Activation Energy (E_a)

- E_a value indicates that how **temp. changes** during processing or storage affect the ***k*** value of the reaction.

- The higher **E_a value** of the reaction, the more **sensitive** for the reaction to **temp. changes during storage or processing.**

- E_a value is specific for each chemical, microbial and enzymatic reaction.

√ E_a cannot be directly measured.

√ **E_a is calculated from Arrhenius equation.**

This equation (described by Svante Arrhenius in 1889) gives the relationship **between *k* and temp.** of processing or storage.

- Therefore, we need *k* and temp. values to determine E_a

Arrhenious equation

$$k = k_o e^{-Ea/RT}$$

- k: Reaction rate constant (for any reaction order)
- k_o: frequency factor (same unit as k)
- E_a: Activation energy of the reaction (cal/mole of J/mole)
- R: Gas constant (1.987 cal/(mole K) or 8.314 J/(mole K)
- T: Temperature (**K**)

Take *ln* of both sides

$$\ln k = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T}\right) + \ln k_o$$

$$\updownarrow \quad \updownarrow \quad \updownarrow \quad \updownarrow$$

$$y = a \quad x + b$$

- Find the equivalence of this equ. on $\log_{10}$

To determine E_a value graphically

- √ First identify the quality factor of concern and then determine ***k*** values at least at **three different temp**., preferably at five different processing or storage temp.
- √ Then, plot *k* values vs 1/T values.
  - **Using aritmetic graph paper:** Take ***ln* of *k* values** and reciprocal of temp. values in Kelvin and then plot ***ln k*** vs **1/T**. **Slope** will be equal to $-E_a/R$.
  - **Using semi-log graph paper:** Plot **original *k*** values vs **1/T** values. **Slope** will be equal to $-E_a/2.303R$.
- √ From slope, calculate E_a value.

- Be aware that all *k* values should be in the **same order** and the **same unit** for the calculation of E_a.

- **Reactions that their *k* value (rate) increase with temp. have negative slopes in Arrhenius plot.**

  Therefore, E_a will always be positive.

- "k_o" is equal to intercept value of Arrhenius graph.

  Intercept (b) = ln k_o

Example

Oxidative degradation of aa was determined in orange juice at three different storage temperatures. Determine the E_a value (kJ/mole) for the degradation of aa.

AA contents in orange juice stored at various temp.

Temperature (°C)	Time (h)	AA content (mg mL^{-1})
23	20	0.948
	40	0.476
	60	0.004
35	5	1.029
	10	0.758
	20	0.261
45	0	1.200
	5	0.655
	10	0.109

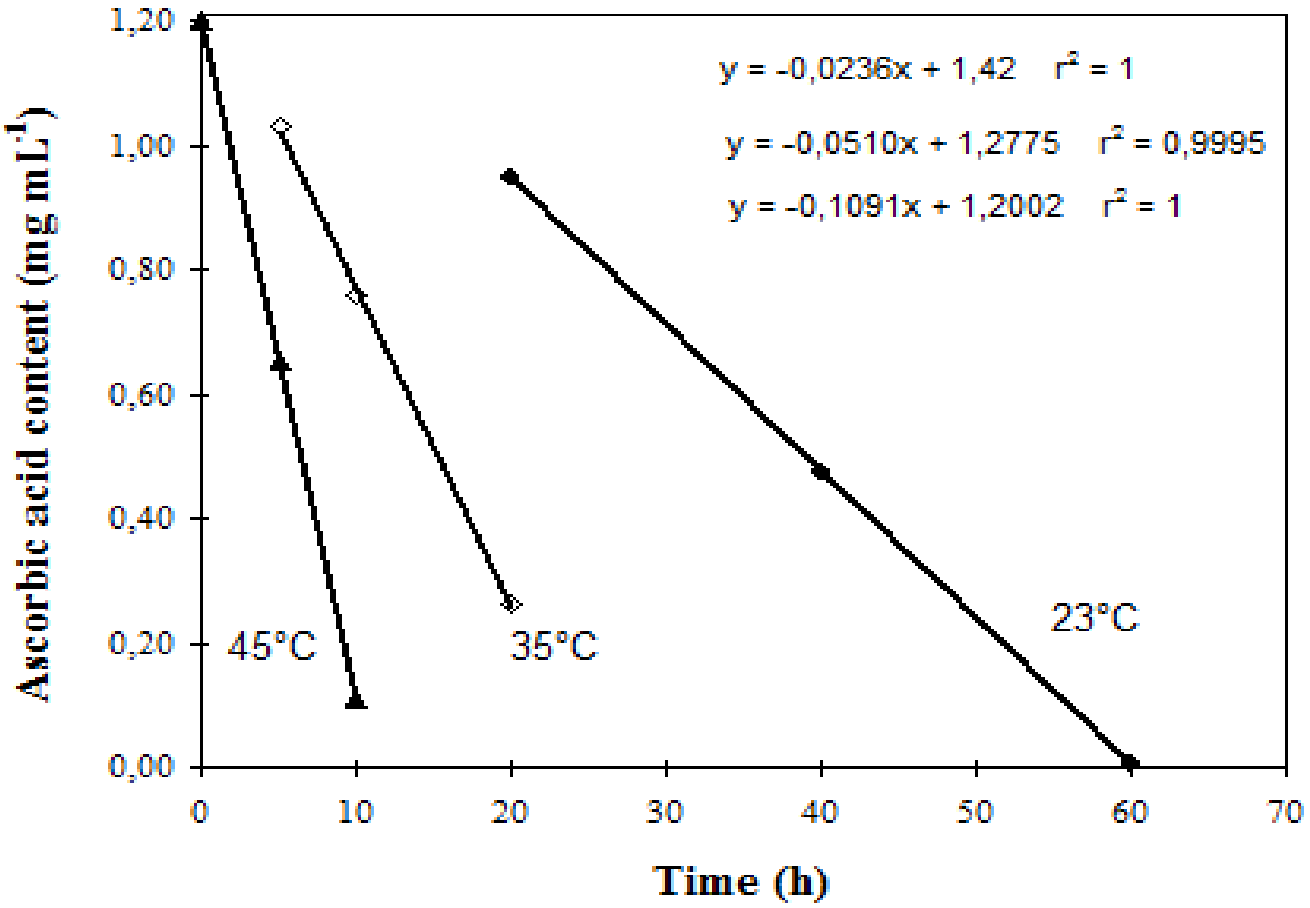
Example

Oxidative degradation of aa was determined in orange juice at three different storage temperatures. Determine the E_a value (kJ/mole) for the degradation of aa.

Note: The straight line in arithmetic graph paper was obtained from aa conc. vs time curve.

Solution

Since reaction is zero-order, aa content versus storage period is plotted in arithmetic graph paper.


y = -0,0236x + 1,42 r² = 1
y = -0,0510x + 1,2775 r² = 0,9995
y = -0,1091x + 1,2002 r² = 1
45°C
35°C
23°C
Ascorbic acid content (mg mL-1)
Time (h)
1,20
1,00
0,80
0,60
0,40
0,20
0,00
0
10
20
30
40
50
60
70

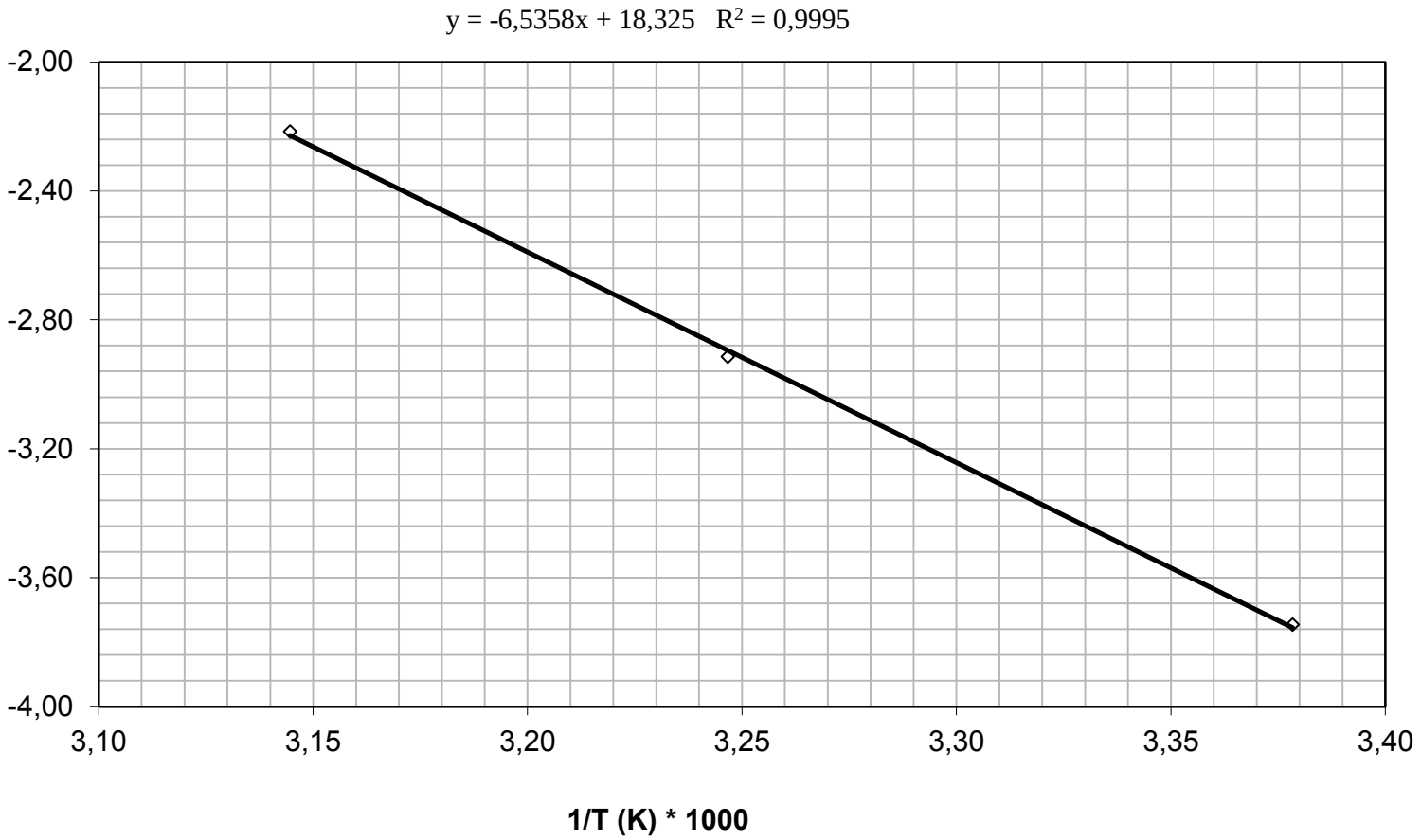
k vales are calculated from slopes

Temperature (°C)	Slopes (mg mL^{-1} h^{-1})	*k* (mg mL^{-1} h^{-1})
23	0.0236	?
35	0.0542	?
45	0.1090	?

Values for Arrhenius plot of aa oxidation

Temp.(°C)	Temp.(K)	$1/Tx10^3$ (K)	k	lnk
23	296	3.38	0.0236	-3,7465
35	308	3.25	0.0542	-2.9151
45	318	3.15	0.1090	-2.2164

Arrhenius plot (*ln k* vs 1/T, arithmetic graph paper)



Calculation of slope

$$\text{Slope} = \frac{-3.60 - (-2.40)}{(3.35 - 3.17) \times 10^{-3}}$$

or;

$$\text{Slope} = \frac{-3.60 - (-2.40)}{0.00335 - 0.00317}$$

$$\text{Slope} = -6667\ \text{K}$$

Calculation of E_a

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

$$-6667\ \text{K} = \frac{-E_a}{1.987\ \text{(unit?)}}$$

$$E_a = 13\,246\ \text{(unit?)}$$