Standard microbiological approach to calculating z values, and consequences of approximations

Dr Tomas Skoglund

Based on the article
-On the common misuse of a constant z-value for calculations of thermal inactivation of microorganisms
https://doi.org/10.1016/j.jfoodeng.2021.110766
Outline

► Thermal inactivation of microorganisms – Basics
► Temperature dependence of kinetics
► Arrhenius – $E_a$ vs. $z$-value
► Reference temperature, $T_r$, and Calculations with constant $z=z_r$ at $T \neq T_r$
► Examples
\[ N = N_0 e^{-kt} \]

\[ k = k_0 e^{\frac{E_a}{RT}} \]
\[ = k_0 10^{-\frac{E_a}{\ln(10)RT}} \]

\[ D = \ln(10)/k \]

\[ D_r = \ln(10)/k(T_r) \]

\[ L = \log \left( \frac{N_0}{N} \right) = \frac{F}{D_r} = \int_0^t 10^{\frac{T(t)-T_r}{z}} dt \]

\[ F = \int_0^t 10^{\frac{T(t)-T_r}{z}} dt \]

\[ z = \frac{\ln(10) RT T_r}{E_a} \]

\[ z_r = \frac{\ln(10) RT_r^2}{E_a} \]
Let's take it from the beginning.

Arrhenius' plot

Thermal Death Time (TDT) plot

Decimal reduction time, s

Temperature (°C)

ln k

$\frac{E}{R}$
Thermal inactivation of microorganisms
Basics

► Target microorganism for the product?
  ● Pathogen or
  ● Food spoilage

► Kinetics
  ● First order kinetics – Two representations
    o Reaction rate (frequency factor), $k$ (SI-unit s\(^{-1}\))
    o Decimal reduction time, $D$ (SI-unit s)
  ● Temperature dependence – Two representations
    o Arrhenius activation energy, $E_a$ (SI-unit J/mol)
    o $z$-value, (SI-unit K or °C)

\[
D = \frac{\ln(10)}{k}
\]

\[
z = \frac{\ln(10)RT_r}{T/E_a}
\]

\[
z_r = \frac{\ln(10)RT_r}{T/E_a}
\]

\[
\ln(10) \approx 2.303
\]
$E_a$ vs. $z$-value (TDT (Thermal Death Time) plot from Bigelow 1921)
$E_a$ vs. $z$-value (Data from Bigelow 1921)
$E_a$ vs. $z$-value (Data from Bigelow 1921)

Arrhenius’ plot

$D = \frac{\ln(10)}{k}$

Bigelow’s TDT plot
$E_a$ vs. $z$-value – lin/log regression

\[
D = \frac{\ln(10)}{k}
\]

Arrhenius’ plot

Bigelow’s TDT plot
$E_a$ vs. $z$-value – lin/log regression

**Arrhenius’ plot**

$$D = \frac{\ln(10)}{k}$$

$\Delta(\log(1/D)) = 1$

$E_a = \ln(10)R/\Delta(1/T)$

**Bigelow’s TDT plot**

$\Delta(\log(D)) = 1$

$D_z$
**$E_a$ vs. $z$-value – lin/log regression** (Data from Bigelow 1921)

$D = \frac{\ln(10)}{k}$

**Arrhenius’ plot**

**Bigelow’s TDT plot**

Let’s have a closer look!

Straight line fits well

Straight line fits well here too!!
$E_a$ vs. $z$-value – lin/log regression (Data from Bigelow 1921)

A larger $R^2$-difference would be expected, had the temperature range been wider or the experiments more accurate.
Comments on the representations/models

$E_a$ vs. $z$-value

Activation energy ($E_a$)
- A bit hard to interpret
- Empirically proven and theoretically explained

$z$-value for decimal reduction time ($D$)
- Easy to interpret
- Established in calculations of process lethality ($F$ values, also denoted “sterilization value”)
- Often used inaccurately as constant, despite its temperature-dependent relationship to $E_a$

But does it matter?
Comments on the representations/models

$E_a$ vs. $z$-value


For **narrow temperature ranges** within which the temperature dependence of the $z$-value can be neglected, the $z$-value expresses the increase in temperature [°C] necessary for obtaining the same effect in 1/10 of the time. In practice, however, the line is not straight (dotted line) and this cannot be neglected in the discussion of **larger temperature ranges**, as will be shown later. **Many investigations have demonstrated** the constancy of the energy of activation in a large number of reactions. The representation in Fig. 6.11 should therefore be used in calculations.

But how narrow?
As we will see, ”narrow” is narrow indeed!
The problem with constant $z$ – An example

$D$ plot vs. temperature based on Arrhenius (constant $E_a$) for Natural thermophilic flora, Milk (high D)
The problem with constant $z$ – An example

$D$ plot vs. Temperature based on Arrhenius (constant $E_a$) for Natural thermophilic flora, Milk (high D)
The problem with constant $z$ – An example

$D$ plot vs. Temperature based on Arrhenius (constant $E_a$) for Natural thermophilic flora, Milk (high D)

$z = \ln(10) RT_r T/E_a = z_r T/T_r$

$z_r = z(T = T_r) = \ln(10) RT_r^2/E_a$

$\zeta_{135{\degree}C} = 11.0{\degree}C$
Example – Calculation of holding time in a UHT line

Direct-steam injection with flash cooling: Temperature profile 80 °C – 138 °C – 81 °C

\[ L = \frac{F}{D_r} = \int_0^{t_h} \frac{T - T_r}{D_r} \frac{T - T_r}{z_r} \frac{T - T_r}{T} \, dt \]

Constant temperature \[ \Rightarrow L = \frac{t_h}{10} \frac{\vartheta - \vartheta_r T_r}{z_r T} \]

**μ-organisms (pathogen and spoilage)**

<table>
<thead>
<tr>
<th></th>
<th>( \vartheta_r )</th>
<th>( D_r )</th>
<th>( z_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clostridium botulinum spores</td>
<td>121.1 °C</td>
<td>12 s</td>
<td>10.0 °C</td>
</tr>
<tr>
<td>Natural thermophilic flora, Milk (high D)</td>
<td>121.1 °C</td>
<td>26.4 s</td>
<td>10.3 °C</td>
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Reference:
- Text books, e.g. H.-G. Kessler, Food and Bio Process Engineering
- W. G. Bigelow, "The logarithmic nature of thermal death curves,"

\[ T_r = \vartheta_r + 273.15 K \]

<table>
<thead>
<tr>
<th>Target logred, ( L )</th>
<th>12</th>
<th>6</th>
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<tr>
<td>Accurate holding time</td>
<td>( \frac{12 \times 12}{138-121.1} ) \times \frac{121.1+273.15}{138+273.15} = 3.5 \text{ s} )</td>
<td>( \frac{6 \times 26.4}{138-121.1} ) \times \frac{121.1+273.15}{138+273.15} = 4.2 \text{ s} )</td>
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<td>Inaccurate holding time</td>
<td>( \frac{12 \times 12}{138-121.1} ) \times \frac{121.1+273.15}{138+273.15} = 2.9 \text{ s} )</td>
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Example – Calculation of holding time in a UHT line

Direct-steam injection with flash cooling: Temperature profile 80 °C – 138 °C – 81 °C

\[ L = \frac{F}{D_r} = \int_0^{t_h} 10^{\frac{T-T_r}{z}} \frac{dT}{D_r} = \int_0^{t_h} 10^{\frac{T-T_r}{z}} \frac{dT}{T} \]

Constant temperature \( \Rightarrow L = \frac{t_h 10^{\frac{\vartheta-\vartheta_r T_r}{z_r} T}}{D_r} \)

\[ t_h = \frac{L D_r}{10^{\frac{\vartheta-\vartheta_r T_r}{z_r} T}} \]

\[ T_r = \vartheta_r + 273.15 \, K \]

### μ-organisms

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<td>( (F_0 = 2.40 , \text{min}) 3.5 , \text{s} )</td>
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14% TOO SHORT
Example – Calculation of holding time

Difference between using approximation with constant $z = z_r$ and temperature dependence of $z$

Relative error of $t_h = 10 - \frac{(T - T_r)^2}{T z_r} - 1$

$\theta$ [°C]

$\text{Clostridium botulinum spores}$

$\text{Natural thermophilic flora}$

Dr. Tomas Skoglund, 2023
Example – Calculation of holding time

Difference between using approximation with constant $z=\text{z}_r$ and temperature dependence of $z$

![Diagram showing holding time vs. temperature for Clostridium botulinum spores and Natural thermophilic flora. The green line represents accurate calculation, while the dashed red line represents an inaccurate calculation with a constant $z$.](image-url)
Error calculations of $F$

$T$ deviation from $T_r$ for different $T_r$ and with $z_r = 10.0 \, ^{\circ}C$

![Graph showing $\Delta T = T - T_r$ deviation for different $T_r$ values with $z_r = 10.0 \, ^{\circ}C$.]
Error calculations of $F$

$T$ deviation from $T_r$ for different $T_r$ and $z_r$

Relative error of $F = 10 \frac{(T - T_r)^2}{T z_r} - 1$
A direct heating & flash cooling system
80 – 138 (4 s) – 81 °C

\[ \log \left( \frac{N_0}{N} \right) \text{ and } F \text{ based on constant } z \]

Clostridium botulinum spores:
\[ L = \log \left( \frac{N_0}{N} \right) \]
\[ F \]

Natural thermophilic flora (high D):
\[ L = \log \left( \frac{N_0}{N} \right) \]
\[ F \]

A direct heating & flash cooling system
80 – 138 (4 s) – 81 °C

\[ L = 5.8 < 6 \]

\[ F(\text{constant } z) = 2.98 \Rightarrow L = 2.98 \times 60/26.4 = 6.8 > 6 \]
An indirect heating & cooling system
96 – 123 – 137 (2 s) – 29 °C

Clostridium botulinum spores:

\[ L = \log\left(\frac{N_0}{N}\right) \]

\[ F \]

\[ F \text{ based on constant } z \]

Natural thermophilic flora (high D):

\[ L = \log\left(\frac{N_0}{N}\right) \]

\[ F \]

\[ F \text{ based on constant } z \]

\[ L = 12.4 >> 6 \]

\[ F(\text{constant } z) = 6.06 \Rightarrow L = 6.06*60/26.4 = 13.8 >> 6 \]
Conclusion

- **Temperature dependence**
  - Follows Arrhenius equation, linear $\log(k)$ vs. $1/T$
  - Seemingly, but inaccurately linear $\log(D)$ vs. $T$

- **Constant $z = z_r$ (for $T \neq T_r$)**
  - overestimation of $L$ and $F$
  - underestimation of required holding times
  - not negligible errors

- **To avoid compromising food safety and quality:** Use $z = \ln(10)RT_r/E_a = z_r T/T_r$
  - Particularly important for direct heating systems
Thank you!
Questions?
Tomas Skoglund’s professional background

I studied engineering physics at the Faculty of Engineering (Lund Institute of Technology, LTH) at Lund University and obtained my Master of Science degree (Eng. Phys) 1978. The year 2007 a PhD degree was obtained. During my early years after education I worked with automatic control engineering (at Volvo Aero), acoustics and vibrations consultations (at Ingemansson Akustik) and with research and education (at the Department of Physics at Lund University / Faculty of Engineering, LTH).

From 1982 I was employed at Alfa-Laval and Tetra Pak with a range of assignments and studies:

• 2012 – 2020 Senior Technology Specialist (Heat Treatment & Math. Modeling & Simulation)
• 2001 – 2012 Senior Development engineer and project manager
• 2004 – 2007 PhD studies (part time) at the Faculty of Engineering at Lund University
• 1982 – 2001 Department manager, Environmental manager, Technical product manager, Project manager, Food plant and line automation engineer.

After retirement 2020 I have worked as self-employed consultant in combination with independent private researcher at NovaUmbra.

I am married since 1978 and have three grown-up children with their own families.