Compensating for the Compensation Effect Using Simulated and Experimental Kinetics from the Bakken and Red River Formations, Williston Basin, North Dakota*

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Abstract

The application of the Arrhenius equation to the problem of petroleum generation promises to predict hydrocarbon generation rates given experimentally defined kinetic parameters and temperature. There are several ways to determine kinetic parameters. In most, if not all of these methods, small variations in experimental conditions result in a linear covariance between activation energy (Ea) and the natural log of the frequency factor (A). This covariance is usually referred to as the compensation effect, the underlying cause of which is debated. However, experimental compensation effects frequently include frequency factors that are thermodynamically impossible. Based on thermodynamic arguments, the frequency factor should be largely unaffected by temperature and as a consequence be nearly constant. The covariance in A and Ea is explained from a statistical standpoint by noting that random experimental errors, particularly in temperature, result in "best fit" solutions to some experimental variable, usually temperature. Solutions for Ea and A that incorporate these errors lie within an extremely elongated ellipse that coincides with the compensation effect.

An analytical solution exists that relates the harmonic mean of experimental temperatures containing random errors to the slope of the resulting compensation effect. "Compensation effects" from numerical simulations of programmed pyrolysis experiments

containing random temperature errors are consistent with the analytical solution. Furthermore, calculated compensation effects using experimental temperatures are very close to the compensation effect obtained from non-isothermal kinetic analyses of samples from the Bakken (Mississippian-Devonian) and Red River (Ordovician) formations. The compensation effect is largely due to temperature errors that may be corrected to a constant value of A using the harmonic mean of the peak reaction temperatures. Assuming a constant frequency factor allows "correct" activation energies to be obtained. When done, corrected values of Ea from the Bakken (Type II) change more rapidly with depth than do samples from the Red River (Type I). A map of "corrected" activation energies from the Bakken Formation is consistent with current notions of the formation's thermal maturity within the Williston Basin of North Dakota.

References Cited

Barrie, P.J., 2012, The mathematical origins of the kinetic compensation effect, the effect of random experimental errors: Phys. Chem., v. 14, p. 318-326.

Krug, R.R., et al., 1976, Statistical interpretation of enthalpy-entropy compensation: Nature, v. 261, p, 566-567.
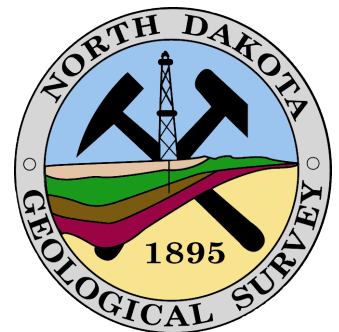
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NORTH DAKOTA

Reaction Kinetics

How Fast

How Much

$$dx/dt = Ae^{\frac{-E_a}{RT}}$$

$$dx = A\int_{t}^{t_{n+1}} e^{\frac{-E_a}{RT}} dt$$

Kerogen Property

- E_a - Activation Energy (kJ/mole)
- A – Frequency Factor (1/t)
- R – Gas constant

Overburden Property

- T – Temperature (^oK)
- t – Time

Source Bed Property

- x – moles kerogen ("richness")

Kissinger Equation: Determination of Kinetic Parameters using Nonisothermal Experiments

$$-\ln (\beta/T_p^2) = E_a/R \, (1/T_p) - \ln (A \, R/E_a)$$
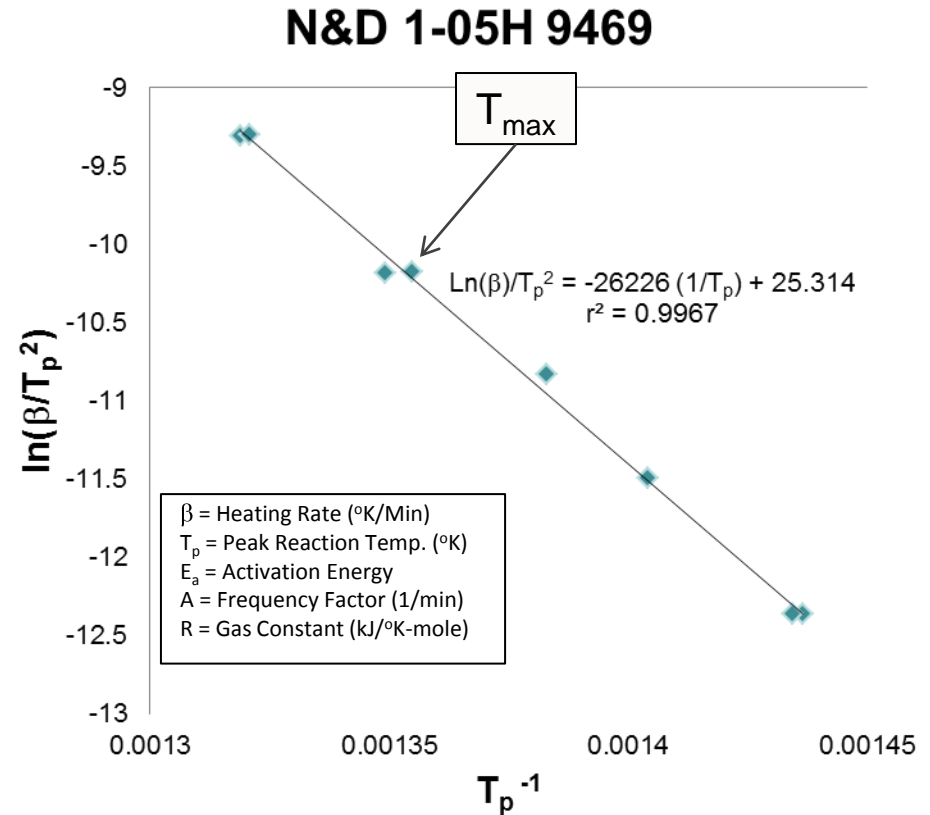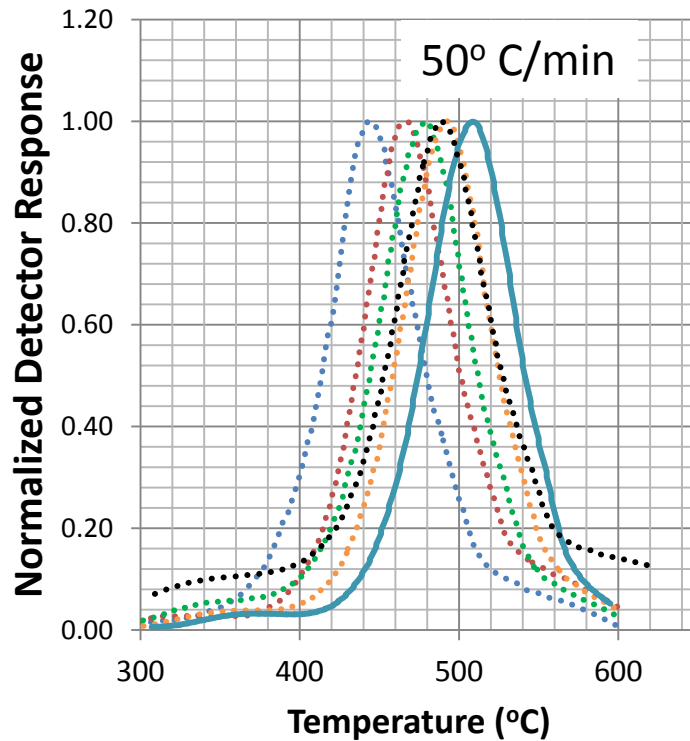
Where:

E_a = Activation Energy (kJ/mole)

A = Frequency Factor (min^{-1})

R = Gas constant (kJ/^{o}K – mole)
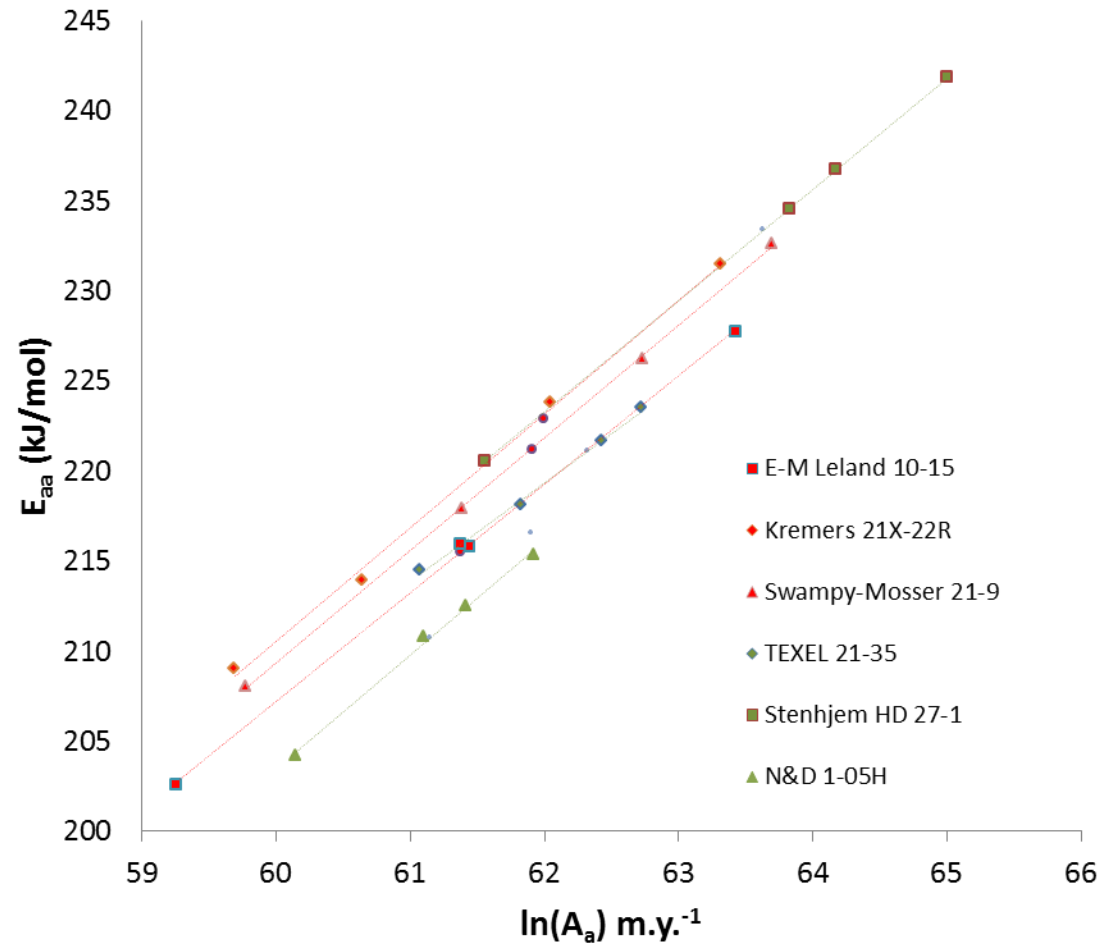
T_p = Peak Reaction Temperature (^{o}K)

β = Heating rate (^{o}K/min)

Change in Peak Reaction Temperature as a Function of Heating Rate

N&D 1-05H 9469

T_{max}

$Ln(\beta)/T_p^2 = -26226\,(1/T_p) + 25.314$
$r^2 = 0.9967$

β = Heating Rate (^oK/Min)
T_p = Peak Reaction Temp. (^oK)
E_a = Activation Energy
A = Frequency Factor (1/min)
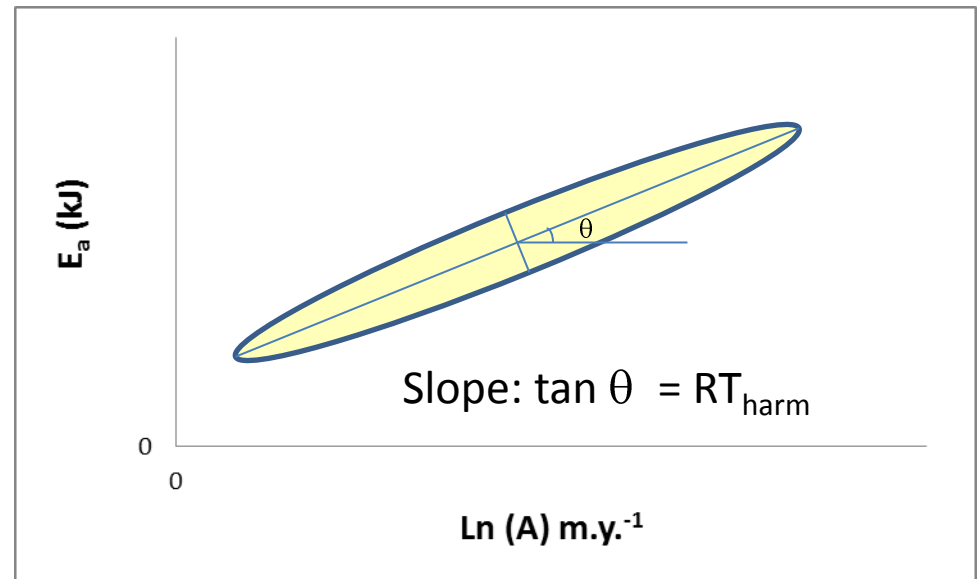R = Gas Constant (kJ/^oK-mole)

$$\ln(\beta/T_p^2) = -(E_a/R)T_p^{-1} + \ln(AR/E_a)$$

Raw Data: Now what?

Statistical Compensation Effect

- Caused by random measurement errors.

- Because E_a and A are not independent, errors produce various best fit linear regressions that result in solutions for E_{aa} and A_a that fall within an error ellipse.

Slope: $\tan \theta = RT_{harm}$

E_a (kJ)

Ln (A) m.y.$^{-1}$

The "Error Ellipse"

- $ratio = \sqrt{\dfrac{r^2(T^2+1)}{1-r^2}}$

Where:
   ratio = major axis : minor axis length
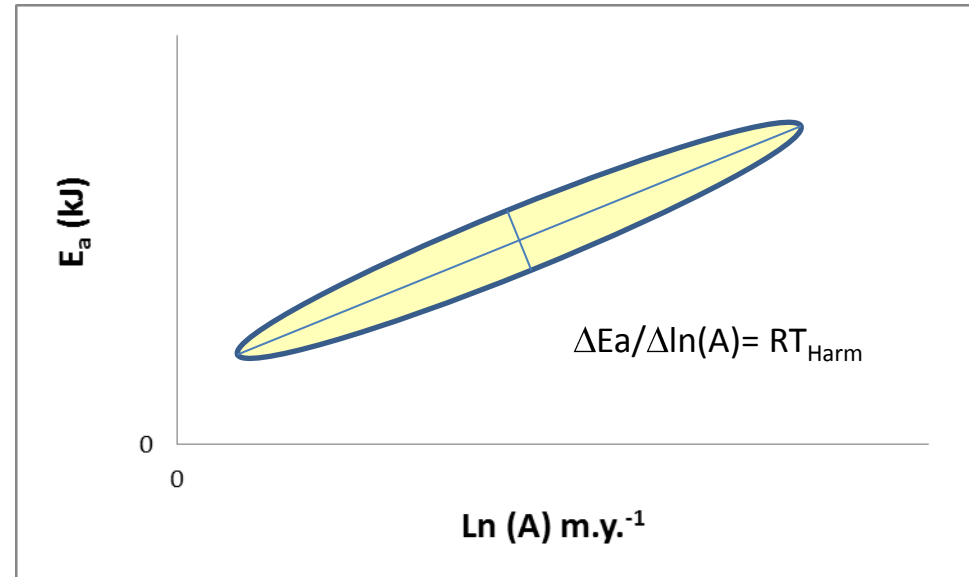   r = correlation coefficient (near 1)
   T = harmonic mean of temperature $^\circ K$
   R = Gas constant
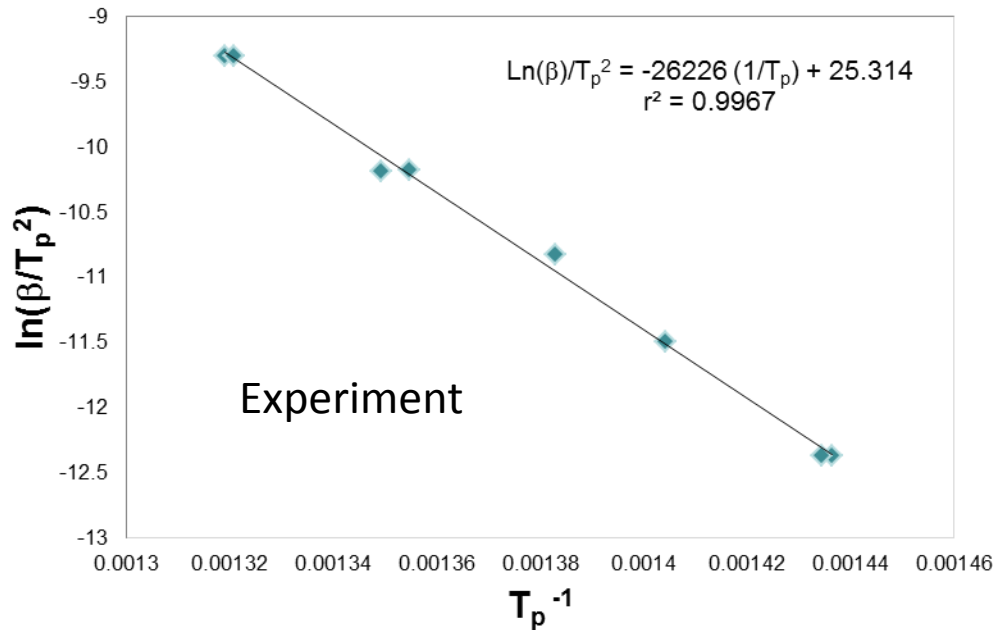Ratio >> 1000:1 for experiments here.

Foot wide and a mile long

"Ellipse" is essentially a line in which the slope of the major axis is the product of the harmonic mean of the temperatures used and the gas constant.

$\Delta Ea/\Delta ln(A) = RT_{Harm}$

Krug, R.R. et al. ,1976, Statistical interpretation of enthalpy-entropy compensation: Nature 261, 566-567

Barrie, P.J., 2012, The mathematical origins of the kinetic compensation effect:1. the effect of random experimental errors. Phys. Chem. Chem. Phys., 2012, 14, 318-326.

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$$\ln(\beta/T_p^2) = -26226\,(1/T_p) + 25.314$$
$$r^2 = 0.9967$$

Experiment

X-axis: T_p^{-1}

Y-axis: $\ln(\beta/T_p^2)$

Apparent Solution

Possible Equivalent Solutions

- Experiment
- Error "Ellipse"

X-axis: $\ln(A)$ m.y.$^{-1}$

Y-axis: E_a (kJ/mol)

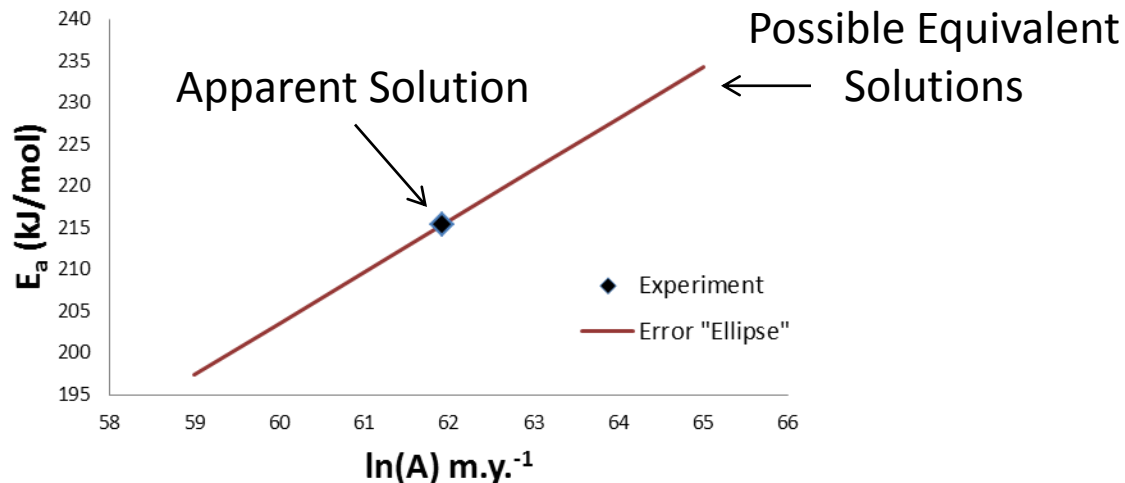$$\ln(\beta/T_p^2) = -E_a/R\,(1/T_p) + \ln(A\,R/E_a)$$

- Error Ellipse
  - All possible solutions.
 - Slope = $T_{harm} *R$
    - Dependent upon experimental design (β).
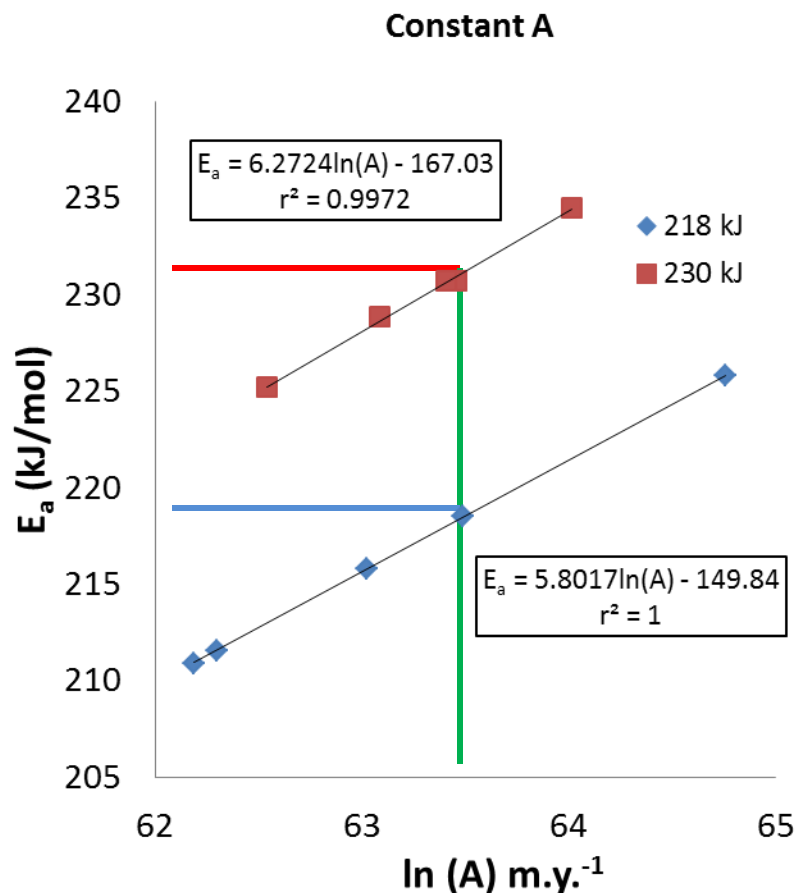   - Function of errors in measuring T_p

Random Temperature Error Simulations

- Kissinger Equation

- Nonisothermal analysis
- $\ln(\beta/T_p^2) = -E_a/R\,(1/T_p) + \ln(A\,R/E_a)$

- Solve for β given E_a, A and T_p
- Add normally distributed error with a fixed variance to T_p – call it T_{pe}
- Plot $\ln(\beta/T_{pe}^2)$ versus $(1/T_{pe})$
- Calculate linear regression
- Solve for apparent activation energy E_{aa} and apparent frequency factor A_a
- Given:
  - E_a = 235 kJ/mol
  - A = 1×10^{14} sec^{-1}
- Solution for this example:
  - E_{aa} = 231 kJ/mol
  - A_a = 3.3 X 10 ^{15} sec^{-1}

$\ln(\beta/T_p^2) = -27833(1/T_p) + 25.493$
$r^2 = 0.999$
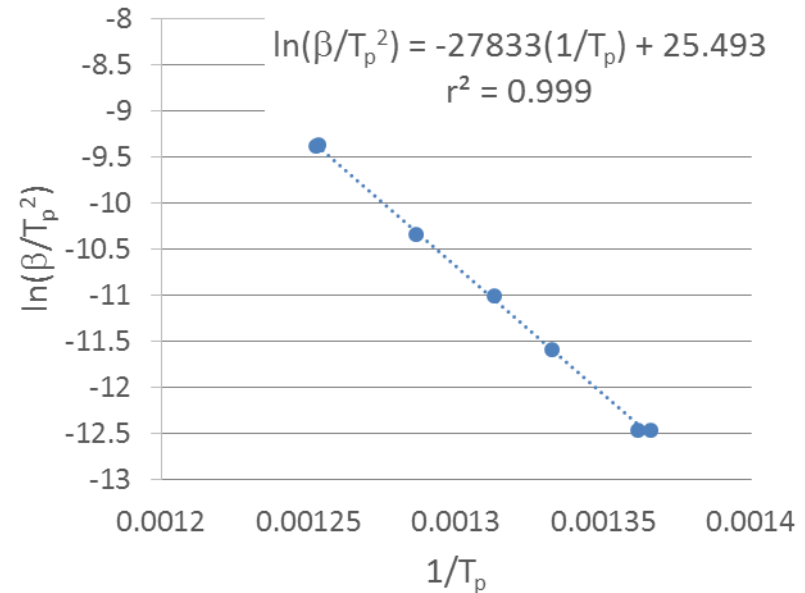
T_p (°C)	β	T_{peC} (°C)	T_{peK} (°K)	$1/T_{pek}$	$\ln(\beta/T_{pek}^2)$
460	2.06	461.21	734.36	0.001362	-12.4758
460	2.06	458.99	732.14	0.001366	-12.4697
477	5.16	477.26	750.41	0.001333	-11.5995
489	9.65	488.61	761.76	0.001313	-11.0045
503	19.53	504.17	777.32	0.001286	-10.3396
524	53.78	524.70	797.85	0.001253	-9.37892
524	53.78	525.20	798.35	0.001253	-9.38017

Simulated Statistical Compensation Effect: Constant A

Constant A

$E_a = 6.2724\ln(A) - 167.03$
$r^2 = 0.9972$

◆ 218 kJ
■ 230 kJ

$E_a = 5.8017\ln(A) - 149.84$
$r^2 = 1$

E_a (kJ/mol) vs ln (A) m.y.$^{-1}$

- Ln (A) = 63.319 (m.y.$^{-1}$)
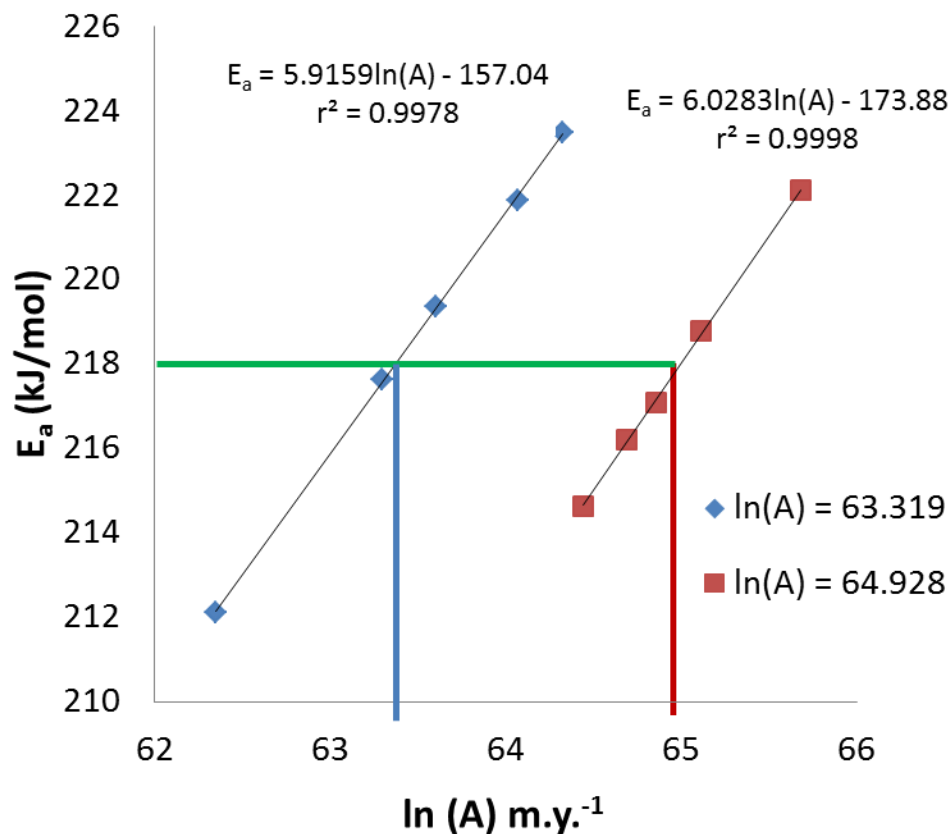
- 218 kJ/mol
  - Harmonic mean * R = 5.88
  - Slope = 5.80

- 230 kJ/mol
  - Harmonic mean * R = 6.21
  - Slope = 6.27

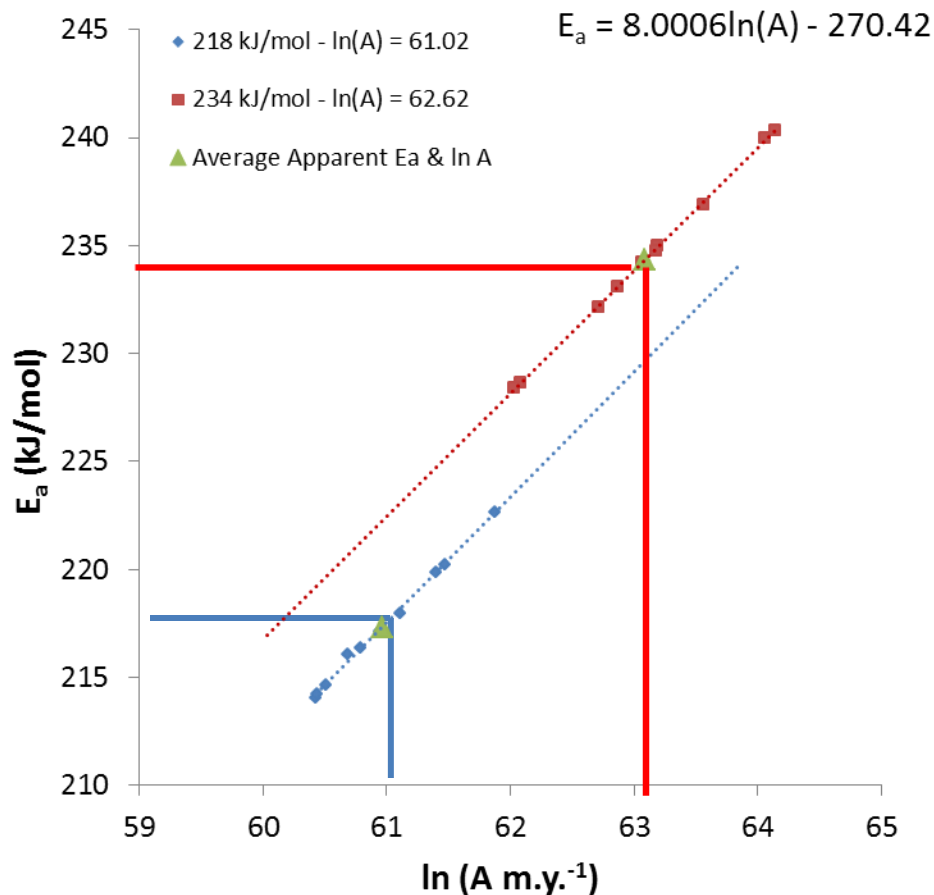# Simulated Statistical Compensation Effect: Constant E_a

- $E_a = 218$ kJ/mol

- $\ln(A) = 63.319$ (m.y.$^{-1}$)
  - Harmonic mean $*$ R $= 5.88$
  - Slope $= 5.92$

- $\ln(A) = 64.928$ (m.y.$^{-1}$)
  - Harmonic mean $*$ R $= 6.21$
  - Slope $= 6.03$

Simulated Statistical Compensation Effect: Both E_a and A Differ

- Simulations
  - 10 runs
  - Normal distribution of error.
  - Fixed variance
  - Dotted lines – regression for each data set
- Blue data
  - E_a = 218 kJ/mol
  - A = 1 X 10^{13} sec^{-1}
- Red data
  - E_a = 234 kJ/mol
  - A = 5 X 10^{13} sec^{-1}
- Green Triangles
  - Average E_a and ln(A)
  - Heavy black line – regression through average Ea and ln A
  - Slope does not equal statistical compensation effect

$E_a = 8.0006\ln(A) - 270.42$

Legend:
- 218 kJ/mol - ln(A) = 61.02
- 234 kJ/mol - ln(A) = 62.62
- Average Apparent Ea & ln A

Y-axis: E_a (kJ/mol)
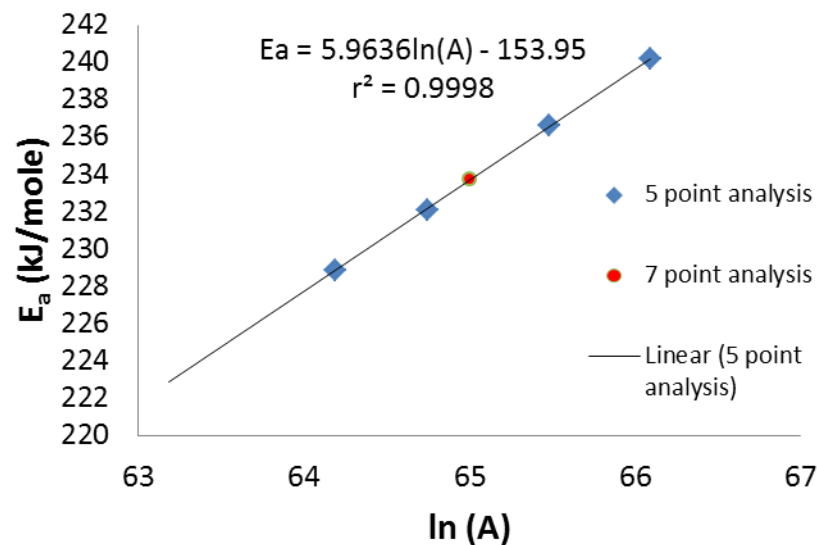X-axis: ln (A m.y.$^{-1}$)

Statistical Compensation Effects in Experimental Data

- Williston Basin, North Dakota.
  - Devonian-Miss. Bakken Fm.
    - Organoclastic
    - Regional anoxia
  - Ord. Red River Formation
    - Carbonate hosted
    - Local anoxia

- Experimental Method
- Nonisothermal Pyrolysis
  - 5 heating rates
    - 2,5,10,20,50 ^{o}K/min.
    - Duplicate runs using 2 and 50°K/min. heating rates.
  - Determined apparent E_a and A using the Kissinger method.

# Statistical Compensation Effect: Within Sample Error

- Old Engine Oil 16-4H
  - API: 33061005210000
  - Upper Bakken: 9011' TVD
- Analysis involves 7 "runs" (Yellow circle)
  - 2 @ 2°/min
  - 1 @ 5°/min
  - 1 @ 10°/min
  - 1 @ 20°/min
  - 2 @ 50°/min
  - R x Harmonic Mean = 6.04

- Error analysis involves four analyses using different combinations of five points (Blue squares)
  - 1 @ 2°/min
  - 1 @ 5°/min
  - 1 @ 10°/min
  - 1 @ 20°/min
  - 1 @ 50°/min

$$E_a = 5.9636 \ln(A) - 153.95$$
$$r^2 = 0.9998$$

- 5 point analysis
- 7 point analysis
- Linear (5 point analysis)

Results from the Error Analysis

E_{aa}	240.19	236.62	232.09	223.69
$\ln(A_a)$	66.10	66.10	64.75	64.19
$R*T_{harm}$	6.04	6.05	6.10	6.04

Statistical Compensation Effect between samples within a well.

33053023570000
STENEHJEM HD 27 1
ORYX ENERGY CO.

T_{harm} X R = 6.24

$E_{aa} = 6.1726 \ln(A) - 159.39$
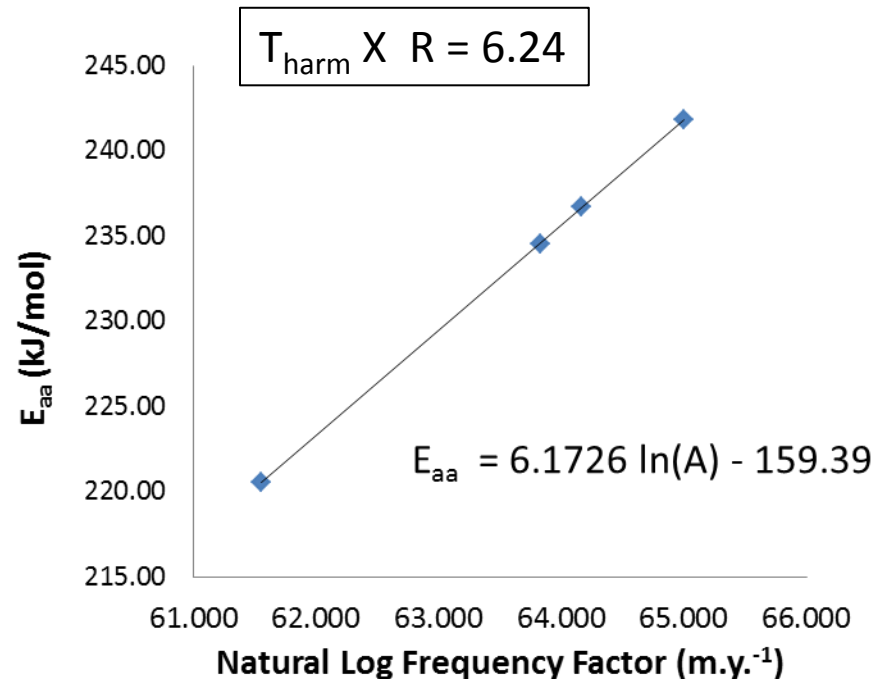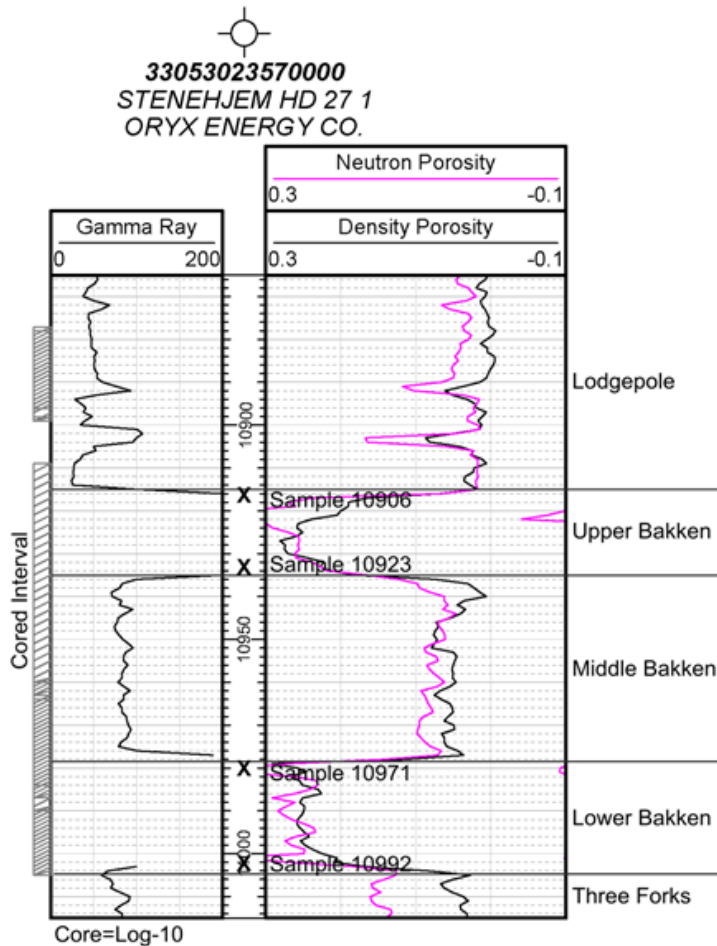
$\ln(A_a)$ (m.y.$^{-1}$)	E_{aa} (kJ/mole)	Harmonic Mean (^{o}K)	T_{max} (^{o}C)
61.555	220.59	750.51	452
64.999	241.85	751.57	451
64.171	236.74	751.33	451
63.829	234.52	752.13	451

Statistical Compensation Effect Between Wells

"Mature" Tmax = 451°C   "Immature" Tmax = 429°C

"Mature"

$E_{aa} = 6.1726 \ln(A) - 159.39$

$T_{harm} \times R = 6.25$

"Immature"

$E_{aa} = 6.3311 \ln(A) - 176.42$

$T_{harm} \times R = 6.04$

Apparent Activation Energy (kJ/mol)

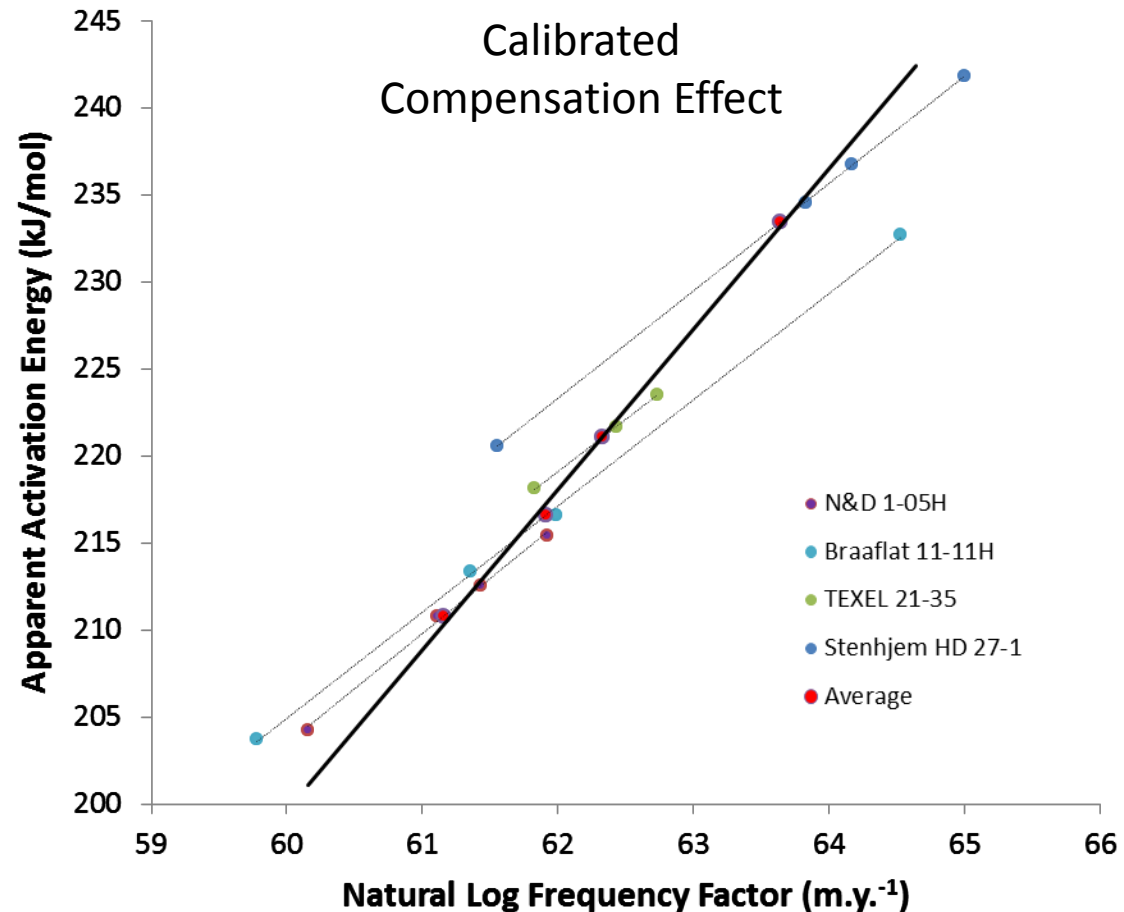Natural Log Frequency Factor (m.y.$^{-1}$)
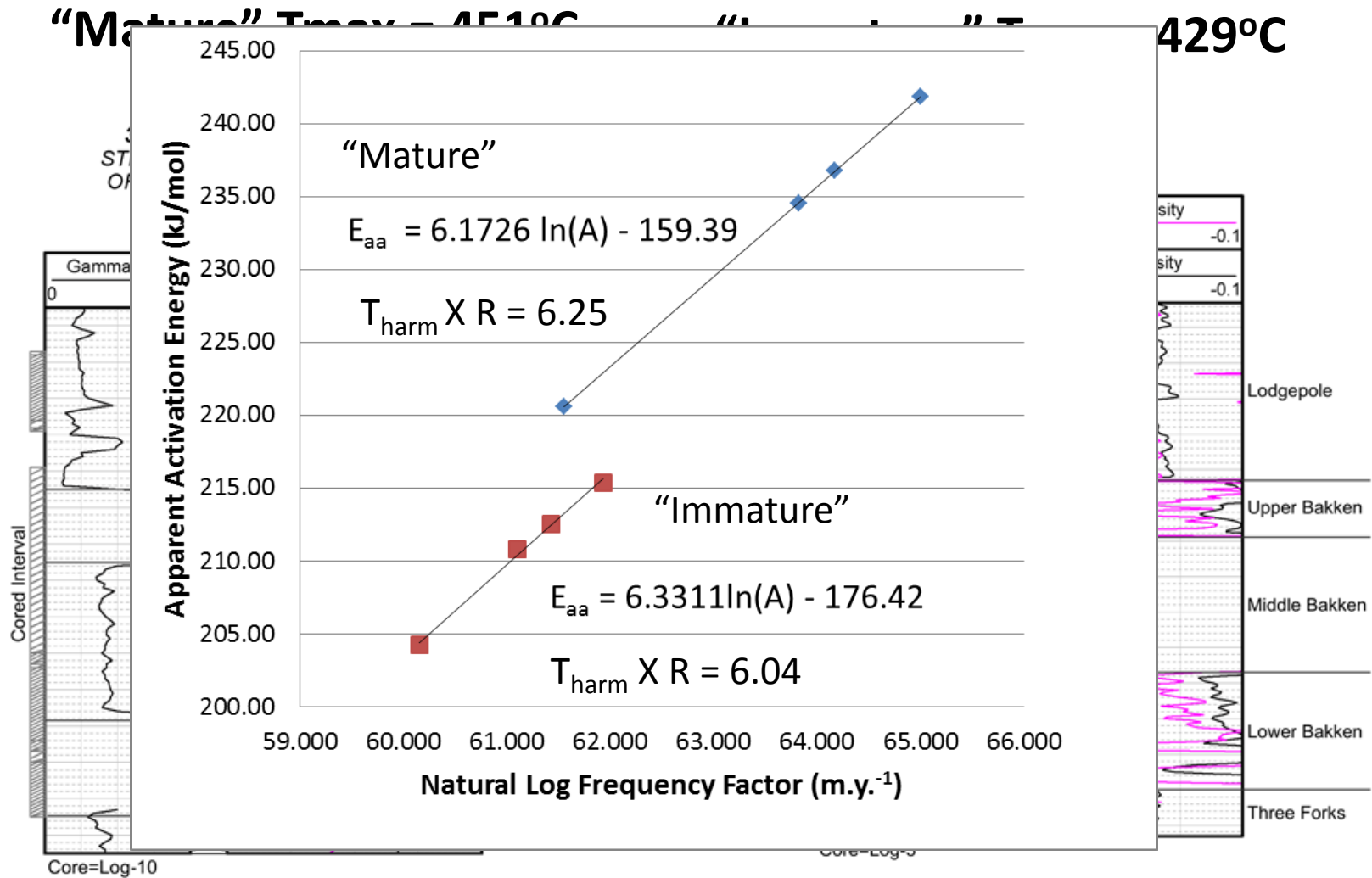
Compensating for the Compensation Effect

Compensation
effect from four
wells

Average E_{aa} and
$\ln(A_a)$ for each
well (red circles).

Linear fit to
average E_{aa} and
$\ln(A_a)$

Calibrated Compensation Effect

Apparent Activation Energy (kJ/mol)

Natural Log Frequency Factor (m.y.$^{-1}$)

- N&D 1-05H
- Braaflat 11-11H
- TEXEL 21-35
- Stenhjem HD 27-1
- Average

Compensation Effect: Red River (Ord.)

Three wells with samples that obey the same statistical compensation effect (parallel dotted lines).

The average E_{aa} and ln (A_a) are shown by red circles.

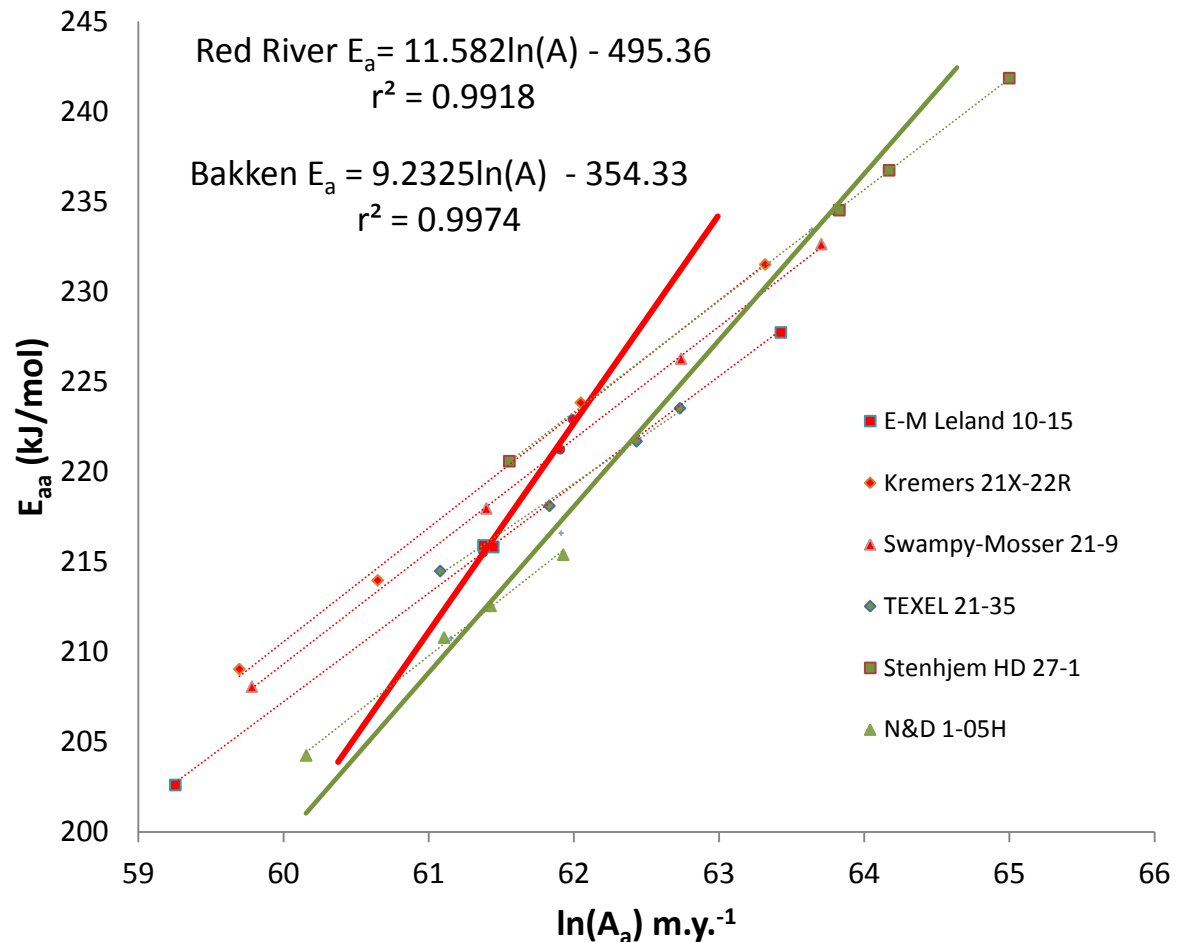Regression (heavy black line) through the average values is significant.

Slope of the average data regression is not consistent with the statistical compensation effect.
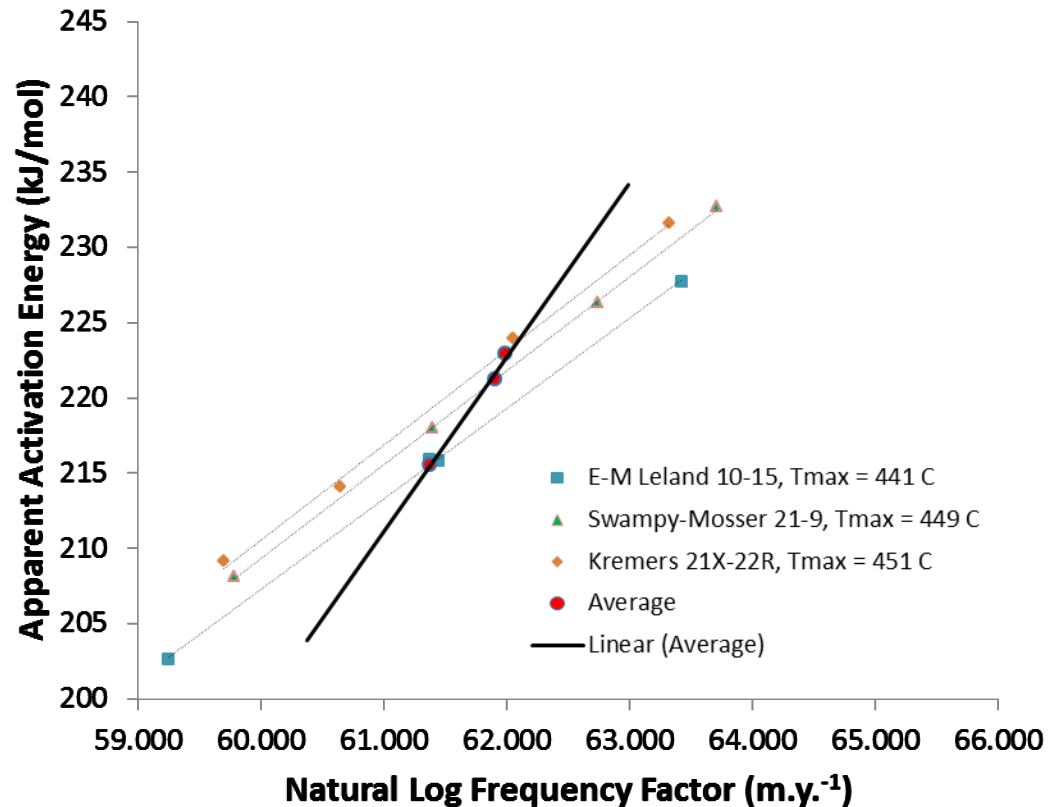
Well Name	API	Slope	T_{harm}*R	Mean Ea kJ/mol	Mean ln(A) m.y.$^{-1}$	Mean T_{max} °C
Kremers 21X-22R	33033000440000	6.27	6.32	222.92	61.99	441
Swampy-Mosser 21-9	33023003280000	6.21	6.25	221.24	61.91	449
E-M Leland 10-15	33075012860000	6.13	6.02	215.52	61.38	451

Compensation Effect Between Formations

- Red River in red

- Bakken in green

- Regression slope between samples between formations:
  - not equal to statistical compensation effect.
 - not equal to each other.

Red River $E_a = 11.582\ln(A) - 495.36$
$r^2 = 0.9918$

Bakken $E_a = 9.2325\ln(A) - 354.33$
$r^2 = 0.9974$

Legend:
- E-M Leland 10-15
- Kremers 21X-22R
- Swampy-Mosser 21-9
- TEXEL 21-35
- Stenhjem HD 27-1
- N&D 1-05H

Y-axis: E_{aa} (kJ/mol)

X-axis: $\ln(A_a)$ m.y.$^{-1}$

Compensating for the statistical compensation effect.

Given a single E_{aa} and $\ln(A_a)$
(cross-filled circle)

Find the harmonic mean from the temperatures used. (Green Line)

Find the intersection between the statistical compensation effect and calibrated compensation effect
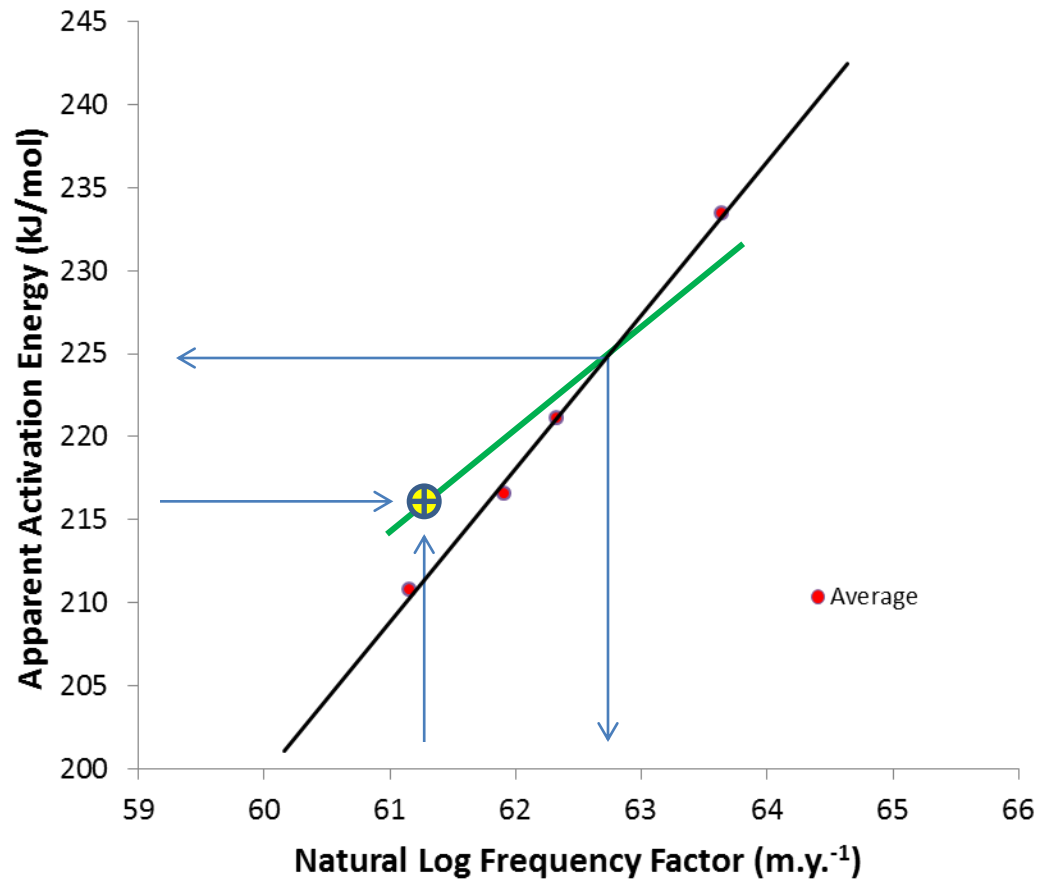
Conclusions

- Statistical compensation effects in simulated and experimental kinetic analyses of the Bakken and Red River Formations are consistent with random measurement errors.

- Kinetic parameters that are coincident with a particular statistical compensation effect may be equivalent.

- The slope of the statistical compensation effect is given by the harmonic mean of the temperatures used and the gas constant.

- Minimum requirements to adequately describe kinetics from nonisothermal pyrolysis:
  - apparent E_a
  - apparent A
  - Harmonic mean of the temperatures used.

- There is no unique solution without knowledge of either E_a or A and Harmonic mean of temperatures used.

Thank You