Linear Least-Squares Application in Chemical Kinetic Data

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Advanced Linear Algebra, Spring 2014
Outline

1. Chemical Perspective
   - Elementary Reactions
   - Arrhenius Equation

2. Least-Square Methods
   - Preliminaries
   - Normal Equations
   - QR Decomposition
   - Cholesky Factorization
   - SVD
Outline

1. **Chemical Perspective**
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   - SVD
Elementary Reactions

\[ A + B \rightarrow C + D \]

\[ NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g) \]
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Arrhenius Equation

\[ k = Ae^{-E_a/RT} \]
**Arrhenius Equation**

\[ k = Ae^{-\frac{E_a}{RT}} \]

\[ \ln k = -\frac{E_a}{R} \frac{1}{T} + \ln A \]
The Arrhenius equation is given by:

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

And the linear least-squares equation is:

\[ y = m x + b \]
Arrhenius Equation

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

\[
y = mx + b
\]

\[
A = e^b = e^{\ln k}
\]

\[
E_a = -mR
\]
Arrhenius Equation

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

\[ y = m x + b \]

\[ k = m T_0 + b \]

\[ A = e^b = e^\ln k \]

\[ E_a = -mR \]
Arrhenius Equation

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

\[ y = mx + b \]

\[ k = mt_0 + b \]

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

\[ A = e^b = e^{\ln k} \]

\[ E_a = -mR \]
**Arrhenius Equation**

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

\[
y = m x + b
\]

\[
k = m T_0 + b
\]

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

\[
k = T x
\]

\[
A = e^b = e^{\ln k}
\]

\[
E_a = -mR
\]
Table: Temperature Dependence of the Rate Constant in the Formation of Nitrogen Dioxide and Oxygen Gas

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$k$ ($M^{-1}s^{-1}$)</th>
<th>$\ln k$</th>
<th>$\frac{1}{T}$ ($K^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$1.21 \times 10^{10}$</td>
<td>23.216</td>
<td>$3.33 \times 10^{-3}$</td>
</tr>
<tr>
<td>325</td>
<td>$1.67 \times 10^{10}$</td>
<td>23.539</td>
<td>$3.08 \times 10^{-3}$</td>
</tr>
<tr>
<td>350</td>
<td>$2.20 \times 10^{10}$</td>
<td>23.841</td>
<td>$2.86 \times 10^{-3}$</td>
</tr>
<tr>
<td>375</td>
<td>$2.79 \times 10^{10}$</td>
<td>24.052</td>
<td>$2.67 \times 10^{-3}$</td>
</tr>
<tr>
<td>400</td>
<td>$3.45 \times 10^{10}$</td>
<td>24.264</td>
<td>$2.50 \times 10^{-3}$</td>
</tr>
<tr>
<td>425</td>
<td>$4.15 \times 10^{10}$</td>
<td>24.449</td>
<td>$2.35 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Arrenhius 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

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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.
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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 $Tx = k$ is also a solution to $T^*T x = T^*k$, the normal equations, where the function $r(x) = \|Tx - k\|^2$ is minimized.
Normal Equations

\[ T^* T x = T^* k \]

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

\[ m = -1256.73203263 \Rightarrow E_a = 10.44847012 \text{ kJ mol}^{-1} \]

\[ b = 27.405755138 \Rightarrow A = 7.983038593 \times 10^{11} \]
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QR Decomposition
via the Gram-Schmidt Procedure

Use when...
- rounding errors are present
- speed is not important
QR Decomposition
via the Gram-Schmidt Procedure

Use when...
- rounding errors are present
- speed is not important

Benefits:
- $T$ can be any size
- $T$ has full rank so $x$ will always be unique
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

\[
T = [t_1 | t_2]
\]

\[
= [u_1 | u_2] \begin{bmatrix} 1 & -\frac{t_1^* t_2}{t_1^* t_1} \\ 0 & 1 \end{bmatrix}^{-1}
\]

Gram-Schmidt on \( t_1 \) and \( t_2 \)

\[
= [q_1 | q_2] \begin{bmatrix} \frac{1}{\|u_1\|} & -\frac{t_1^* t_2}{t_1^* t_1} \\ 0 & \frac{1}{\|u_2\|} \end{bmatrix}^{-1}
\]

\( u_1 \) and \( u_2 \) scaled by their norm

\[
= QR
\]
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: \( R \mathbf{x} = Q^* \mathbf{k} \)

\[
m = -1256.73203263 \quad \Rightarrow \quad E_a = 10.44847012 \ \text{kJ/mol}
\]

\[
b = 27.405755138 \quad \Rightarrow \quad A = 7.983038593 \times 10^{11}
\]

Notes:

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

Use when...

- no rounding errors
- speed is important
Cholesky Factorization

Use when...

- no rounding errors
- speed is important

Benefits:

- \( T \) can be any size
- \( T \) has full rank so \( x \) will always be unique
**Definition**

If \( \langle x, Ax \rangle > 0 \) for all \( x \) then \( A \) is a symmetric positive definite matrix where \( x \neq 0 \).

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

\( T \) is a symmetric positive definite matrix.
**Theorem**

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

\[ T^* T = A = \begin{bmatrix} a & y^* \\ y & B \end{bmatrix} \]

\[
= \begin{bmatrix} \sqrt{a} & 0^* \\ \frac{1}{\sqrt{a}} y & l \end{bmatrix} \begin{bmatrix} 1 & 0^* \\ 0 & B - \frac{1}{a} yy^* \end{bmatrix} \begin{bmatrix} \sqrt{a} & \frac{1}{\sqrt{a}} y^* \\ 0 & l \end{bmatrix}
\]

\[ = G_1^* A_1 G_1 \]

After \( n \) iterations:

\[ A = G_n^* \ldots G_2^* G_1^* I G_1 G_2 \ldots G_n = G^* G \]
Note:
The entry in the upper left corner of the matrix $B - \frac{1}{a}yy^*$ is always positive.

$$a = \langle e_2, A_1 G_1^{-1} e_2 \rangle > 0 \quad \text{where} \quad x = G_1^{-1} e_2$$
Cholesky Factorization

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

\[ = \begin{bmatrix} 6.90 \times 10^{-3} & 0 \\ 2.4322 & 0.29093 \end{bmatrix} \begin{bmatrix} 6.90 \times 10^{-3} & 2.4322 \\ 0 & 0.29093 \end{bmatrix} \]

\[ = G^* G. \]
Chemical Perspective

Least-Square Methods

Summary

Preliminaries
Normal Equations
QR Decomposition
Cholesky Factorization
SVD

Cholesky Factorization

From the normal equations: \( G^* G x = T^* k \)

\[
\begin{align*}
m &= -1256.74352341 \quad \Rightarrow \quad E_a &= 10.44856565 \ \frac{kJ}{mol} \\
b &= 27.4057876928 \quad \Rightarrow \quad A &= 7.983289484 \times 10^{11}
\end{align*}
\]
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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 $x$ will always be unique
Theorem

*If $T$ is a real $m \times n$ matrix then there exists orthogonal matrices $U = [u_1|...|u_m]$ and $V = [v_1|...|v_n]$, 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 $T^*T$.**
The eigenvalues of $T^*T$, $\delta_1, \delta_2$, are $\{6.72278 \times 10^{-7}, 6\}$

The singular values of $T$ are $s_1 = \sqrt{\delta_1} = 8.199 \times 10^{-4}$ and $s_2 = \sqrt{\delta_2} = 2.4495$

$$S = [s_1 e_1 | s_2 e_2] = \begin{bmatrix} 8.199 \times 10^{-4} & 0 \\ 0 & 2.4495 \\ 0 & 0 \\ 0 & 0 \\ 0 & 0 \end{bmatrix}$$
The eigenvectors for $\delta_1$ and $\delta_2$ are $x_1$ and $x_2$

$$V^* = [x_1|x_2]^* = \begin{bmatrix} -0.999996 & 0.002798 \\ -0.002798 & -0.999996 \end{bmatrix}$$
SVD

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

\[
\mathbf{U} = [\mathbf{y}_1 | \mathbf{y}_2 | \mathbf{y}_3 | \mathbf{y}_4 | \mathbf{y}_5 | \mathbf{y}_6] = \\
\begin{bmatrix}
-0.6484 & -0.4082 & -0.6426 & -0.3462 & -0.0027 & -0.0339 \\
-0.3435 & -0.4082 & 0.6061 & 0.3246 & -0.4845 & -0.2459 \\
-0.0752 & -0.4082 & 0.3353 & 0.1676 & 0.5944 & 0.7266 \\
0.1565 & -0.4082 & 0.1014 & 0.3999 & -0.0264 & -0.5969 \\
0.3638 & -0.4082 & -0.1078 & -0.7408 & 0.4113 & 0.2215 \\
0.5468 & -0.4082 & -0.2924 & 0.1949 & -0.4920 & -0.0713 \\
\end{bmatrix}
\]
From the normal equations, $SV^*x = U^*k$, 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 $b = U^*k$, then solve the system $C^*Cx = C^*b$.

$m = -1256.73203461 \Rightarrow E_a = 10.44847014 \frac{kJ}{mol}$

$b = 27.4057551435 \Rightarrow A = 7.983038637 \times 10^{11}$

Note: When $T$ is rank deficient, $x$ is given directly.
Summary

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

<table>
<thead>
<tr>
<th>Calculation Method</th>
<th>$E_a$ (kJ/mol)</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimation</td>
<td>10.4</td>
<td>$8.0 \times 10^{11}$</td>
</tr>
<tr>
<td>Normal Equations</td>
<td>10.44847012</td>
<td>$7.983038593 \times 10^{11}$</td>
</tr>
<tr>
<td>QR Decomposition</td>
<td>10.44847012</td>
<td>$7.983038593 \times 10^{11}$</td>
</tr>
<tr>
<td>Singular Value Decomposition</td>
<td>10.44847014</td>
<td>$7.983038637 \times 10^{11}$</td>
</tr>
<tr>
<td>Cholesky Factorization</td>
<td>10.44856565</td>
<td>$7.983289484 \times 10^{11}$</td>
</tr>
</tbody>
</table>
**Summary**

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

$E_a = 10.5 \text{ kJ/mol}$

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

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


[4] Garrido, M.; Larrechi, M.; Rius, F. Multivariate curve resolution-alternating least squares and kinetic modeling applied to


[8] Sundberg, R.; *Statistical aspects on fitting the Arrhenius equation*; Chemometrics and Intelligent Laboratory Systems; Vol 41; 1998; pp 249-252.