Linear Least-Squares Application in Chemical Kinetic Data

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Advanced Linear Algebra, Spring 2014

Outline

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Elementary Reactions

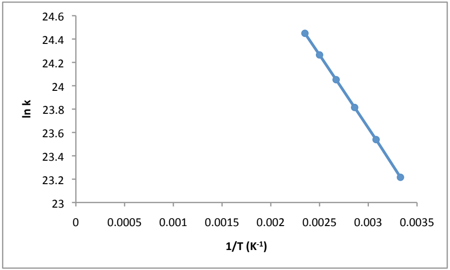
$$A + B \rightarrow C + D$$

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

Outline

Arrhenius Equation

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



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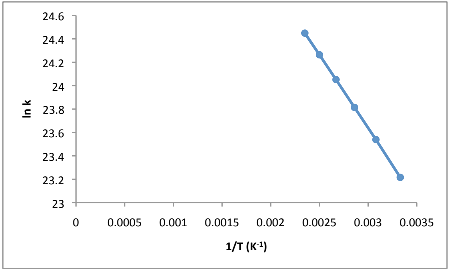
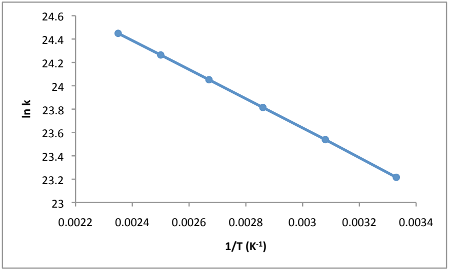


$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$



Arrhenius Equation

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$
$$y \quad = \quad m \quad x \quad + \quad b$$

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$$y = m \; x + b$$

$$A = e^b = e^{\ln k}$$
$$E_a = -mR$$

Arrhenius Equation

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$$y = m \; x + b$$

$$\mathbf{k} = m \; \mathbf{T_0} + b$$

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Arrhenius Equation

$$\ln k = \frac{-E_a}{R}\frac{1}{T} + \ln A$$

$$y \;=\; m \;\; x \;+\; b$$

$$\mathbf{k} \;=\; m \;\; \mathbf{T_0} \;+\; b$$

$$\begin{bmatrix} k_1 \\ k_2 \\ \vdots \\ k_n \end{bmatrix} = \begin{bmatrix} t_1 & 1 \\ t_2 & 1 \\ \vdots & \vdots \\ t_n & 1 \end{bmatrix} \begin{bmatrix} m \\ b \end{bmatrix}$$

$$A = e^b = e^{\ln k}$$

$$E_a = -mR$$

Arrhenius Equation

$$
\begin{aligned}
\ln k &= \frac{-E_a}{R}\frac{1}{T} + \ln A \\
y &= m \quad x + \quad b \\
\mathbf{k} &= m \quad \mathbf{T_0} + \quad b \\
\begin{bmatrix} k_1 \\ k_2 \\ \vdots \\ k_n \end{bmatrix} &= \begin{bmatrix} t_1 & 1 \\ t_2 & 1 \\ \vdots & \vdots \\ t_n & 1 \end{bmatrix} \begin{bmatrix} m \\ b \end{bmatrix} \\
\mathbf{k} &= T \quad \mathbf{x}
\end{aligned}
$$

$$
\begin{aligned}
A &= e^b = e^{\ln k} \\
E_a &= -mR
\end{aligned}
$$

Arrhenius Equation

Table : Temperature Dependence of the Rate Constant in the Formation of Nitrogen Dioxide and Oxygen Gas

T (K)	k $(M^{-1}s^{-1})$	$\ln k$	$\frac{1}{T}$ (K^{-1})
300	1.21×10^{10}	23.216	3.33×10^{-3}
325	1.67×10^{10}	23.539	3.08×10^{-3}
350	2.20×10^{10}	23.841	2.86×10^{-3}
375	2.79×10^{10}	24.052	2.67×10^{-3}
400	3.45×10^{10}	24.264	2.50×10^{-3}
425	4.15×10^{10}	24.449	2.35×10^{-3}

Arrhenius Equation

$$\begin{bmatrix} 3.33 \times 10^{-3} & 1 \\ 3.08 \times 10^{-3} & 1 \\ 2.86 \times 10^{-3} & 1 \\ 2.67 \times 10^{-3} & 1 \\ 2.50 \times 10^{-3} & 1 \\ 2.35 \times 10^{-3} & 1 \end{bmatrix} \begin{bmatrix} m \\ b \end{bmatrix} = \begin{bmatrix} 23.216 \\ 23.539 \\ 23.841 \\ 24.052 \\ 24.264 \\ 24.449 \end{bmatrix}$$

Outline

Preliminaries

Theorem

If T is size $m \times n$ with $m \geq n$, then T has full rank if and only if its columns form a linearly independent set.

$$T = \begin{bmatrix} t_1 & 1 \\ t_2 & 1 \\ \vdots & \vdots \\ t_n & 1 \end{bmatrix}$$

T has full rank.

Outline

Normal Equations

Use when...

- no rounding errors
- speed is important

Normal Equations

Use when...

- no rounding errors
- speed is important

Benefits:

- T can be any size
- T has full rank so $\mathbf{x}$ will always be unique

Normal Equations

Theorem

The least-squares solution to $T\mathbf{x} = \mathbf{k}$ is also a solution to $T^*T\mathbf{x} = T^*\mathbf{k}$, the normal equations, where the function $r(\mathbf{x}) = \|T\mathbf{x} - \mathbf{k}\|^2$ is minimized.

Normal Equations

$$T^* T\mathbf{x} = T^*\mathbf{k}$$

$$\begin{bmatrix} 4.7656 \times 10^{-5} & 0.01679 \\ 0.01679 & 6 \end{bmatrix} \begin{bmatrix} m \\ b \end{bmatrix} = \begin{bmatrix} 0.40025 \\ 143.334 \end{bmatrix}$$

$m = -1256.73203263 \Rightarrow E_a = 10.44847012 \ \frac{kJ}{mol}$
$b = 27.405755138 \Rightarrow A = 7.983038593 \times 10^{11}$

Outline

QR Decomposition

via the Gram-Schmidt Procedure

Use when...

- rounding errors are present
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QR Decomposition

via the Gram-Schmidt Procedure

Theorem

Suppose that T is an $m \times n$ matrix of rank n. Then there exists an $m \times n$ matrix Q whose columns form an orthonormal set, and an upper-triangular matrix R of size n with positive diagonal entries, such that $T = QR$.

QR Decomposition

via the Gram-Schmidt Procedure

$$\begin{aligned} T &= [\mathbf{t}_1 | \mathbf{t}_2] \\ &= [\mathbf{u}_1 | \mathbf{u}_2] \begin{bmatrix} 1 & \frac{-\mathbf{t}_1^*\mathbf{t}_2}{\mathbf{t}_1^*\mathbf{t}_1} \\ 0 & 1 \end{bmatrix}^{-1} && \text{Gram-Schmidt on } \mathbf{t}_1 \text{ and } \mathbf{t}_2 \\ &= [\mathbf{q}_1 | \mathbf{q}_2] \begin{bmatrix} \frac{1}{\|\mathbf{u}_1\|} & \frac{-\mathbf{t}_1^*\mathbf{t}_2}{\mathbf{t}_1^*\mathbf{t}_1} \\ 0 & \frac{1}{\|\mathbf{u}_2\|} \end{bmatrix}^{-1} && \mathbf{u}_1 \text{ and } \mathbf{u}_2 \text{ scaled by their norm} \\ &= QR \end{aligned}$$

QR Decomposition

via the Gram-Schmidt Procedure

$$T = \begin{bmatrix} 0.4824 & -0.5954 \\ 0.4462 & -0.2926 \\ 0.4143 & -0.0262 \\ 0.3868 & 0.2039 \\ 0.3621 & 0.4098 \\ 0.3404 & 0.5914 \end{bmatrix} \begin{bmatrix} 6.9034 \times 10^{-3} & 2.4322 \\ 0 & 0.2909 \end{bmatrix} = QR$$

QR Decomposition

via the Gram-Schmidt Procedure

From the normal equations: $R\mathbf{x} = Q^*\mathbf{k}$

$$m = -1256.73203263 \;\Rightarrow E_a = 10.44847012 \;\frac{kJ}{mol}$$
$$b = 27.405755138 \;\Rightarrow A = 7.983038593 \times 10^{11}$$

Notes:

- Preserves entry values when calculated over RDF
- Solutions equal to those calculated directly from the normal equations

Outline

Cholesky Factorization

Use when...

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Cholesky Factorization

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- speed is important

Benefits:

- T can be any size
- T has full rank so $\mathbf{x}$ will always be unique

Cholesky Factorization

Definition

If $\langle \mathbf{x}, A\mathbf{x} \rangle > 0$ for all $\mathbf{x}$ then A is a symmetric positive definite matrix where $\mathbf{x} \neq 0$.

$$T^*T = \begin{bmatrix} 4.7656 \times 10^{-5} & 0.01679 \\ 0.01679 & 6 \end{bmatrix}$$

T is a symmetric positive definite matrix.

Cholesky Factorization

Theorem

If T^*T is symmetric positive definite then there exists a unique upper triangular matrix G with positive diagonal entries such that $T^*T = G^*G$.

Cholesky Factorization

Proof:

$$T^*T = A = \left[\begin{array}{c|c} a & \mathbf{y}^* \\ \hline \mathbf{y} & B \end{array}\right]$$

$$= \left[\begin{array}{c|c} \sqrt{a} & \mathbf{0}^* \\ \hline \frac{1}{\sqrt{a}}\mathbf{y} & I \end{array}\right] \left[\begin{array}{c|c} 1 & \mathbf{0}^* \\ \hline \mathbf{0} & B - \frac{1}{a}\mathbf{y}\mathbf{y}^* \end{array}\right] \left[\begin{array}{c|c} \sqrt{a} & \frac{1}{\sqrt{a}}\mathbf{y}^* \\ \hline \mathbf{0} & I \end{array}\right]$$

$$= {G_1}^* A_1 G_1$$

After n interations:

$$A = G_n^* \dots G_2^* G_1^* I G_1 G_2 \dots G_n = G^* G$$

Cholesky Factorization

Note:
The entry in the upper left corner of the matrix $B - \frac{1}{a}\mathbf{y}\mathbf{y}^*$ is always positive.

$$a = \langle \mathbf{e}_2, A_1 G_1^{-1} \mathbf{e}_2 \rangle > 0 \quad \text{where } \mathbf{x} = G_1^{-1}\mathbf{e}_2$$

Cholesky Factorization

$$\begin{aligned} T^*T &= \begin{bmatrix} 4.7656 \times 10^{-5} & 0.01679 \\ 0.01679 & 6 \end{bmatrix} \\ &= \begin{bmatrix} 6.90 \times 10^{-3} & 0 \\ 2.4322 & 0.29093 \end{bmatrix} \begin{bmatrix} 6.90 \times 10^{-3} & 2.4322 \\ 0 & 0.29093 \end{bmatrix} \\ &= G^*G. \end{aligned}$$

Cholesky Factorization

From the normal equations: $G^*G\mathbf{x} = T^*\mathbf{k}$

$m = -1256.74352341 \Rightarrow E_a = 10.44856565 \; \frac{kJ}{mol}$
$b = 27.4057876928 \Rightarrow A = 7.983289484 \times 10^{11}$

Outline

SVD

Use when...

- T is rank deficient
- speed is not important

SVD

Use when...

- T is rank deficient
- speed is not important

Benefits:

- Method is rank revealing
- Only method that holds when T is rank deficient
- T has full rank so $\mathbf{x}$ will always be unique

SVD

Theorem

If T is a real $m \times n$ matrix then there exists orthogonal matrices

$$U = [\mathbf{u}_1|...|\mathbf{u}_m] \text{ and } V = [\mathbf{v}_1|...|\mathbf{v}_n],$$

where U is size m and V is size n, such that $T = USV^*$. S is a diagonal matrix with diagonal entries $\sqrt{\delta_1}, ..., \sqrt{\delta_n}$, where $\delta_1, ..., \delta_n$ are eigenvalues of the matrix T^*T.

SVD

- The eigenvalues of T^*T, δ_1, δ_2, are $\{6.72278\times10^{-7}, 6\}$
- The singular values of T are $s_1 = \sqrt{\delta_1} = 8.199 \times 10^{-4}$ and $s_2 = \sqrt{\delta_2} = 2.4495$

$$S = [s_1\mathbf{e}_1 | s_2\mathbf{e}_2] = \begin{bmatrix} 8.199 \times 10^{-4} & 0 \\ 0 & 2.4495 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}$$

SVD

- The eigenvectors for δ_1 and δ_2 are $\mathbf{x}_1$ and $\mathbf{x}_2$

$$V^* = [\mathbf{x}_1|\mathbf{x}_2]^* = \begin{bmatrix} -0.999996 & 0.002798 \\ -0.002798 & -0.999996 \end{bmatrix}$$

SVD

- $\mathbf{y}_1 = \frac{1}{\sqrt{\delta_1}} T\mathbf{x}_1$ and $\mathbf{y}_2 = \frac{1}{\sqrt{\delta_2}} T\mathbf{x}_2$
- The eigenvectors of TT^* for the zero eigenvalue are $\mathbf{y}_3, \ \mathbf{y}_4, \ \mathbf{y}_5, \$ and $\mathbf{y}_6$

$$U = [\mathbf{y}_1|\mathbf{y}_2|\mathbf{y}_3|\mathbf{y}_4|\mathbf{y}_5|\mathbf{y}_6]$$

$$= \begin{bmatrix} -0.6484 & -0.4082 & -0.6426 & -0.3462 & -0.0027 & -0.0339 \\ -0.3435 & -0.4082 & 0.6061 & 0.3246 & -0.4845 & -0.2459 \\ -0.0752 & -0.4082 & 0.3353 & 0.1676 & 0.5944 & 0.7266 \\ 0.1565 & -0.4082 & 0.1014 & 0.3999 & -0.0264 & -0.5969 \\ 0.3638 & -0.4082 & -0.1078 & -0.7408 & 0.4113 & 0.2215 \\ 0.5468 & -0.4082 & -0.2924 & 0.1949 & -0.4920 & -0.0713 \end{bmatrix}$$

SVD

From the normal equations, $SV^*\mathbf{x} = U^*\mathbf{k}$, we get $\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$ so the system is inconsistent.

Let $C = SV^*$ and $\mathbf{b} = U^*\mathbf{k}$, then solve the system $C^*C\mathbf{x} = C^*\mathbf{b}$.

$m = -1256.73203461 \;\Rightarrow E_a = 10.44847014 \,\frac{kJ}{mol}$
$b = 27.4057551435 \;\Rightarrow A = 7.983038637 \times 10^{11}$

Note: When T is rank deficient, $\mathbf{x}$ is given directly.

Summary

Table : Results of Various Least-squares Methods for the Calculation of the Activation Energy and Frequency Factor

Calculation Method	E_a (kJ/mol)	A
Estimation	10.4	8.0×10^{11}
Normal Equations	10.44847012	$7.983038593 \times 10^{11}$
QR Decomposition	10.44847012	$7.983038593 \times 10^{11}$
Singular Value Decomposition	10.44847014	$7.983038637 \times 10^{11}$
Cholesky Factorization	10.44856565	$7.983289484 \times 10^{11}$

Summary

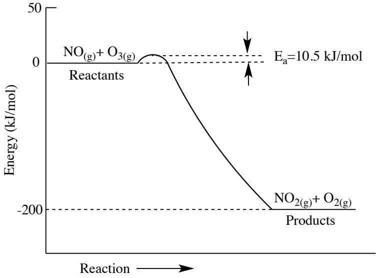

Figure : Energy profile for reaction $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$

$$E_a = 10.448 \; \frac{kJ}{mol} \;\; A = 7.983 \times 10^{11}$$

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