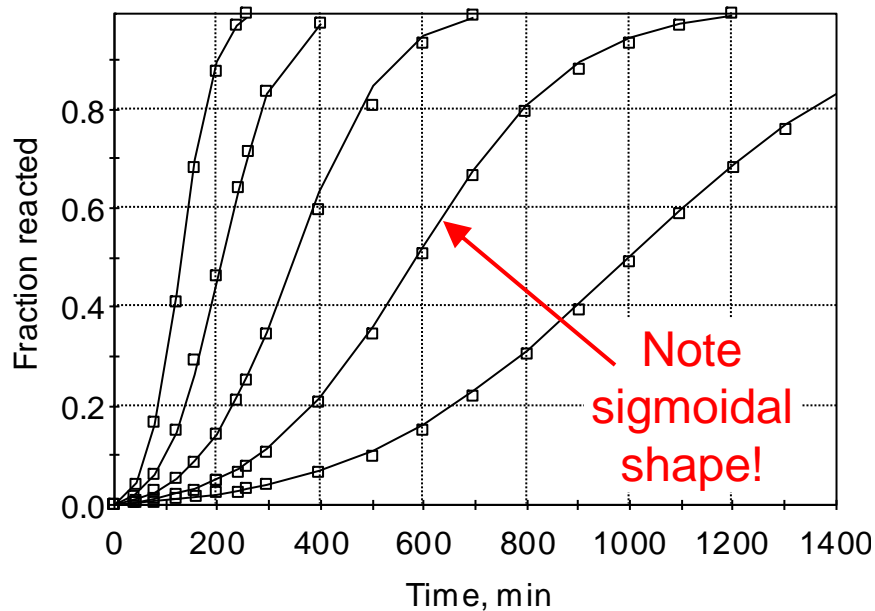
Reynolds and Burnham,  
Energy & Fuels 11, 88-97, 1997



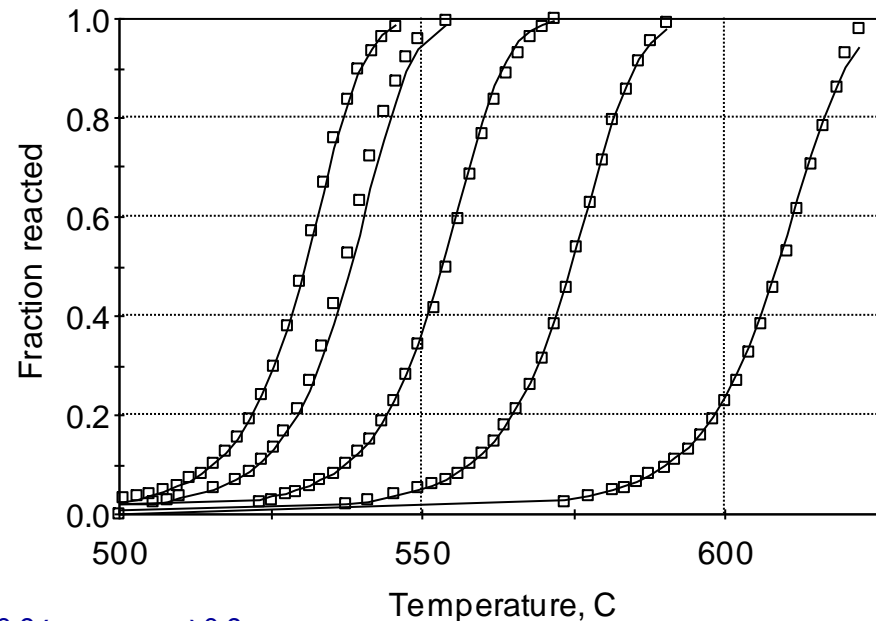
# Polyether-ether-ketone (PEEK) has classic sigmoidal (autocatalytic) reaction characteristics

- Simultaneous Friedman analysis of both data sets gave a roughly constant activation energy of about 58 kcal/mol
- Extended Kissinger analysis of the constant heating rate data gave E of 56.6 kcal/mol and m=1 for the growth parameter

Isothermal reaction 460 to 500 °C



Constant heating rate 0.67 to 19.5 °C/min



Nonlinear regression

$$dx/dt = -kx^{0.9}(1-0.99x)^{0.9}$$

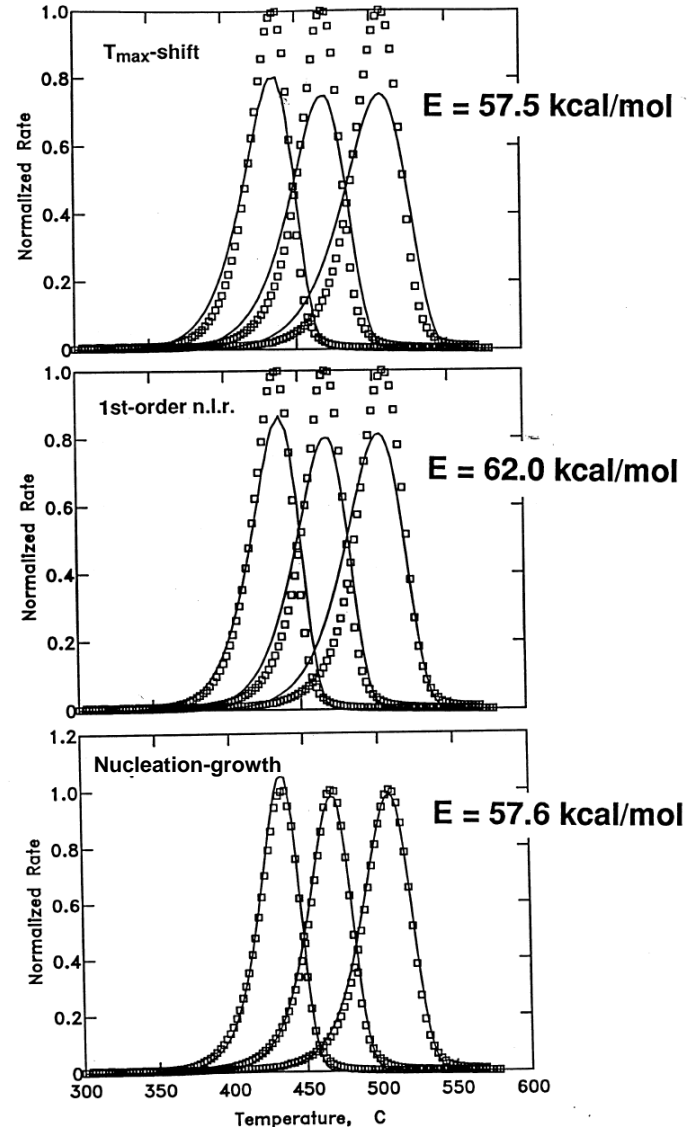
$$k = 7.9 \times 10^{12} \exp(-28940/T) \text{ s}^{-1} \quad [57.5 \text{ kcal/mol}]$$



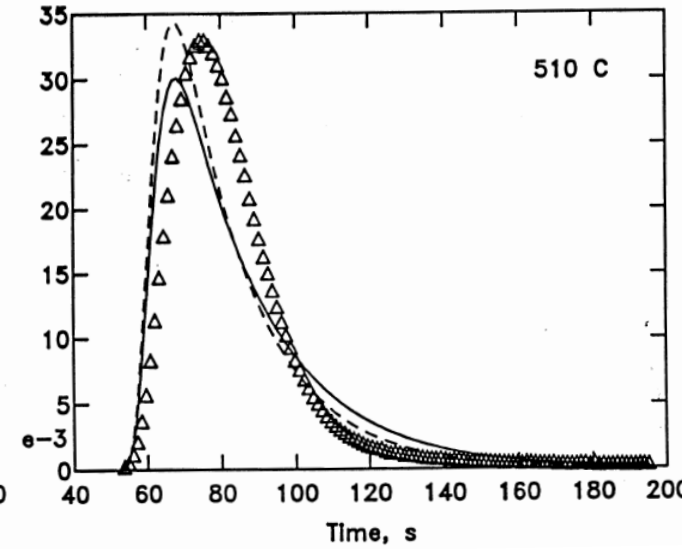
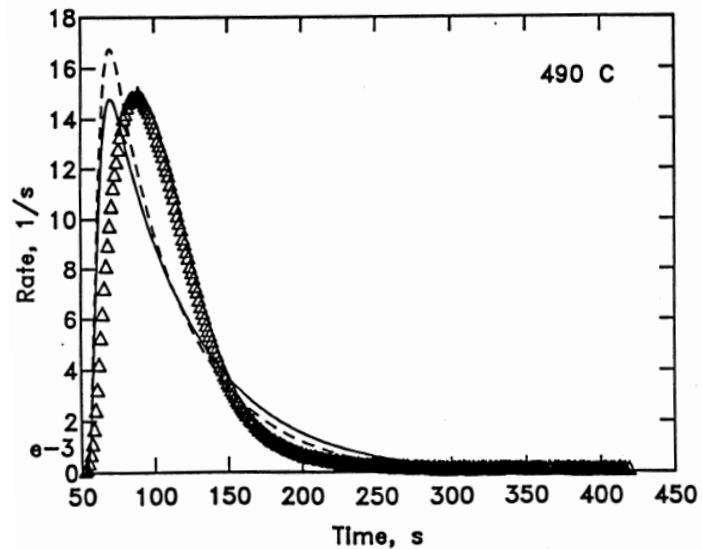
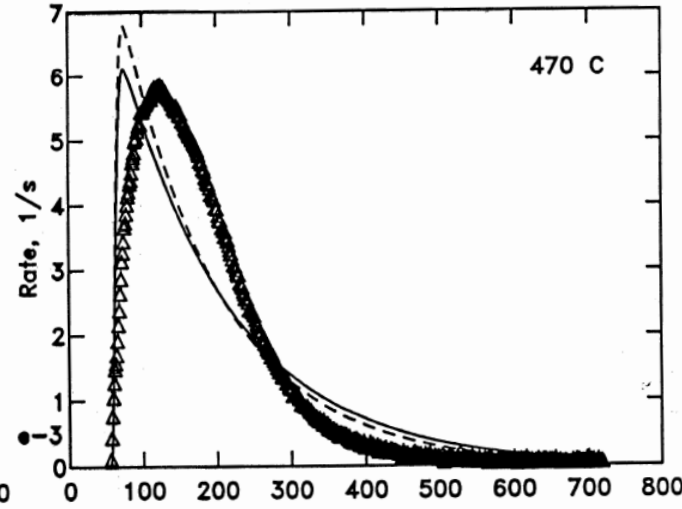
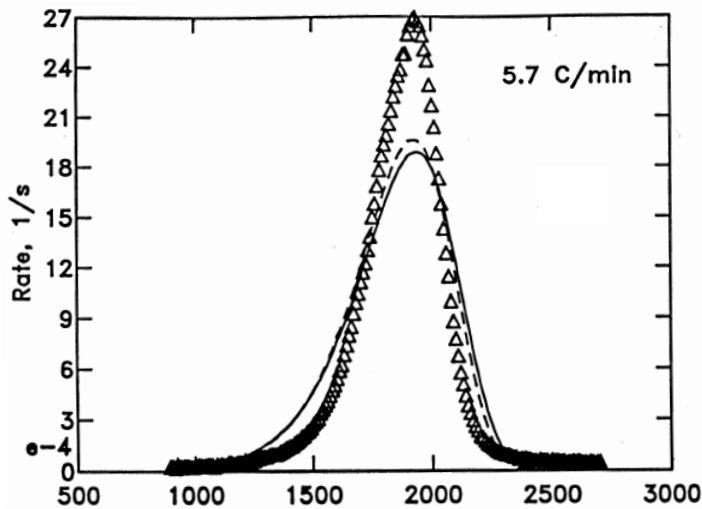
# Frejus Boghead Coal is a Good Example of a Well-Preserved Algal Kerogen



- Profile is only 66% as wide as calculated from Kissinger parameters
- Nonlinear fit of a first-order gives  $E$  greater than Kissinger's method and not a particularly good fit
- The nucleation-growth model gives a good fit to the entire profile with  $E$  close to Kissinger's method



# A 1<sup>st</sup>-Order Reaction Also Fails to Fit Isothermal Data From Fluidized Bed Pyrolysis

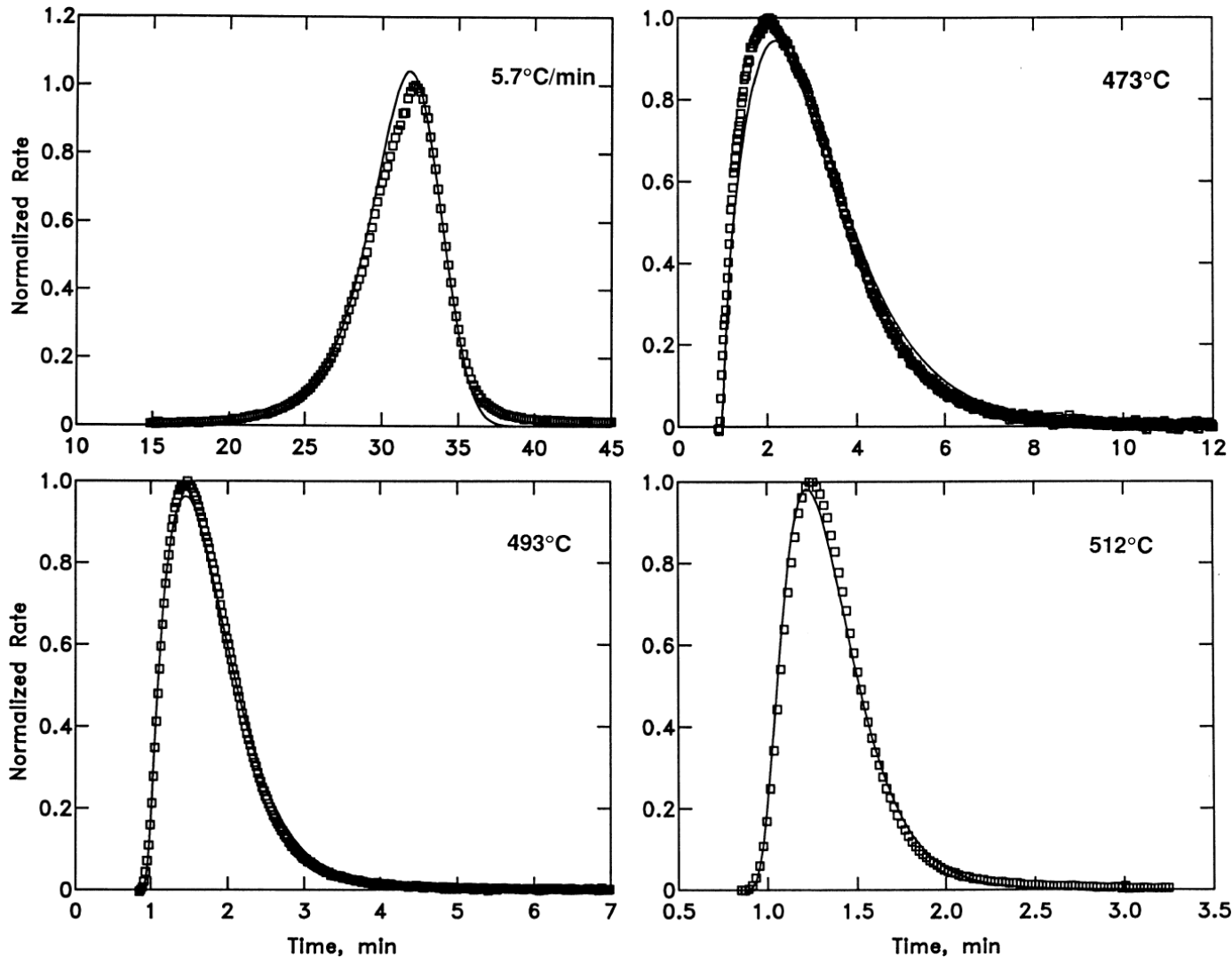


Dashed line:  
Kissinger 1<sup>st</sup>-order  
parameters from  
Pyromat data

Solid line:  
Nonlinear 1<sup>st</sup>-order  
fit to fluidized bed  
data

The slow rise time  
at constant T is  
characteristic of  
an autocatalytic  
reaction

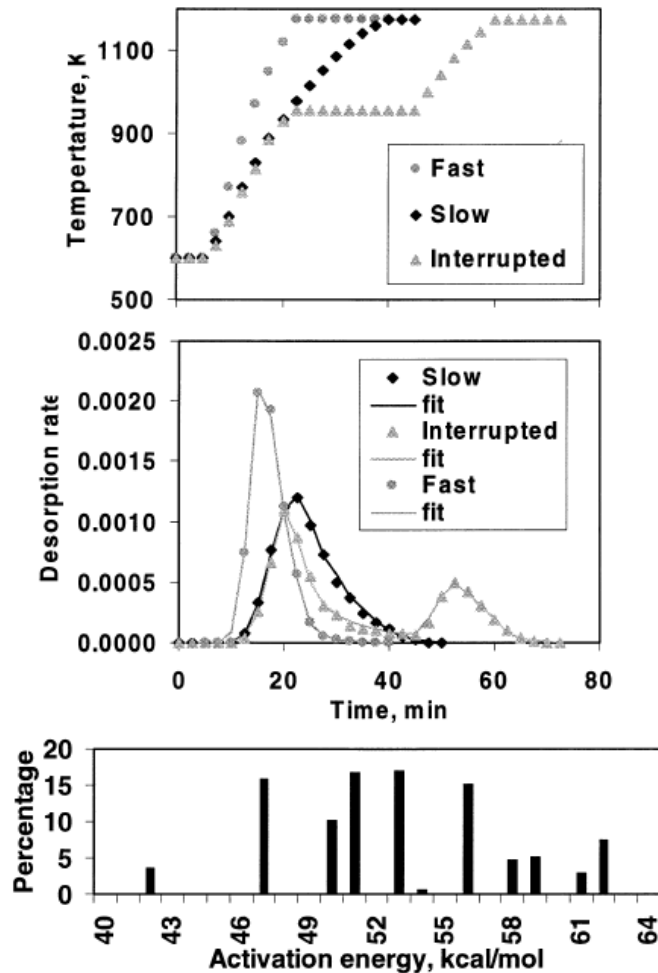
# The Nucleation-Growth model Fits the Frejus Fluidized-Bed Data Very Well, Also



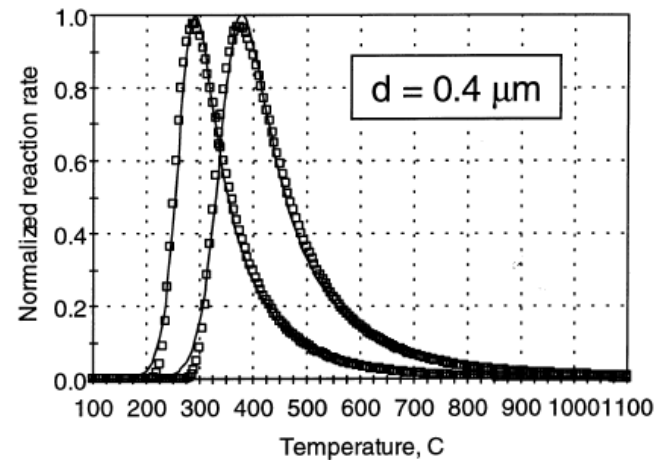
All the fluidized-bed calculations take advantage of the unique ability of Kinetics05 to account for dispersion of the gas signal between the reactor and detector. This is accomplished by using a tracer signal in a fourth column of the data file.

# Surface desorption can follow different kinetic laws

Thermal desorption of CO from soot has an energy distribution



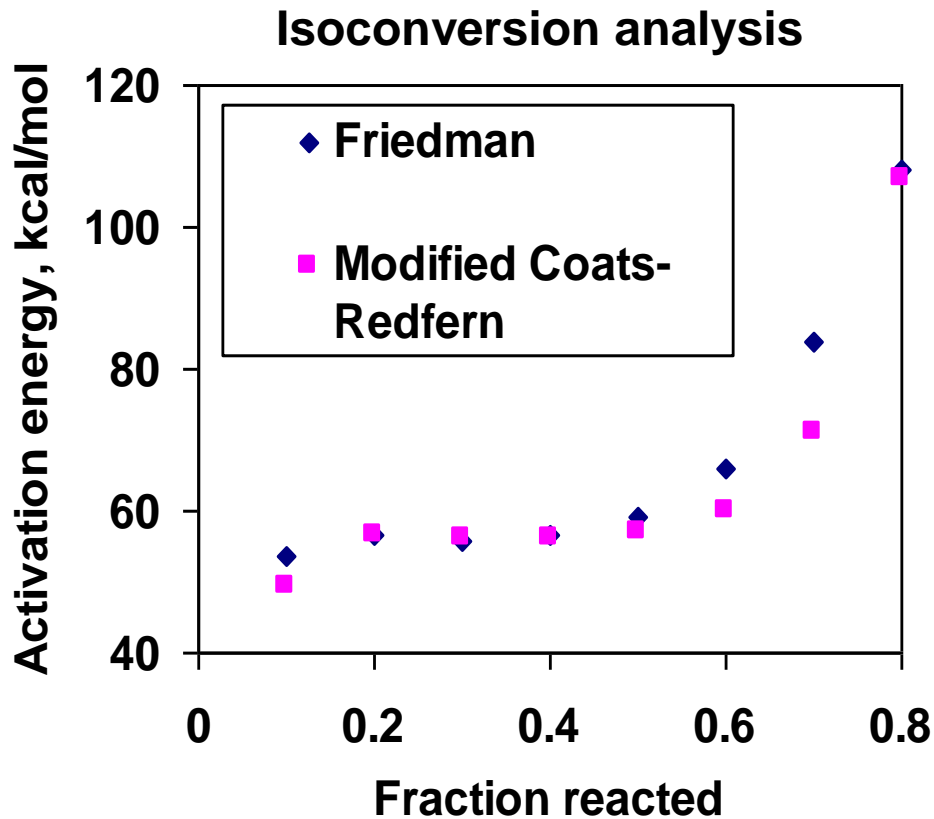
Calculated diffusive release of implanted gas follows nucleation-like kinetics



Parameter	0.2 $\mu\text{m}$	0.4 $\mu\text{m}$	0.6 $\mu\text{m}$
$E$ (kJ/mol)	70.17	70.18	70.04
$A$ ( $\text{s}^{-1}$ )	$9.6 \times 10^3$	$2.45 \times 10^3$	$1.065 \times 10^3$
reaction order, $n$	3.64	3.69	3.73
nucleation order, $m$	0.45	0.45	0.46

The apparent frequency factor scales with depth squared

# Pittsburgh #8 Coal Pyrolysis Requires a Distributed Reactivity Model



## Approximate kinetic parameters

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$E_{50\%}$       57 kcal/mol  
 $A_{50\%}$        $4.1 \times 10^{14} \text{ s}^{-1}$

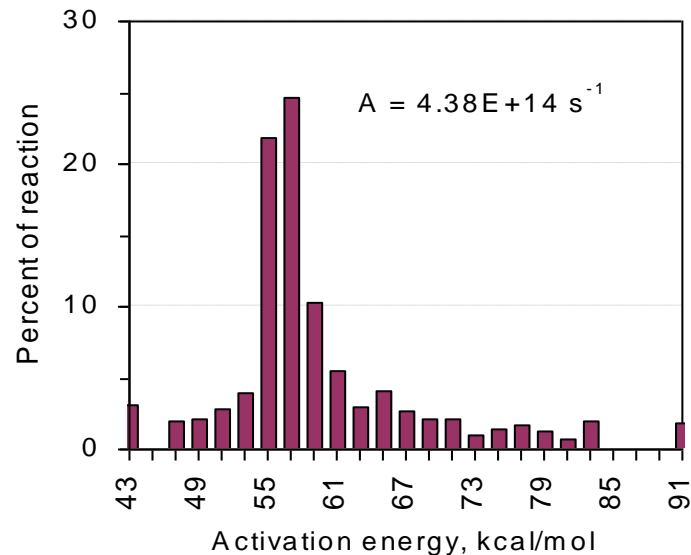
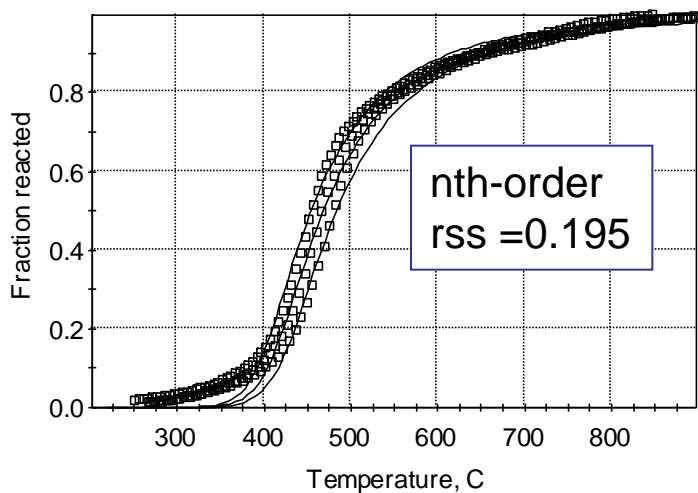
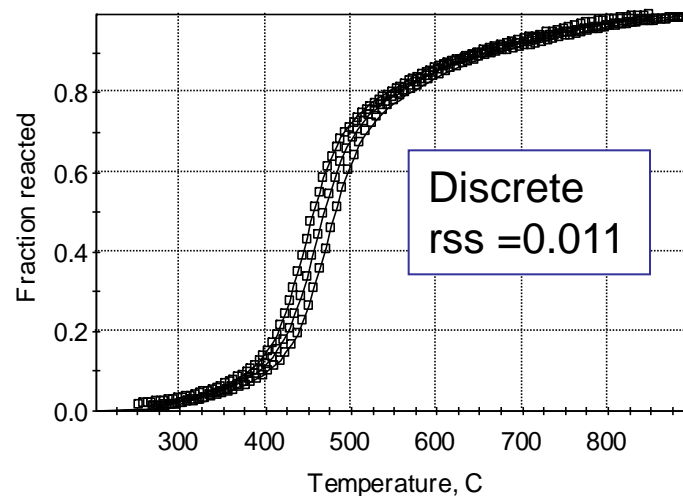
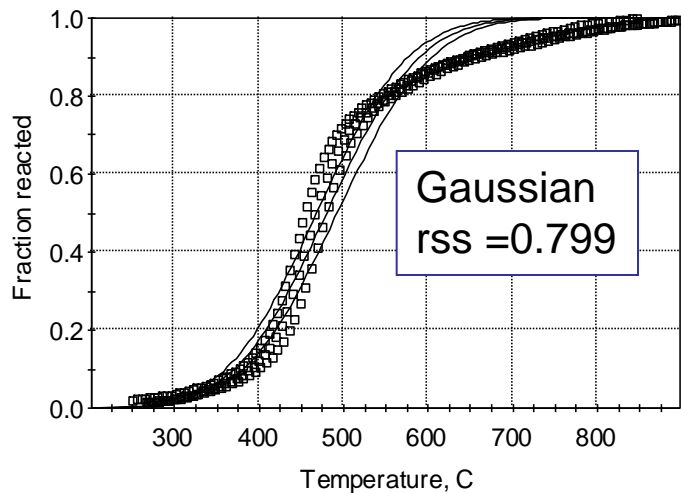
Width relative  
to 1<sup>st</sup>-order rxn    3.6

Asymmetry          2.4  
(skewed to high T)

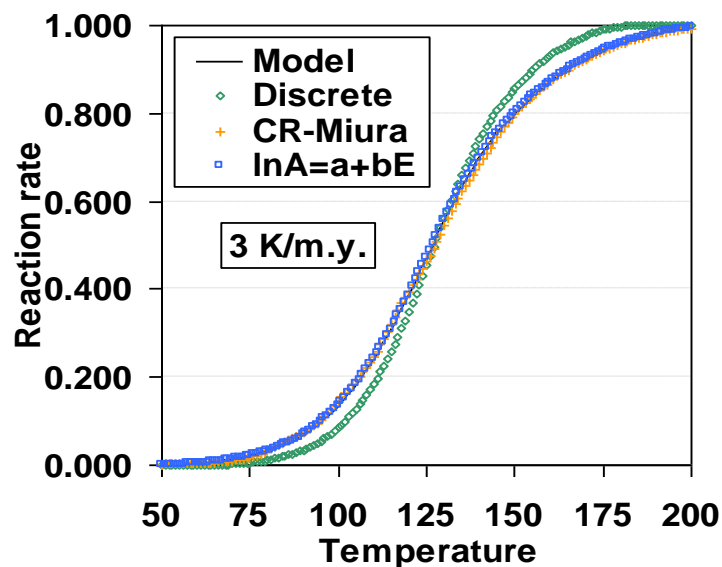
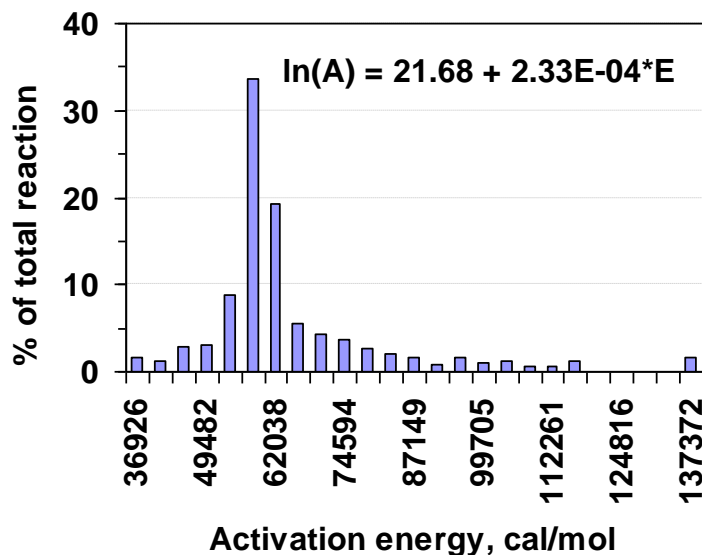
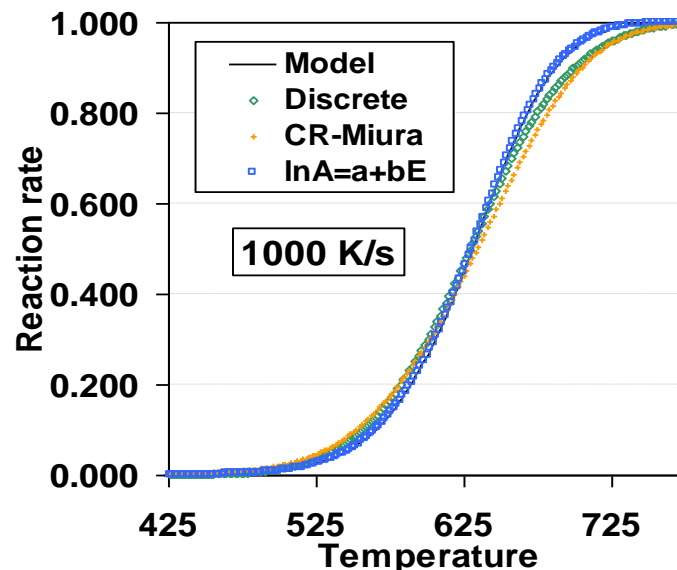
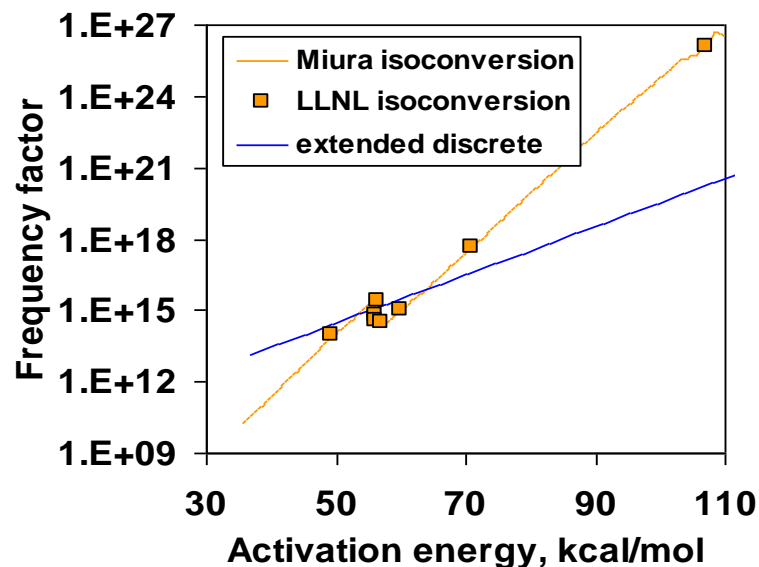
n from width        5.1  
Gaussian  $\sigma$       9.8%

A. K. Burnham and R. L. Braun, Energy & Fuels 13, 1-39, 1999

# The Discrete E Model Easily Provides the Best Fit to Pittsburgh #8 Volatiles



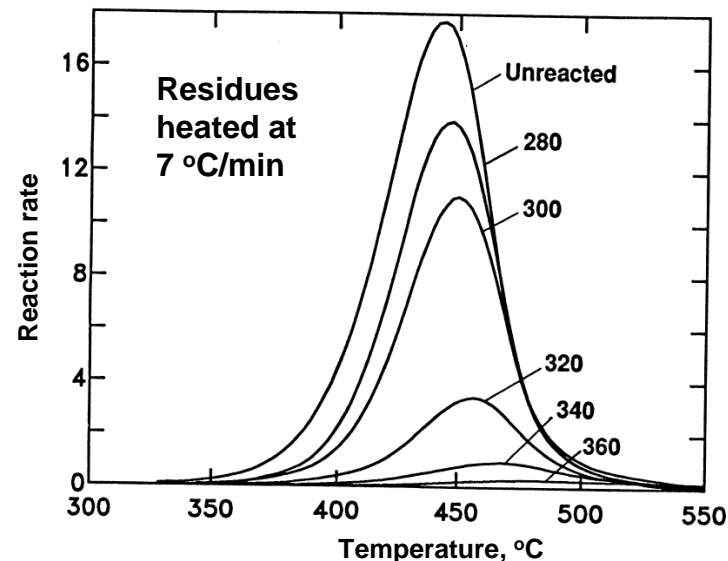
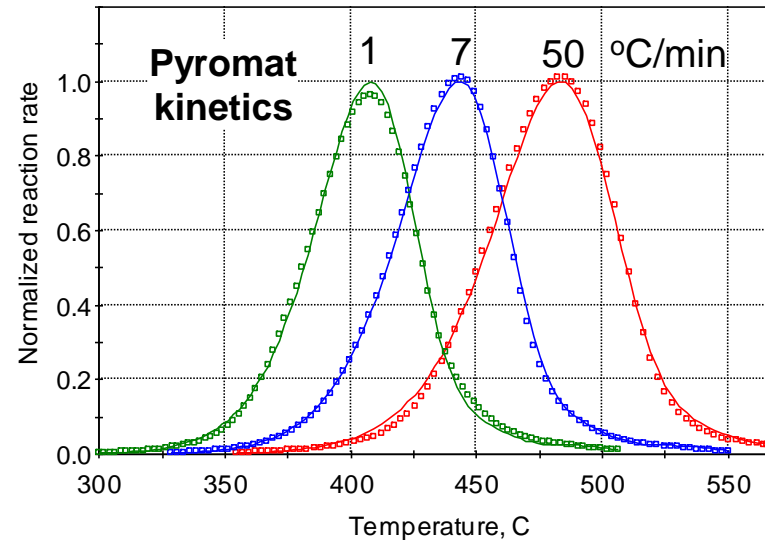
# The Extended Discrete Model Fits Slightly Better and Agrees Better With Isoconversional Analysis



# The Ability of the Discrete Model to Model Residual Activity Has Been Tested

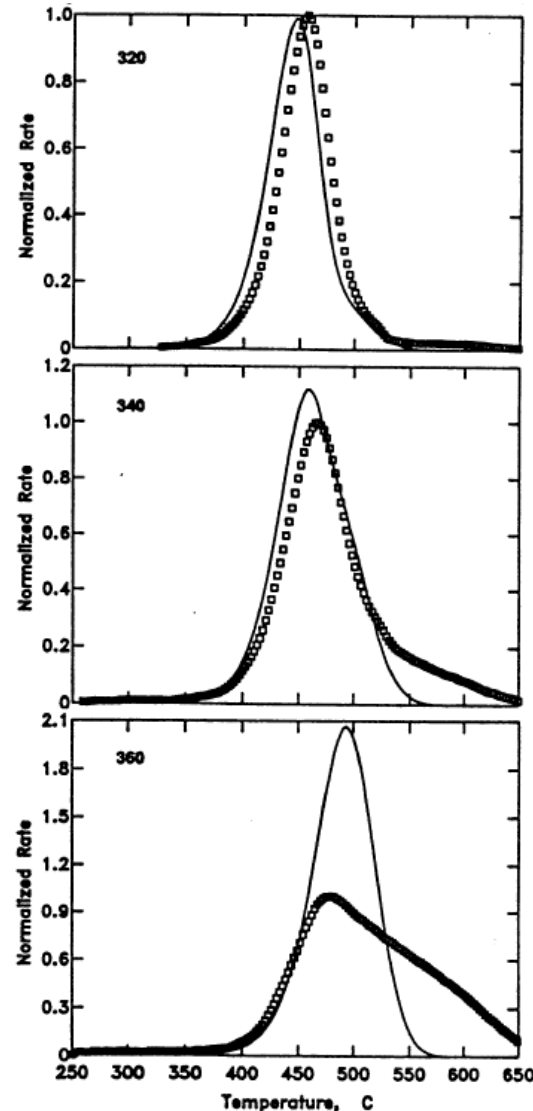
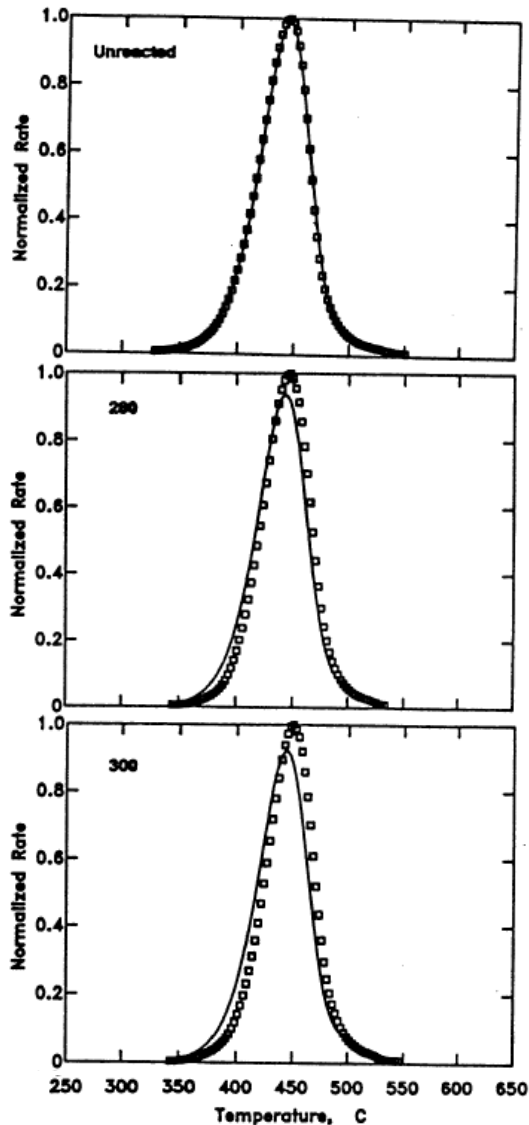
- Measure Pyromat kinetics for an immature sample from the Danish North Sea
- Calculate Pyromat reaction profiles for residues from hydrous pyrolysis (72 h at various temperatures)
- The comparison uses the Apply feature with a thermal history combining the hydrous pyrolysis and Pyromat thermal histories

Burnham et al, Org. Geochem.  
23, 931-939, 1995



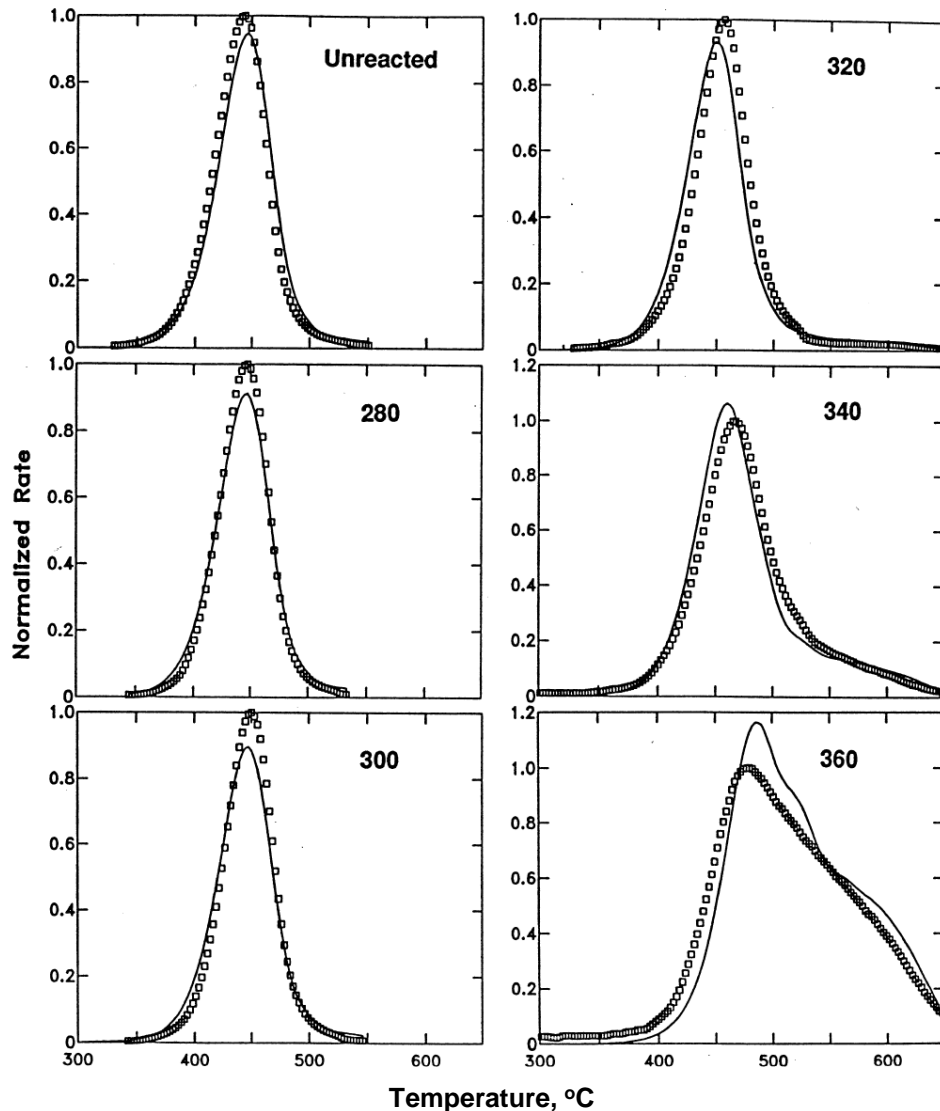


# The Original Sparse Distribution Did Poorly at High Conversions



- Distributed E kinetics should be able to predict the reactivity of the residue if the model is rigorously correct
- The model qualitatively predicts the increase in  $T_{\max}$  with maturation
- The model does not do well for T above 550 °C, because the original signal was low and possibly because the baseline was clipped too much

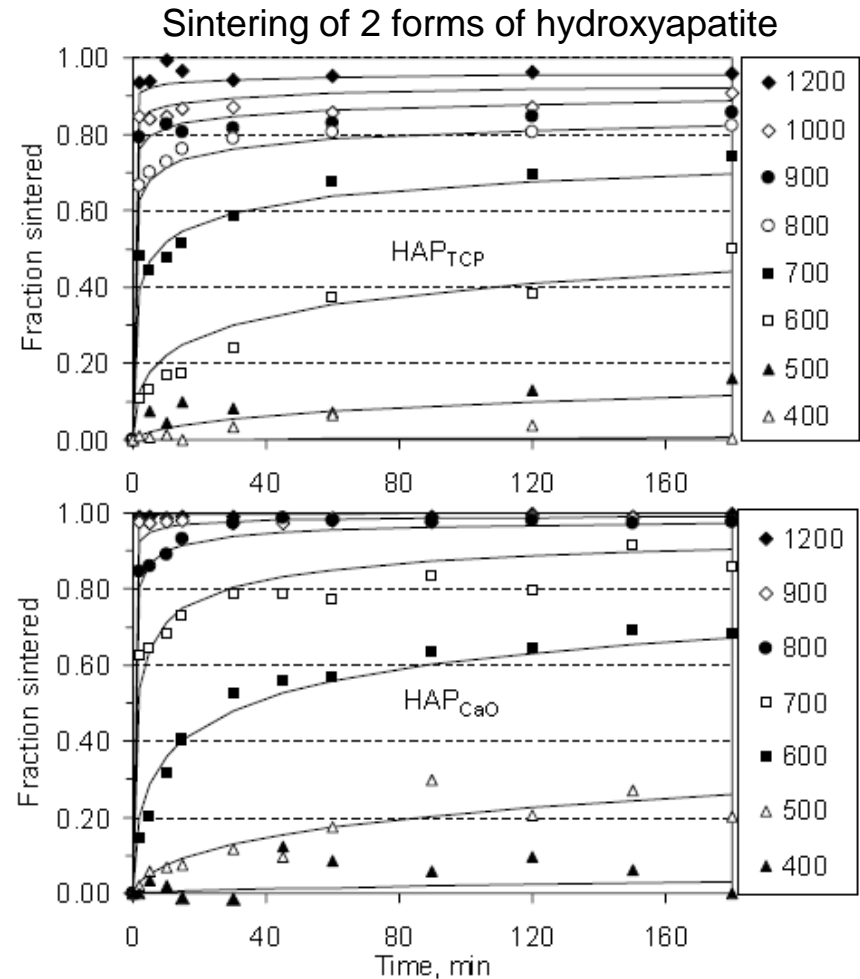
# Agreement is Improved by Fitting All Samples Simultaneously



- All thermal histories include both the hydrous pyrolysis and Pyromat heating phases
- The fit to the unreacted sample is not quite as good as when it is fitted by itself
- The frequency factor and principal activation energy shifted up slightly, with a net increase of about 5 °C in the predicted T of petroleum formation
- The parallel reaction model is verified within the accuracy of the data

# The Distributed Reactivity Approach Can Also Model Sintering

- Sintering is a highly deceleratory process, with an apparent limit that superficially increases with temperature
- Sintering is commonly modeled by a power law or nth-order model
- Mathematically, the exponent of the power law is related to reaction order:  $n=1+1/\nu$
- Conceptually, reaction order can be interpreted as a distribution of diffusion lengths
- Adding a Gaussian E distribution can account for the spectrum of defects leading to mobile material



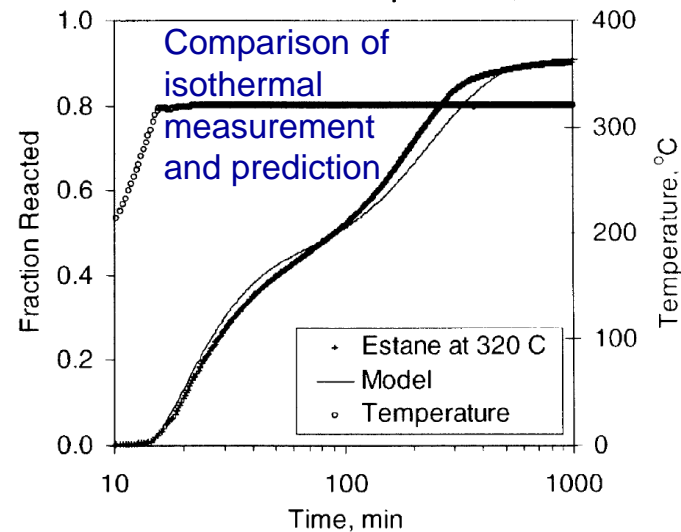
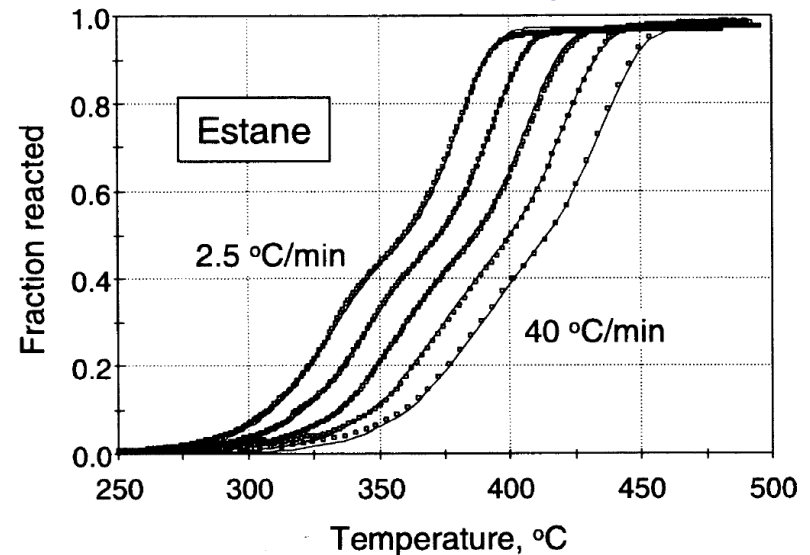
Fraction sintered =  $1-S/S_0$  where S is surface area  
Burnham, Chem. Eng. J. **108**, 47-50, 2005 59

# Kinetics05 can fit reactions with distinct individual components

- The 1st order, nth order, nucleation-growth, Gaussian, and Weibull models can fit up to three independent peaks, but simultaneous regression on all parameters is not reliable
- With strongly overlapping peaks, guidance from the isoconversional analysis and a manual Kissinger analysis can help pick good initial guesses
- A multiple step refinement of subsets of the parameters can give a good model

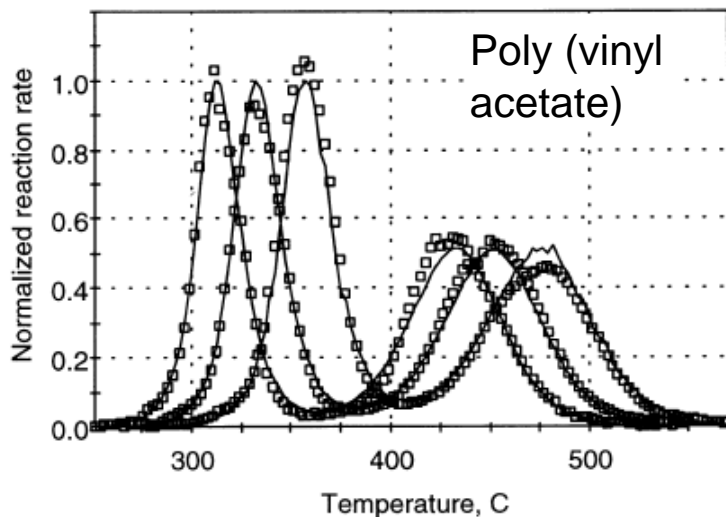
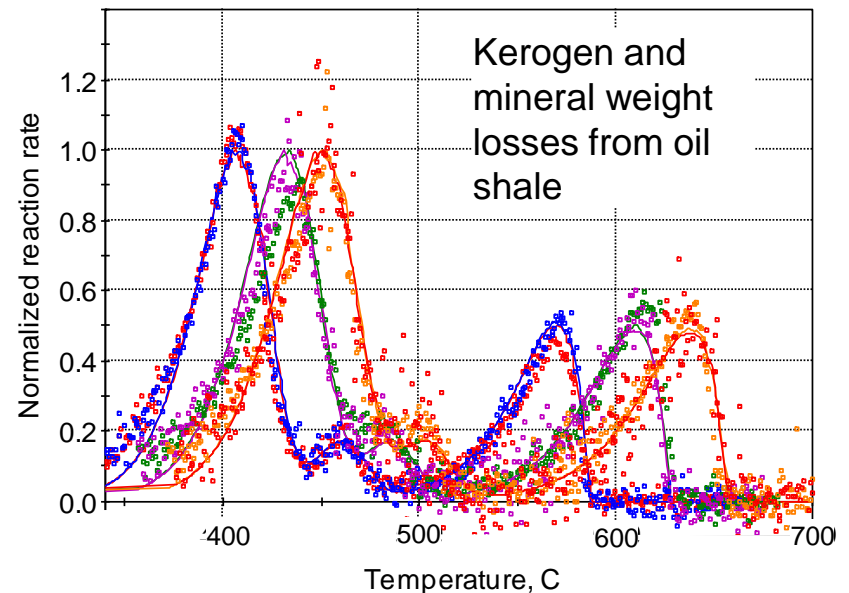
Burnham and Weese, *Thermochimica Acta* **426**, 85-92, 2005

Fit to 2 independent nucleation-growth reactions



# Sometimes reaction profiles have better separated multiple peaks

- With minimally overlapping peaks, splitting the data and doing an initial separate analysis is a useful first step
- Subsequent fitting of the entire profile using the separate results as initial guesses improves the likelihood of a robust convergence



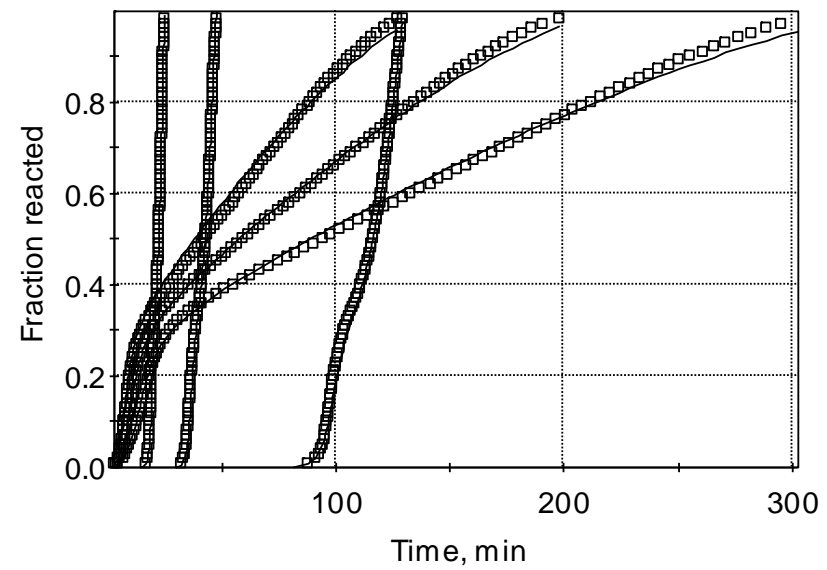
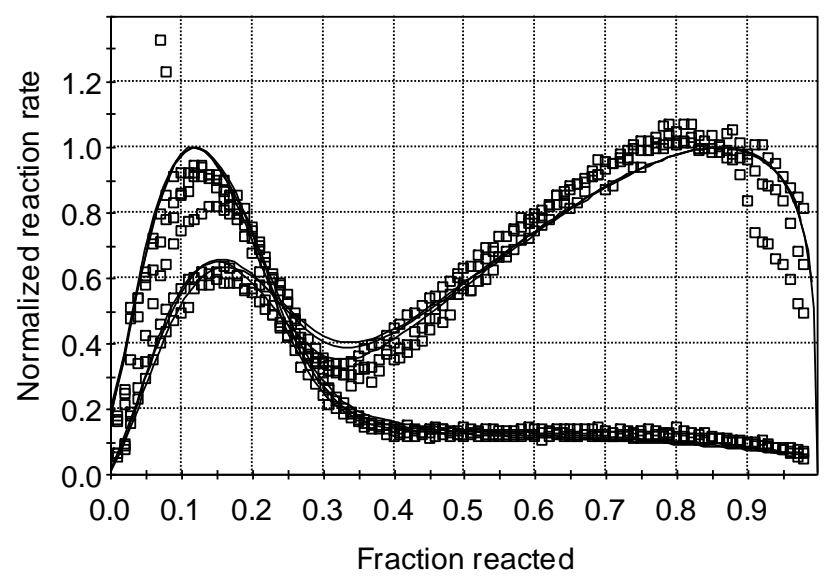
PVAc

1<sup>st</sup> peak: nth-order nucleation-growth reaction

2<sup>nd</sup> peak: nth-order reaction

A. K. Burnham and R. L. Braun, Energy & Fuels  
13, 1-39, 1999

# Two-Step Ammonium Perchlorate Kinetics From TGA Mass Loss Can Predict DSC Heat Flow



## Kinetic parameters

<u>Rxn 1</u>	27% of total	<u>Rxn 2</u>	73% of total
A	$1.36 \times 10^7 \text{ s}^{-1}$	A	$4.19 \times 10^6 \text{ s}^{-1}$
E	22.8 kcal/mol	E	26.6 kcal/mol
m	1.00	m	0.00
n	1.96	n	0.28

Decomposition:  
nucleation-growth

Sublimation:  
receding interface

