Example

The influence of temperature on death rate of bacterial spores is illustrated by the experimental data given in the following table. Determine the activation energy and frequency factor involved in describing this reaction.

Death rates of bacterial spores at various temperatures

Temperature (°F)	Death rates (min^{-1})
220	– 0.0363
225	– 0.0685
230	– 0.1330
235	– 0.2470
240	– 0.4550

Convert temperatures from Fahrenheit to Kelvin

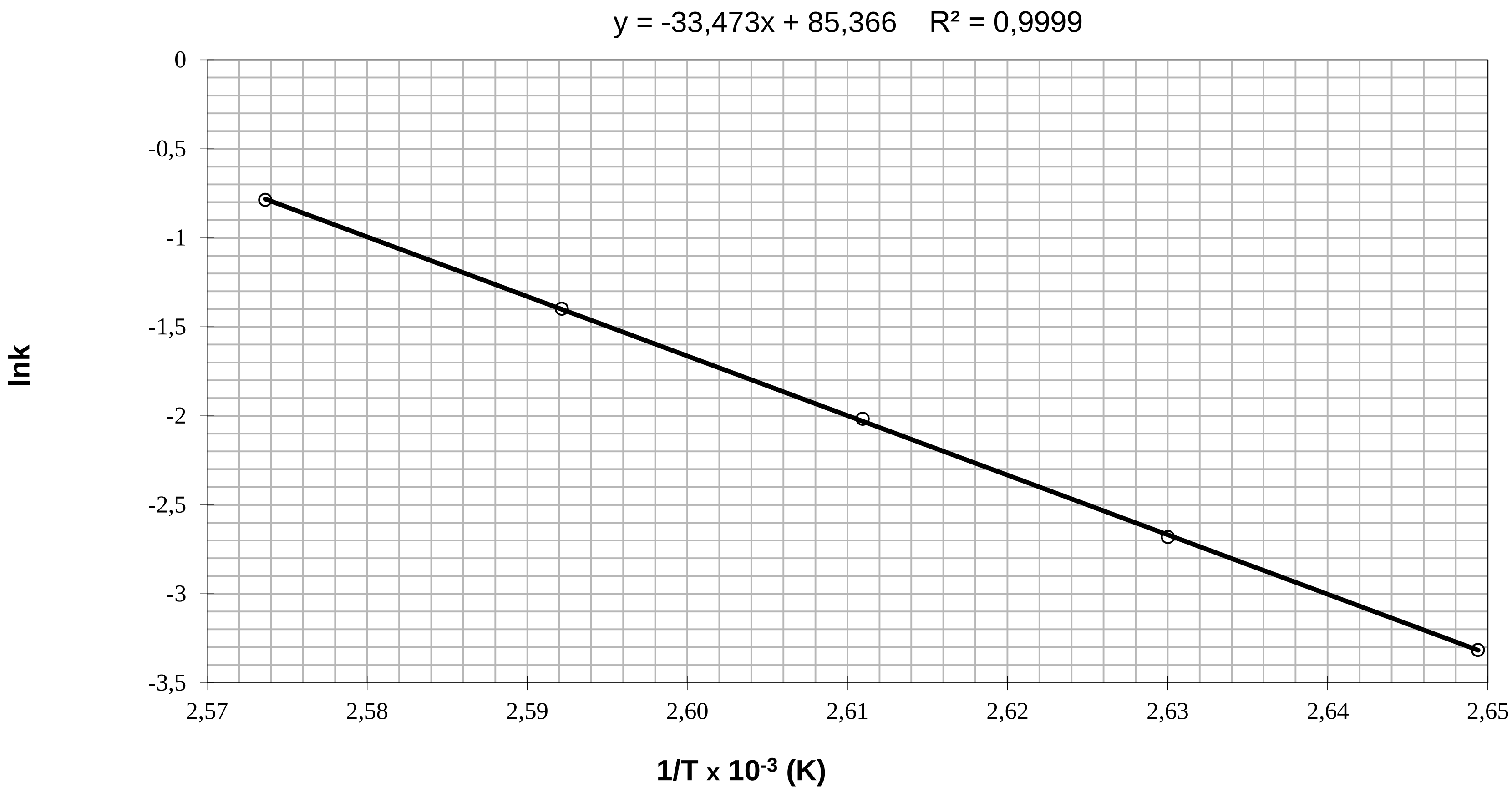
Temp.(°F)	Temp.(°C)	Temp.(K)
220	104	377
225	107	380
230	110	383
235	113	386
240	116	389

Table Data for Arrhenius plot

(for arithmetic graph paper)

Temp. (K)	1/T (1/K)	$1/T \times 10^3$ (1/K)	k	– lnk
377	0.00265	2.65	0.0363	3.3159
380	0.00263	2.63	0.0685	2.6809
383	0.00261	2.61	0.1330	2.0174
386	0.00259	2.59	0.2470	1.3984
389	0.00257	2.57	0.4550	0.7875

Arrhenius plot (lnk vs 1/T, arithmetic)



Calculation of slope

$$\text{Slope} = \frac{-2.5 - (-1.5)}{(2.624 - 2.595) \times 10^{-3}}$$

Slope = – 34 483 K

Calculation of E_a

$$\text{Slope} = -\frac{E_a}{R}$$

$$-34\,483\text{ K} = \frac{-E_a}{1.987\ \text{(unit?)}}$$

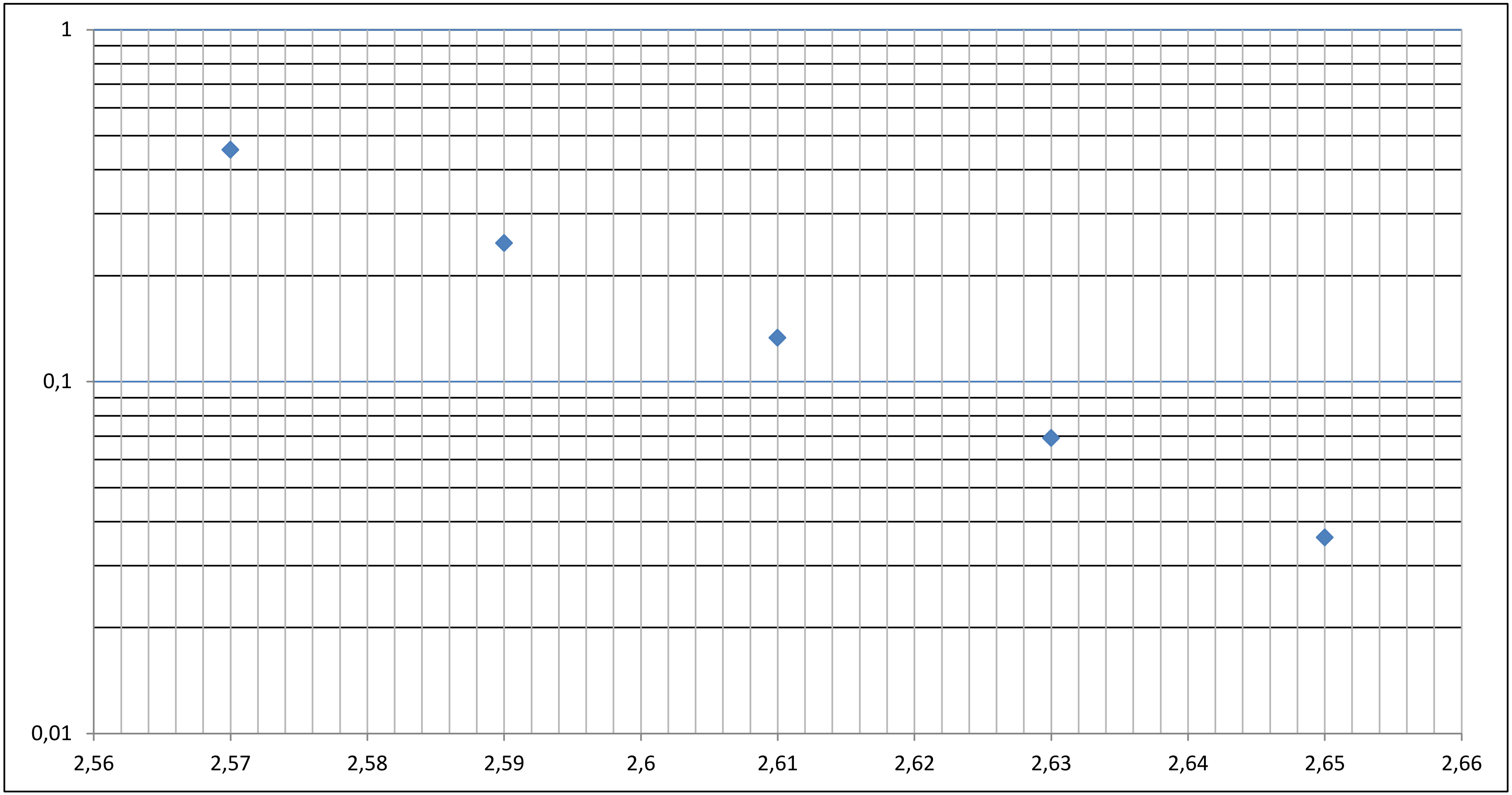
$$E_a = 68\,276\ \text{(unit?)}$$

Table Data for Arrhenius plot

(for semi-log graph paper)

Temp. (K)	**1/T (1/K)**	**$1/T \times 10^3$ (1/K)**	**k**
377	0.00265	2.65	0.0363
380	0.00263	2.63	0.0685
383	0.00261	2.61	0.1330
386	0.00259	2.59	0.2470
389	0.00257	2.57	0.4550

Arrhenius plot (k vs 1/T, semi-log)



Calculation of slope

$$\text{Slope} = \frac{\log 0.04 - \log 0.2}{(2.647 - 2.596) \times 10^{-3}}$$

Slope = – 13 705 K

Calculation of E_a

$$\text{Slope} = -\frac{E_a}{2.303 \times R}$$

$$-13\,705\ \text{K} = \frac{-E_a}{2.303 \times 1.987\ \text{(unit?)}}$$

$$E_a = 62\,715\ \text{(unit?)}$$

E_a values for important reactions in foods

- E_a values for the chemical, microbial and enzymatic reactions affecting the quality of foods change between **2–150 kcal/mol.**

Importance of Ea value

1) *k* values of reactions with high E_a value is affected more by temp. changes.

2) Magnitude of E_a indicates that which temperature (**<u>refrigerated, room or processing</u>**) the chemical, microbial or enzymatic reactions will occur.

- Reactions affecting the quality of foods are much less affected by the temp. changes, compared to the **undesirable** microbial and enzymatic reactions affecting the foods.

Reactions with low Ea (2 –15 kcal/mol)

(Reactions for fat soluble components as well as reactions catalyzed by enzymes)

1) Reactions catalyzed by enzymes
2) Degradation of carotenoids
3) Degradation of chlorophylls
4) Oxidation of fatty acids

Reactions with intermediate E_a (15–30 kcal/mol)

Components soluble in water

1) Degradation of vitamins (aa and thiamine)

2) Degradation of water soluble pigments (anthocyanins)

3) Maillard browning (betwwen aa and sugars)

Reactions with high E_a (50–100 kcal/mol)

1) Inactivation of m.o.'s (bacterial spores)

2) Inactivation of enzymes (PPO, pectinmethyl esterase, lipoxygenase)

Reactions with very high Ea (100 – 150 kcal/mol)

Inactivation of heat-stable enzymes
(such as lipase and protease in milk)

Reactions with low Ea (2 –15 kcal/mol)

- E_a value of fat soluble food components is low.
- This is because oxidation of these components is catalyzed by either enzymes or metal ions, such as copper and iron.
- These reactions are not affected by temperature changes.
- These reactions occur at regrigerated temperatures (below 10^{o}C, mosly 4^{o}C).

Reactions with intermediate Ea (15–30 kcal/mol)

- Water soluble components.
- These reactions occur at room temperature.

Reactions with high and very high Ea (100 – 150 kcal/mol)

- Inactivation of m.o.'s and enzymes
- Not important at refrigerated temperatures and room temperatures.
- Only important at process temperatures, in other words, at high temperatures.

HTST or LTLT?

Definetly HTST !!!

- HTST processing will inactivate the undesirable m.o.'s as well as undesirable enzymes, while the degradation of quality factors will be limited.
- This can be explained by Ea values of m.o.'s, enzymes and quality factors.
- Since the E_a value of quality factors is much less than the E_a value of m.o.'s and enzymes spoiling the foods, **HTST process** will result in increasing the inactivation of m.o.'s and enzymes, and at the same time, destruction of quality factors will be minimum.

Q_{10} value
(temperature coefficient)

- Used for reporting temp. dependence of reactions of generally quality factors. (related to the self-life of foods)
- Defined as the increase in the rate of the reaction (***k*** value) when the temp. is increased by 10^{o}C (18°F). If a **reaction rate (*k*)** doubles with a 10^{o}C change in temp., then, $Q_{10} = 2$.
- Generally, in **food storage**, a 10^{o}C reduction in storage temp. will increase shelf-life by a factor of **2**.

- ***Q*<u>$_{10}$</u> value depends on temp. and should not be used over a wide range of temp.**

- Q_{10} value can be calculated from the data when food product has been stored at two or more temp. regardless of whether or not they are 10°C apart.

Calculation of Q_{10}

If the temp. difference between two *k* values is exactly 10^oC:

$$Q_{10} = \frac{\text{reaction rate } (k_2) \text{ at } T + 10°C}{\text{reaction rate } (k_1) \text{ at } T°C}$$

If temp. difference between the two *k* values is higher than 10°C:

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{10/(T_2 - T_1)}$$

Example 5.2

Dried apricots were exposed to warm air at 40^o-60^{o}C to remove SO_2 and the formation of browning were observed during this process. The reaction rate constants obtained during this process were given in Table 5.3. Which kinetic parameters can you calculate from the *k* values for this reaction?

- Calculate the kinetic parameters which show the temp. dependence of brown color formation in dried apricots.

Note: Calculate these kinetic parameters in «**SI**» unit system, if applicable.

Tablo 5.3 Reaction rate constants for the formation of brown color in dried apricots exposed to various temperatures

Temp. (°C)	**k (10^3 x h^{-1})**			
40	1.77 (0.813)			
50	3.96 (0.996)			
60	21.23 (0.975)			

Tablo 5.3 Reaction rate constants for the formation of brown color in dried apricots exposed to various temperatures

Temp. (°C)	**k (10^3 x h^{-1})**	**Q_{10} 40°–50°C**	**Q_{10} 50°–60°C**	**Q_{10} 40°–60°C**
40	1.77 (0.813)			
50	3.96 (0.996)			
60	21.23 (0.975)			

Calculation of Q_{10}

$$Q_{10}\,(40°–50°) = \frac{k_{50oC}}{k_{40oC}}$$

$$Q_{10}(40°–60°)=\left(\frac{k_{60oC}}{k_{40oC}}\right)^{10/(60-40)}$$

$$Q_{10}\,(50°–60°) = \frac{k_{60oC}}{k_{50oC}}$$

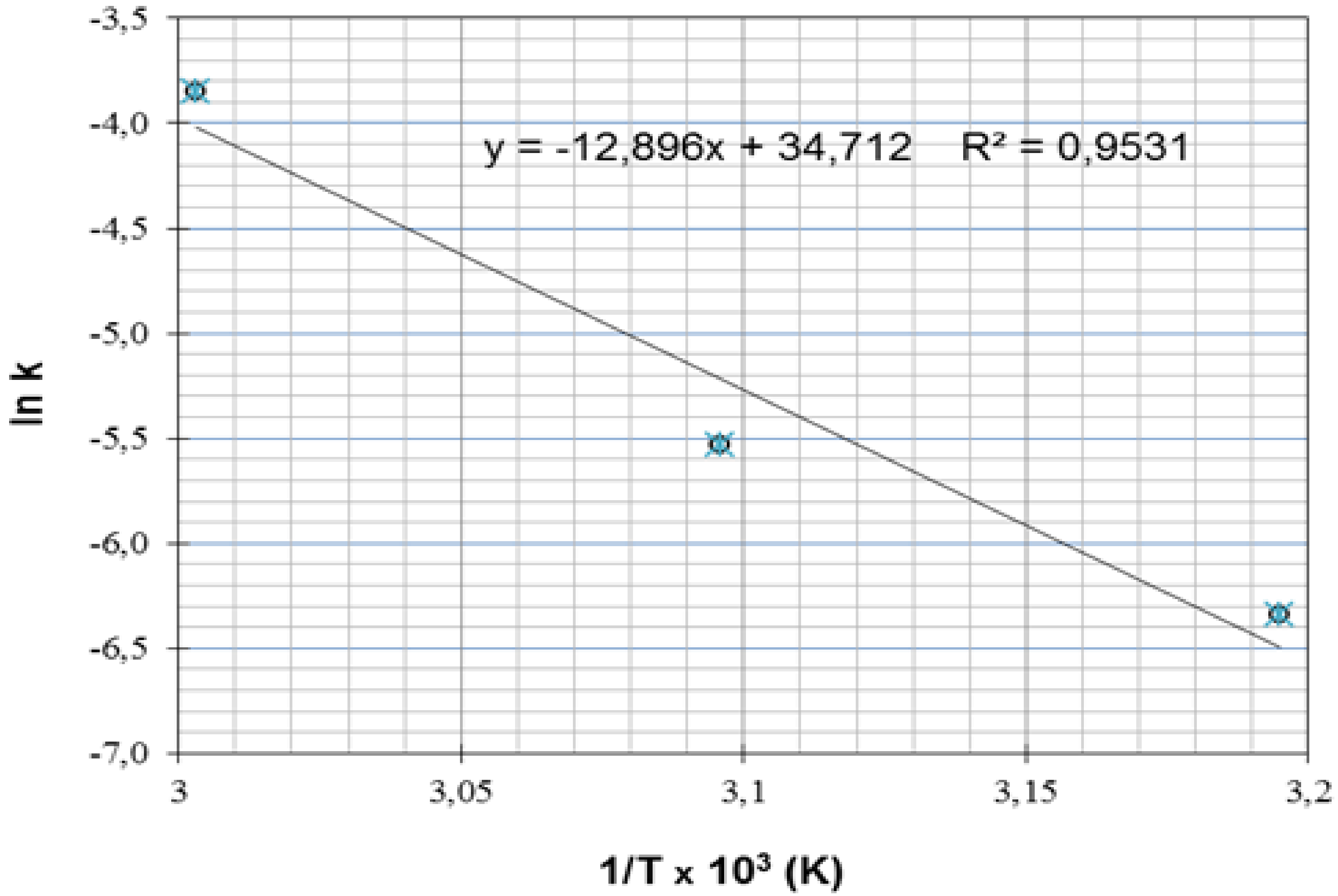
Calculated Q_{10} values

Temp. (°C)	k (10^3 x h^{-1})	Q_{10} 40°–50°C	Q_{10} 50°–60°C	Q_{10} 40°–60°C
40	1.77			
50	3.96	**2.24**	**5.36**	**3.46**
60	21.23	.		

Calculation of E_a

°C	K	$1/T \times 10^3$ (X)	k	ln k (Y)
40	313	3.20	0.00177	– 6.337
50	323	3.10	0.00396	– 5.532
60	333	3.00	0.02123	– 3.852

Arrhenius plot



Arrhenius equation

$$\ln k = -12\,896\,(1/T) + 34.712, \quad R^2 = 0.9531$$

$$\text{Slope} = -\frac{E_a}{R}$$

$$-12\,896\ \text{K} = \frac{-E_a}{8.314\ \text{J/(mole K)}}$$

$E_a = 107\,217$ J/mole **= 107 kJ/mole**

z value

- Used to show temp. dependence of mostly microbial and enzymatic inactivation rate during mostly heat processing.

- Defined as the **temp. change** **(ΔT)** needed to change D value by a factor of 10.

- Also used to express the temp. dependence of chemical reactions in foods during processing and storage.

- *z* value, like D value, is the kinetic parameter only calculated for **first-order reactions.**

- Unit of *z* value is °C or °F.

Thermal Destruction Curve

(Thermal Inactivation Curve or Thermal Resistance Curve)

- Obtained by plotting D values of m.o. or enzymes against temp. in semi-log graph paper.

- *z*-value is calculated as:
  - Temp. change required for the D-value to change by a factor of 10 (temp. change required for the thermal destruction curve to move one log cycle).

    Or;

  - Equal to the reciprocal of the slope of thermal destruction curve. (slope=-1/*z*)

Definition of D and *z* values

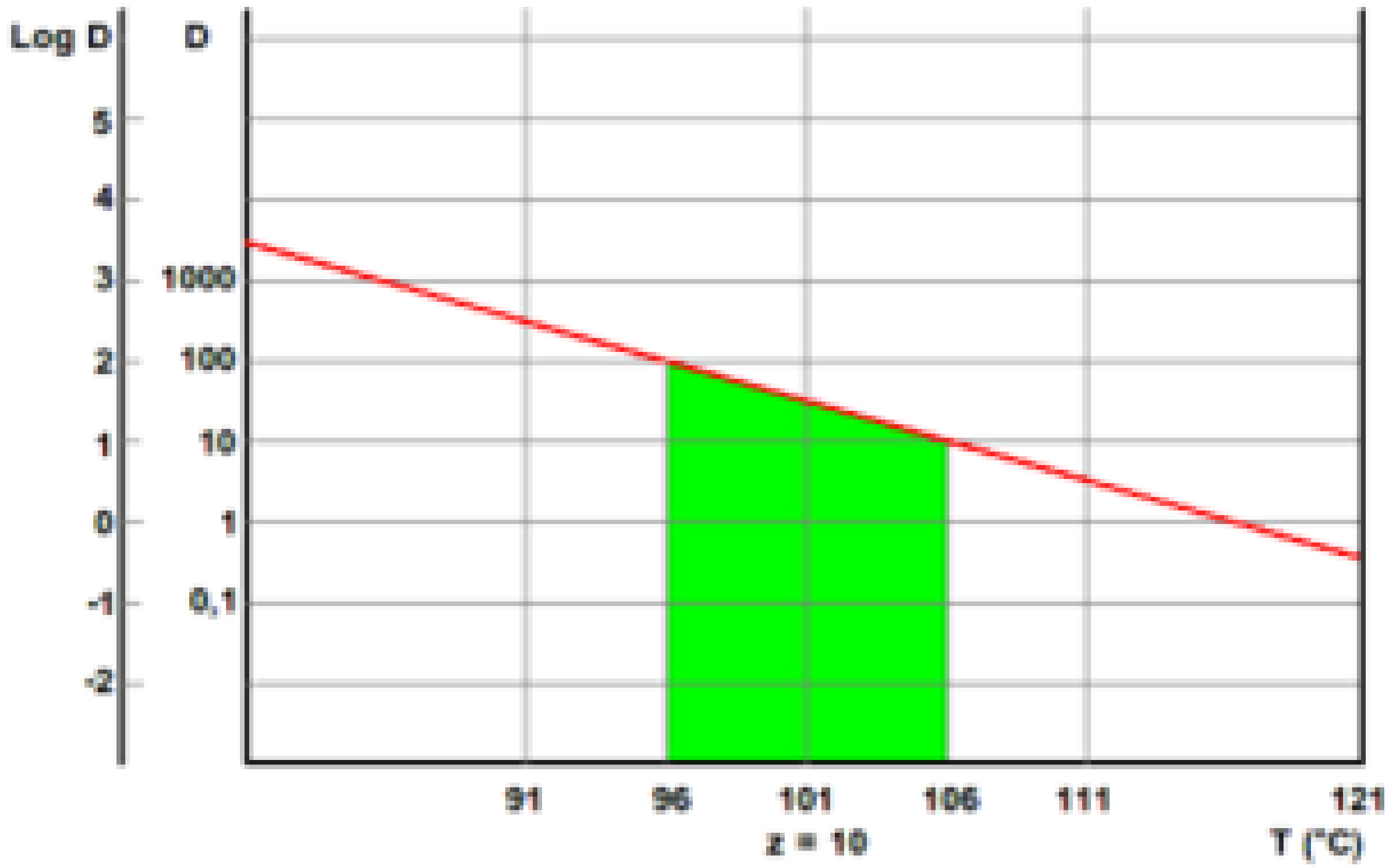
- **D-value:** Gives the time needed at a constant temp. to inactivate 90% of m.o.'s or enzymes. (Unit: **time**)
- ***z*-value:** Shows the the resistance of m.o. or enzymes to temp. changes. (Unit: **temperature**)

Implementation of *z* value

- **The higher the *z*-value**, the less the m.o. is affected from temp. changes.

- **The lower the *z*-value**, the more the m.o. is affected from temp. changes.

Example



- If D-value at 65°C is 4.5 min and z value is 15°C, then calculate the D-values at 80°C and 50°C.

If D-value at 65°C is 4.5 min. and z value is 15^{o}C, then

D-value at 50°C will be ??? min.

D-value at 80°C will be ??? min.

If D-value at 65°C is 4.5 min. and z value is 15°C, then

D-value at 50°C will be 45 min.

D-value at 80°C will be 0.45 min.

z vs E_a

- ***z*-value** is mostly used to show how **temp. changes** affect the inactivation of m.o.'s and enzymes.
- E_a is prefferred to show how **temp. changes** affect the degradation of quality factors.
- E_a and *z*-values are **inversely correlated** with each other. If the E_a value of a given reaction is high, then *z*-value of the same reaction should be low.

Table 5.1 E_a and *z*-values of spore forming bacteria

Bacteria	**E_a value (kcal/mol)**	***z*-value (°F)**
B. stearothermophillus	99	13 (7.2°C)
C. sporogenes	53	23 (12.8°C)
C. botulinum	70	18 (10.0°C)

Table 5.2 E_a and *z*-values of reactions lowering the quality of foods

Quality factor	E_a value (kcal/mol)	*z*-value (°F)
Thiamine	27	45
Riboflavine	23	50
Ascorbic acid	23	50
A vitamin	15	72
Chlorophyll	15	75
Maillard browning	27	45
Lysine	30	38

Example

2000 of *Clostridium sporogenes* spores were inoculated into the tubes containing 5 mL sterile milk in aseptic conditions. The tubes (150 tubes) were subjected to 5 different temperatures and 5 tubes at each temperature were periodically taken and the live organisms in each tube were counted. The arithmetic means of the counts were determined and the live organisms against heating time were plotted in semi-log graph paper. From the straight line in bacterial survivor curve, D values were determined. D values for this spore were given in Table 5.7.

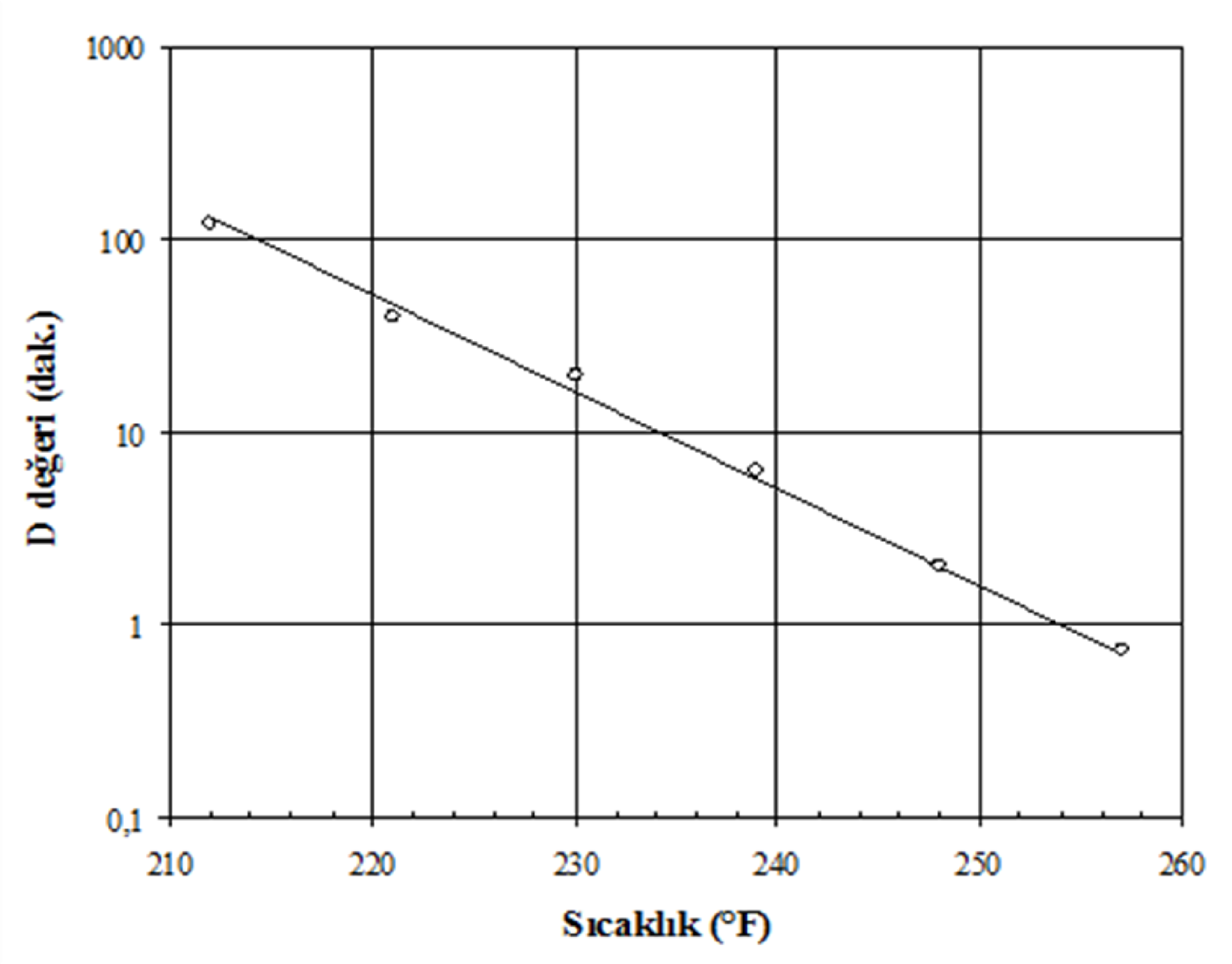
- Determine the *z*-value for *C. sporegenes* spores.

- Compare *z*-value of *C. sporegenes spores* with *z*=7.2^{o}C of *Bacillus stearothermophillus* spores, calculated at 212-257^{o}F.

Table 5.7 D values for *C. sporogenes* spores heated at various temp.'s

Temperature (°F)	D values (min)
212	120
221	40
230	20
239	6.25
248	2.0
257	0.75

Figure 5.3 Thermal destruction curve for *C. sporogenes* spores



Calculation of z value

$z = 254 - 234 =$ **20°F** (11.1°C).

z-value can also be calculated form the reciprocal of the slope of **thermal inactivation curve**.

Comparison of *z* values

- *z* = 11.1°C for *C. sporegenes* spores.
- *z* =7.2°C for *Bacillus stearothermophillus* spores

Comparison of *z* values

Since z=7.2^{o}C for *B. stearothermophillus* spores is smaller than z=11.1^{o}C for *C. sporegenes* spores at the same temp. range, the degradation of *B. stearothermophillus* spores is much more affected (faster degradation) by the temp. changes at 212-257^{o}F, as compared to the degradation of *C. sporegenes* spores.

Example 5.6

Reaction rate constants for the degradation of anthocyanins in sour cherry juice were determined and the values were given in Table 5.8. Calculate ***z* value, Q_{10} values** and **E_a value**.

Table 5.8 Reaction rate constants for the degradation of sour cherry anthocyanins

Temperature (°C)	**k x 10^3 (h^{-1})**
60	12.091
70	28.304
80	78.230

Finding D value

Finding D value

$$D = -\frac{2.303}{k}$$

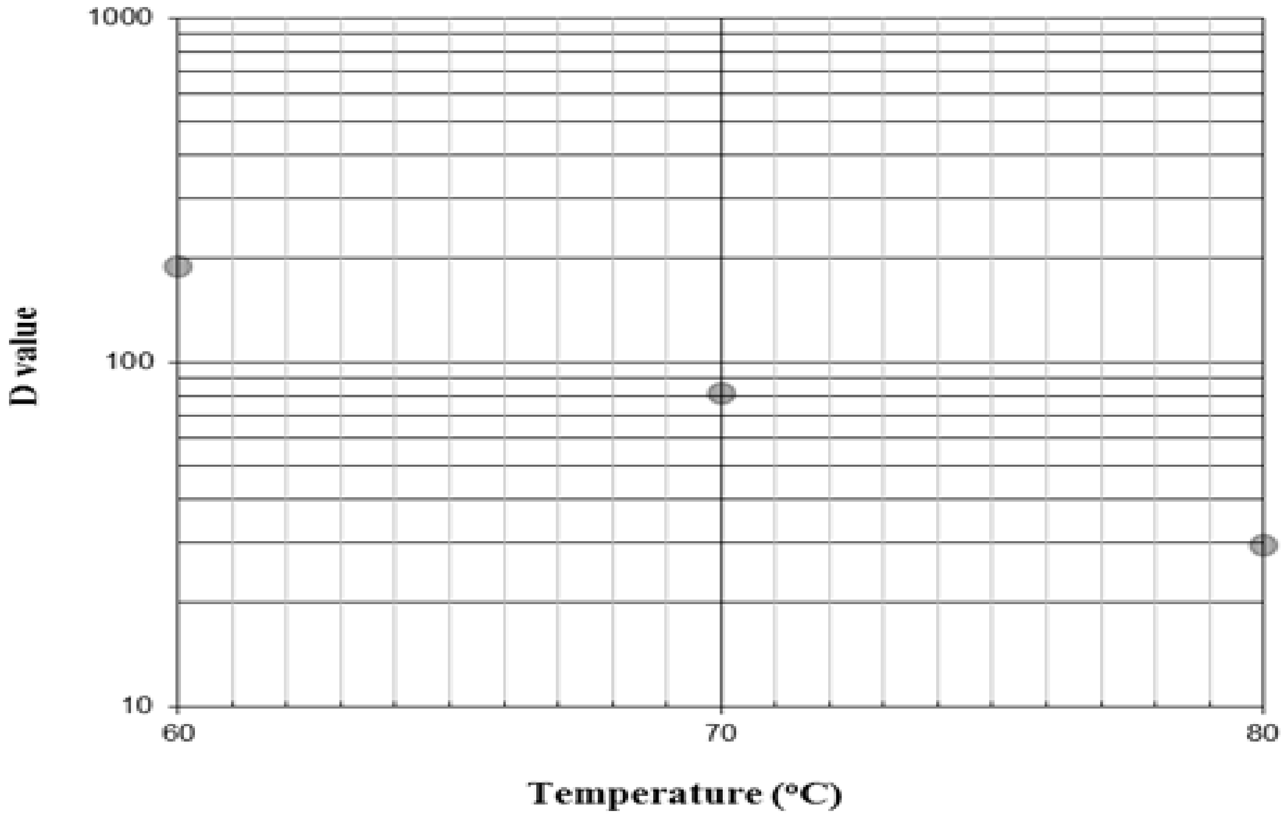
Calculation of D value

- 60°C $\rightarrow$ $-D = -\dfrac{2.303}{-0.01209} = 190\ \text{h}$

- 70°C $\rightarrow$ $-D = -\dfrac{2.303}{-0.028304} = 81.4\ \text{h}$

- 80°C $\rightarrow$ $-D = \dfrac{2.303}{-0.078230} = 29.4\ \text{h}$

Figure 5.5 Thermal inactivation curve for the degradation of anthocyanins in sour cherry juice



Calculation of *z*-value

Calculation of *z*-value from the slope of straight line:

- Slope= $\dfrac{\log 30 - \log 80}{79.8 - 69} = -0.03944\ 1/^{o}C$

$$-0.03944 = -\frac{1}{z}$$

$$z = 25.4^{o}C$$

Calculated E_a value

$E_a = 90\ 905\ \text{J mol}^{-1} = 90.9\ \text{kJ mol}^{-1}$

Calculated Q_{10} value

Q_{10} = 2.34 at 60-70^{o}C

Q_{10} = 2.76 at 70-80^{o}C

Q_{10} = 2.54 at 60-80^{o}C

Example 5.7 : Slope values calculated from semi-log graph for the thermal degradation of anthocyanins in blood orange juice at 70°–90°C were given in Table 5.11. Find out the ***z* value** for the degradation of anthocyanins in blood orange juice at 70°–90°C.

Table 5.11 Slopes for the degradation of anthocyanins in blood orange juice heated at 70°–90°C

Temp. (°C)	-slope x 10^3 (min^{-1})
70	0.80
80	1.40
90	3.30

Calculation of *k* values

Analyzing the **unit of slopes**, degradation of anthocyanins follows **first-order** reaction kinetics.

Calculation of *k* values

$k = 2.303 \times \text{slope}$

Find the D values

$$D = -\frac{2.303}{k}$$

$70°C \rightarrow D = 1251.6 \text{ min} = 20.9 \text{ h}$

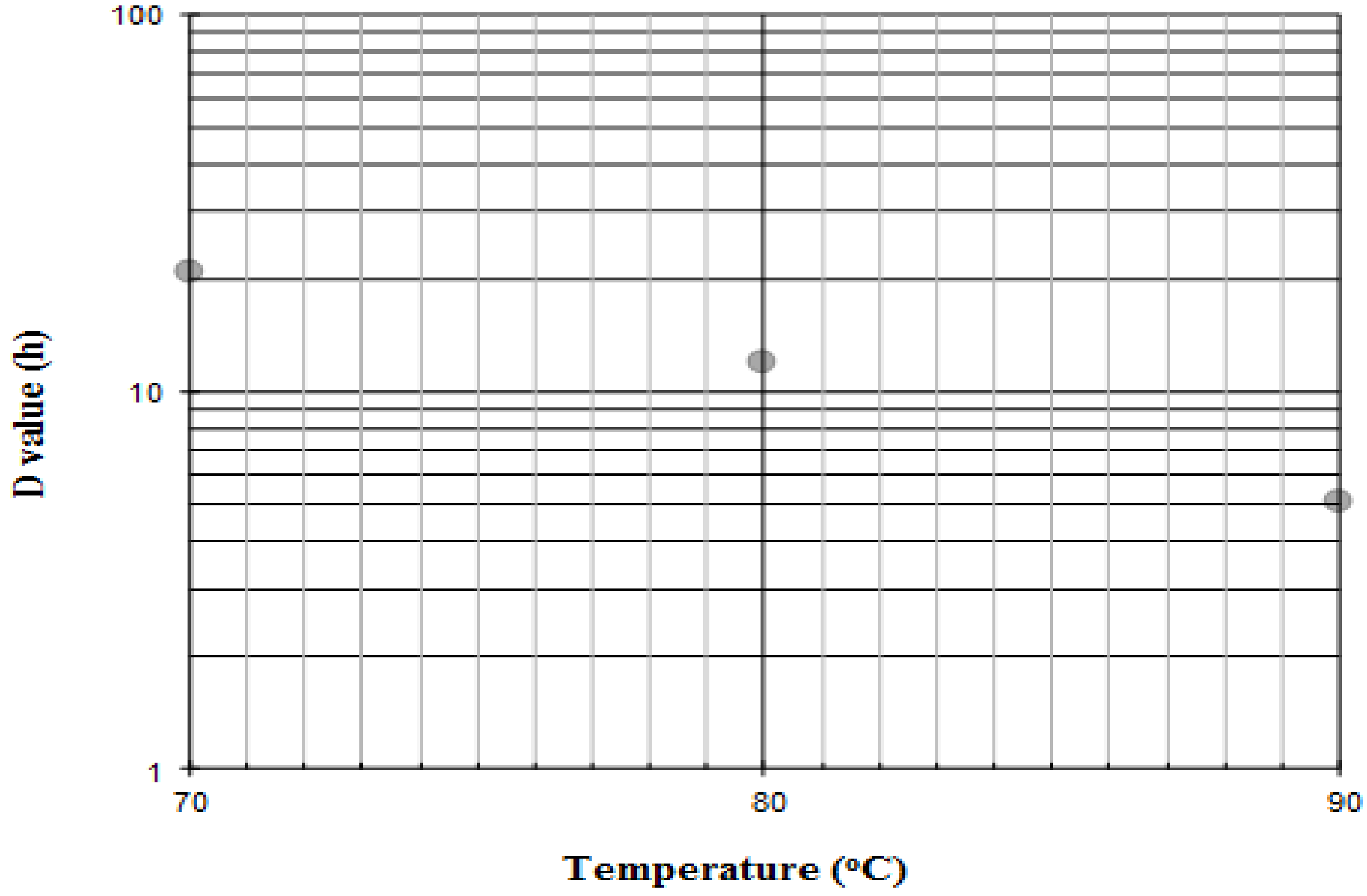
$80°C \rightarrow D = 715.2 \text{ min} = 11.9 \text{ h}$

$90°C \rightarrow D = 303 \text{ min} = 5.1 \text{ h}$

To calculate z value:

Thermal inactivation curve is drawn (**D vs Temp**)

Figure 5.6 Thermal inactivation curve for blood orange anthocyanins



Calculation of z value

$$\text{Slope} = \frac{\log 6 - \log 10}{89 - 81} = -0.02773\ 1/^{o}\text{C}$$

$$-0.02773 = -\frac{1}{z} \rightarrow$$ **z = 36^{o}C**

Example 5.8: 90% of ascorbic acid was degraded in orange juice heated at 90°C for 180 min. Increasing the temperature by 15°C resulted in the decrease in D value by 10 fold. At 90°–105°C, z values for the degradation of ascorbic acid in lemon and grapefruit juices were determined as 12° and 18°C, respectively. Compare the temperature sensitivity of ascorbic acid in these fruit juices.

Answer

- Increasing temp. by 15°C, D value decreased by 10 times. This shows that *z*-value for the degradation of aa in orange juice is 15°C.
- Among juices, the most sensitive aa to temperature changes (increases) is lemon juice ($z=12^oC$) followed by orange ($z=15^oC$) and grapefruit ($z=18^oC$) juices.

Example 5.9: Murakami *et al*. (1998) studied thermal stability of *Alicyclobacillus acidoterrestris* spores at various pH's in buffer solutions and various temp.'s. D values determined in buffer solution at pH= 3 at 88°–95°C were given in Table 5.13. Find out the following kinetic parameters for these spores at 88°–95°C:

a) Q_{10} value,
b) z value,

Table 5.13 D values for the inactivation of *A. acidoterrestris* spores in buffer solution (pH 3) and at 88°–95°C

Temperature (°C)	D (min)
88	24.1
90	14.8
92	6.2
95	2.7

Calculation of *k* values from D values

$$88°C \rightarrow -24.1 = -\frac{2.303}{k} \rightarrow k = 0.096\ min^{-1}$$

$$90°C \rightarrow -14.8 = -\frac{2.303}{k} \rightarrow k = 0.156\ min^{-1}$$

$$92°C \rightarrow -6.2 = -\frac{2.303}{k} \rightarrow k = 0.371\ min^{-1}$$

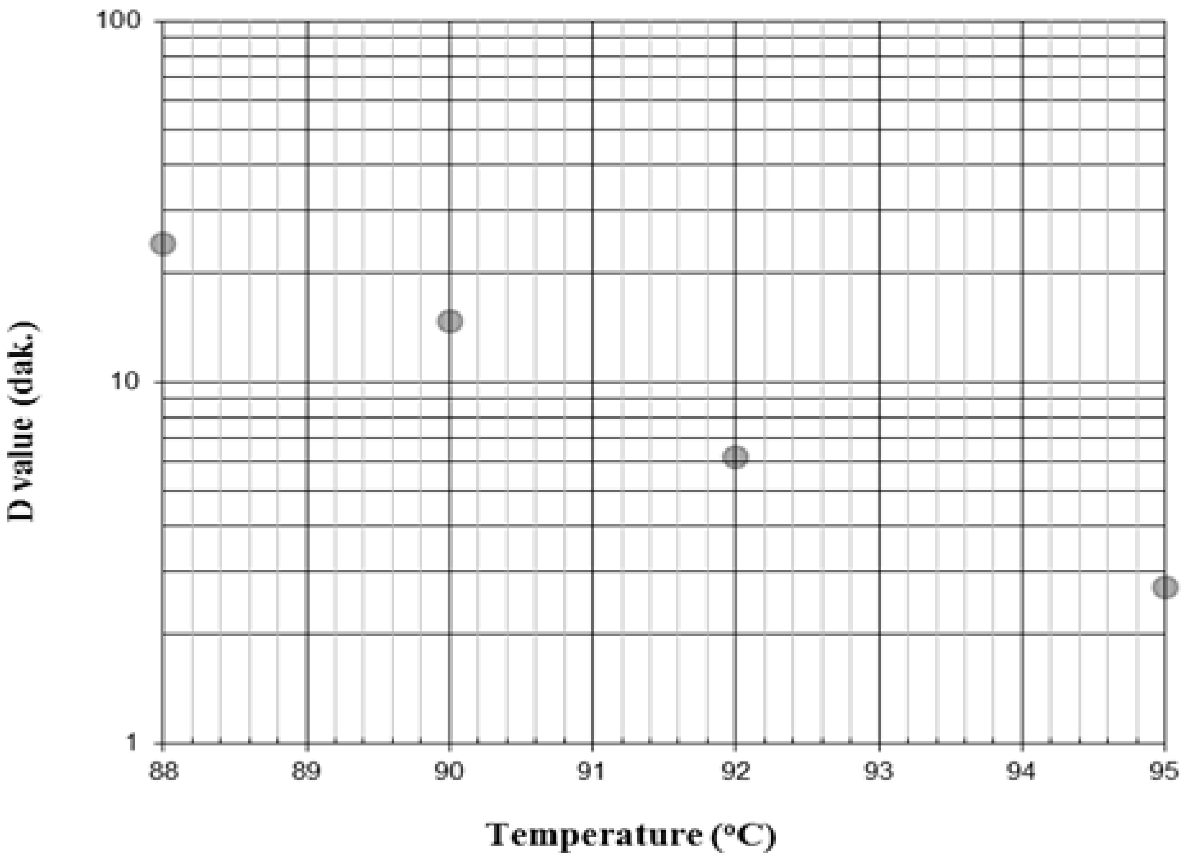
$$95°C \rightarrow -2.7 = -\frac{2.303}{k} \rightarrow k = 0.853\ min^{-1}$$

Calculation of Q_{10} value

$$Q_{10} = \left(\frac{0.853}{0.096} \right)^{10/(95-88)}$$

$$Q_{10} = 22.7$$

Figure 5.8 Thermal inactivation curve for *A. acidoterrestris* spores



Calculation of *z* value

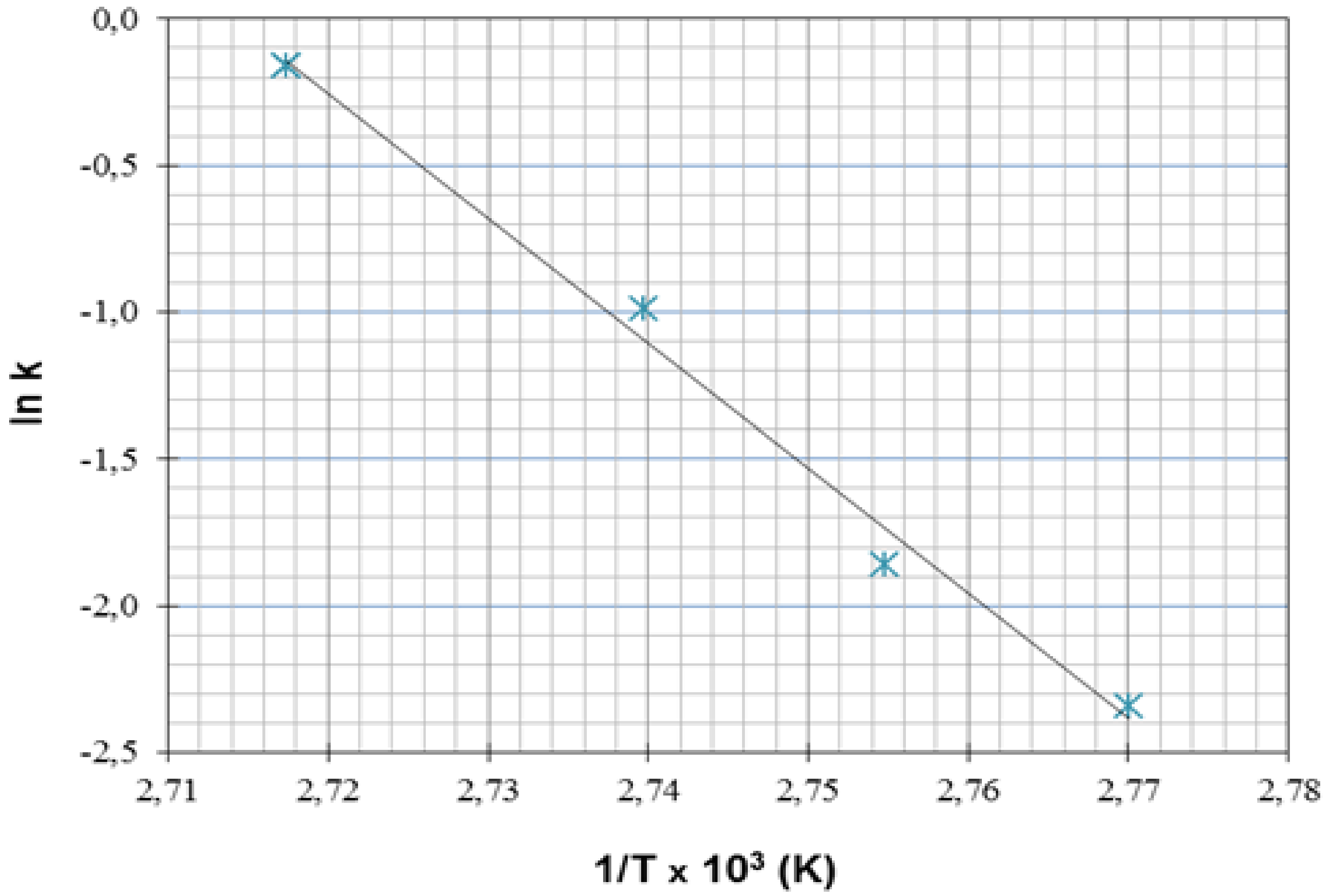
$$\text{Slope} = \frac{\log 4 - \log 10}{93.5 - 90.6} = -0.1372\ 1/^{o}\text{C}$$

$$-0.1372 = -\frac{1}{z}$$

$z = 7.3^{o}\text{C}$

Calculation of E_a value

Arrhenius plot



$$\text{Slope} = \frac{-1.5 - (-0.5)}{(2.749 - 2.726) \times 10^{-3}} = -43\,478 \text{ 1/K}$$

$$\text{Slope} = -\frac{E_a}{R}$$

$$-43\,478 = -\frac{E_a}{1.987}$$

$$E_a = 86\,391 \text{ cal/mole} = 86.4 \text{ kcal/mole}$$

Example 5.10: Reaction rate constants for the removal of SO_2 from dried apricots were calculated in dried apricots stored at 40°, 50° and 60°C (Table 5.16). Calculate:

a) $t_{1/2}$ values (days),
b) D values (days),
c) Q_{10} values (at the range of 40°–50°C and 50°–60°C),

d) E_a value in "**SI**" unit system and compare this E_a value with the E_a=85 (in «SI») of SO_2 removal form raisins at the same temperature range.

e) *z* value.

Table 5.16 "*k*" values for the removal of SO_2 from dried apricots

Temperature (°C)	$-k \times 10^3$ (h^{-1})
40	0.81
50	2.30
60	11.35

Calculation of $t_{1/2}$ values

$$t_{1/2} = -\frac{0.693}{k}$$

$40°C \rightarrow t_{1/2} = 855\ h = 35.6\ days$

$50°C \rightarrow t_{1/2} = 301\ h = 12.5\ days$

$60°C \rightarrow t_{1/2} = 61\ h = 2.5\ days$

Conclusion

As the process temp. increased, $t_{1/2}$ values decreased. Therefore, the increase in temp. caused more SO_2 removal from dried apricots.

Calculation of D values

$$D = \frac{2.303}{k}$$

$40°C \rightarrow D = 2843\ h\ =\ 118.5\ days$

$50°C \rightarrow D = 1001\ h\ =\ 41.7\ days$

$60°C \rightarrow D = 203\ h\ =\ 8.5\ days$

Conclusion

As the process temp. increased, D values decreased. Therefore, as in the case of $t_{1/2}$ values, the increase in temp. caused more SO_2 removal from dried apricots.

Calculation of Q_{10} values

$$Q_{10} = \frac{k_2}{k_1}$$

Calculation of Q_{10} values

$$40°\text{–}50°C \rightarrow Q_{10} = \left(\frac{0.00230}{0.00081}\right) = 2.84$$

$$50°\text{–}60°C \rightarrow Q_{10} = \left(\frac{0.01135}{0.00230}\right) = 4.93$$

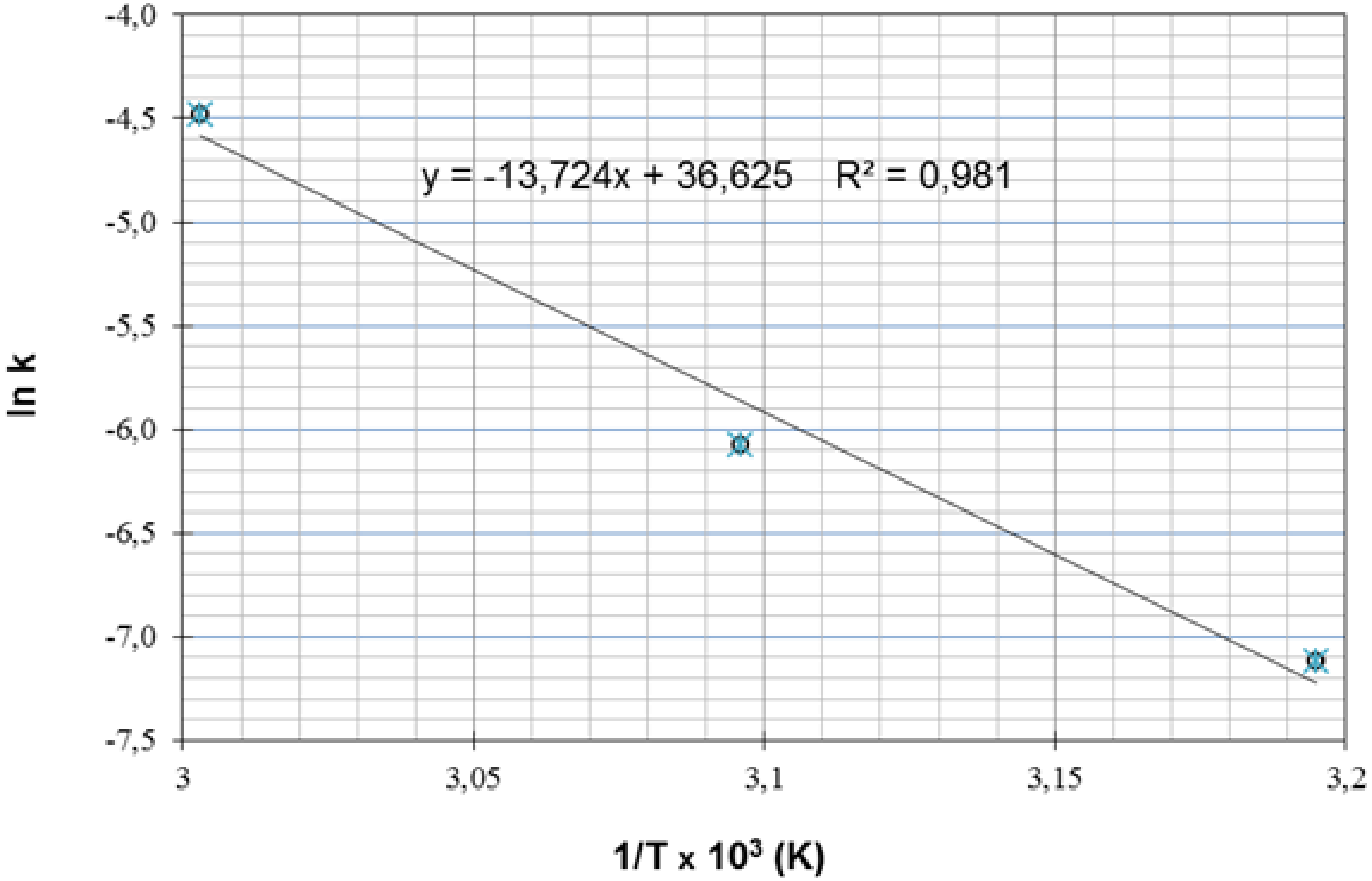
Conclusion

- The calculated Q_{10} values (over 2) indicated that the removal of SO_2 from dried apricots are highly dependent on the temperature.
- At 50°–60°C, increase in tempearture by 10°C resulted in the SO_2 removal rate by app. 5 times in dried apricots. However, this increase was only approximately 3 times at 40°–50°C.
- **Therefore, the removal of SO_2 from dried apricots is more dependent on temperature changes at 50°–60°C than 40°–50°C**.

Table 5.17 Arrhenius data

°C	K	1/T	1/T x (10^3) (X)	k	ln k (Y)
40	313	0.00319	3.19×10^{-3}	0.00081	– 7.12
50	323	0.00310	3.10×10^{-3}	0.00230	– 6.07
60	333	0.00300	3.00×10^{-3}	0.01135	– 4.48

Figure 5.10 Arrhenius graph



Calculation of E_a value

$$\text{Slope} = \frac{-6.5 - (-5.0)}{(3.143 - 3.035) \times 10^{-3}\ (1/K)} = -13\ 889\ K$$

- From the calculated slope, E_a value is calculated from the following equation:

$$\text{Slope} = -\frac{E_a}{R}$$

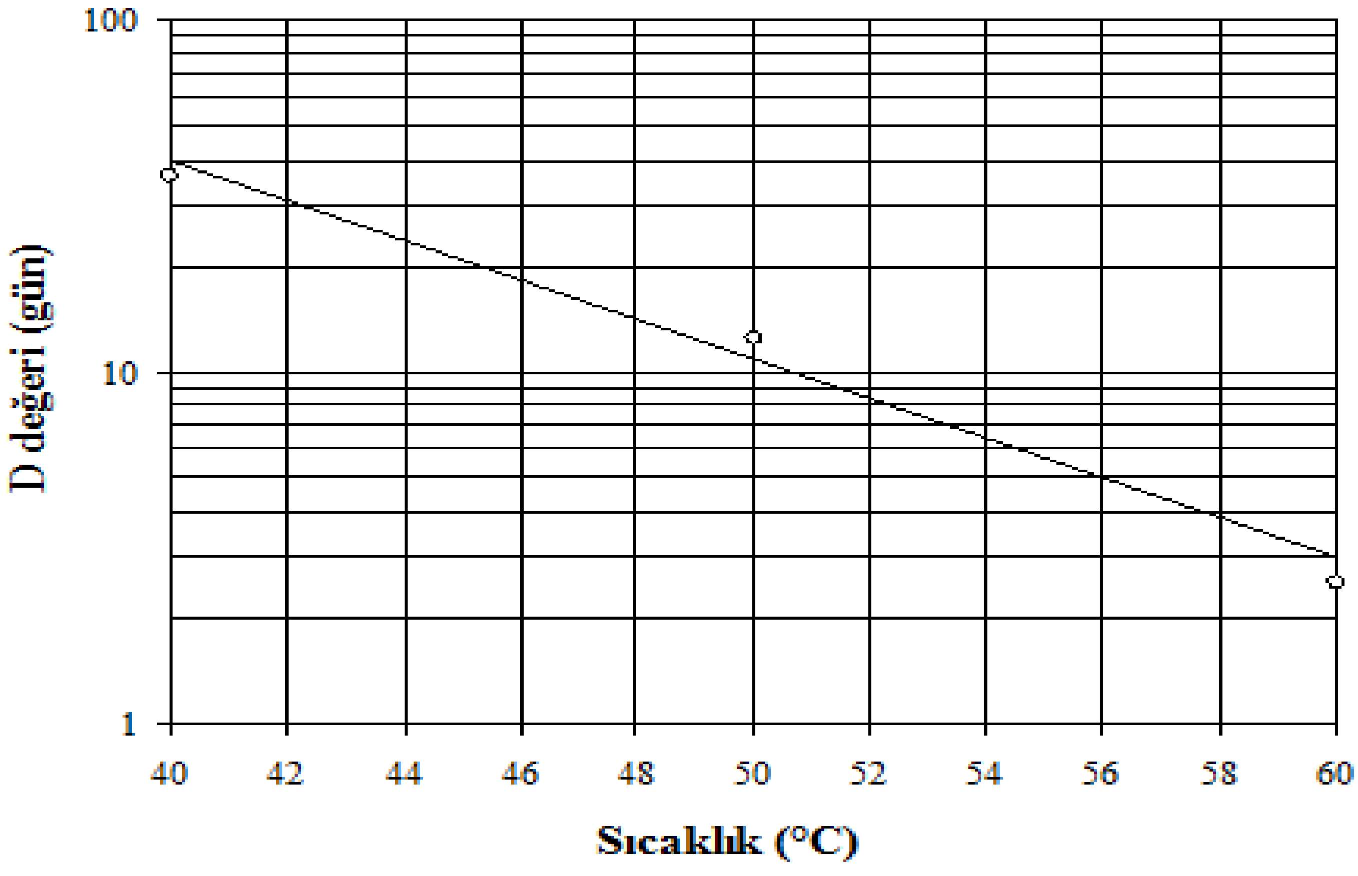
$$-13\ 889\ K = -\frac{E_a}{1.987\ \text{cal/(mole K)}}$$

E_a = 27 597 cal/mole = 27.6 kcal/mole

Table 5.18 “D” values

Temperaure (°C)	**D value (day)**
40	119
50	42
60	9

Figure 5.11 Thermal destruction curve for the removal of SO_2 from dried apricots



Calculation of *z* value

$$\text{slope} = \frac{\log 10 - \log 6}{50.73 - 54.95} = -0.05257\ 1/^{o}C$$

$$\text{slope} = \frac{1}{z}$$

$$-0.05257 = \frac{1}{z}$$

$z = 19°C$

Shelf-life

If Q_{10} for the chemical component in food and shelf-life value of a food determined at any temp., then shelf-life of food at a given temp. can be calculated from the following equation:

$$(Q_{10})^{(T2 - T1)/10} = \frac{\theta_{T1}}{\theta_{T2}}$$

$T_2 > T_1$

θ : Shelf-life of food

Example 5.11: To determine the shelf-life of a food, Q_{10} value of primary quality factor is found to be 3. If shelf-life of this food is determined as 6 mo at 35°C, found out the shelf-life of this food at 20°C.

Shelf-life at 20°C

$$(Q_{10})^{(T2 - T1)/10} = \frac{\theta_{T1}}{\theta_{T2}}$$

$$(3)^{(35 - 20)/10} = \frac{\theta_{20°C}}{6}$$

$$\theta_{20°C} = 31.2 \text{ mo}$$

Thank you for your patient throughout the semester☺))

Good luck for your final☺))