

Lecture 36 CH102 A2 (MWF 11:15 am) Spring 2018

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[TP] For $A \rightarrow B$, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.
 For $C \rightarrow D$, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.
 Compared to the activation energy of $A \rightarrow B$, the activation energy of $C \rightarrow D$ is ...

- 25% 1. smaller
 25% 2. the same
 25% 3. larger
 25% 4. More information needed



1

Lecture 36 CH102 A2 (MWF 11:15 am)

Friday, April 27, 2018

- Complete: Rate versus temperature: E_a and A .
- Catalysis
- Half-life
- Half-life calculations

Next lecture: First law, second law, equilibrium, and kinetics



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Response Counter



6

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$$\ln(k) = (-E_a/R) (1/T) + \ln(A)$$

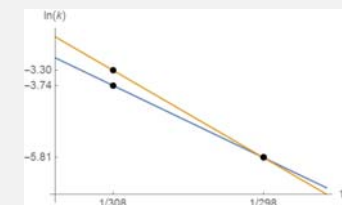
For $A \rightarrow B$, k_{for} is 0.003/min at 25 °C and 0.025/min at 35 °C.

$$\text{slope} = -E_a/R = \frac{\ln(k_{A2}) - \ln(k_{A1})}{1/T_2 - 1/T_1} = -19000 \text{ K}$$

For $C \rightarrow D$, k_{for} is 0.003/min at 25 °C and 0.035/min at 35 °C.

$$\text{slope} = -E_a/R = \frac{\ln(k_{C2}) - \ln(k_{C1})}{1/T_2 - 1/T_1} = -23000 \text{ K}$$

The larger E_a , the greater the temperature dependence.



7

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$$\ln(k) = (-E_a/R) (1/T) + \ln(A)$$

An example to try:

$$k_1 = 43.0 \times 10^{-5} / \text{min}, T_1 = 45 \text{ }^\circ\text{C}$$

$$k_2 = 3.38 \times 10^{-5} / \text{min at } T_2 = 25 \text{ }^\circ\text{C}$$

slope $\rightarrow -12.1 \times 10^3 \text{ K}$
 $E_a \rightarrow -\text{slope } R = +100. \text{ kJ/mol}$

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8

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Catalyst: New path with lower barrier \rightarrow bigger k

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11

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Catalyst: New path with lower barrier \rightarrow bigger k

Only molecules with energy greater than E_a can react

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12

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Catalyst: New path with lower barrier \rightarrow bigger k

The lower E_a , the more molecules with energy at least E_a

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13

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Catalyst: New path with lower barrier → bigger k

Energy (kJ mol^{-1})

Uncatalyzed reaction $E_a = 264 \text{ kJ mol}^{-1}$

Catalyzed reaction $E_a = 118 \text{ kJ mol}^{-1}$

Reactants: $\text{cis-}C_4H_8 + I_2$ (75 kJ mol^{-1})

Products: $\text{trans-}C_4H_8 + I_2$ (14 kJ mol^{-1})

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14

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[Quiz] Compared to temperature dependence of an uncatalyzed reaction, when a catalyst is used, increasing temperature would speed the reaction up ...

25% 1. more
25% 2. the same amount
25% 3. less
25% 4. More information needed

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Response Counter

10

15

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$\ln(k) = (-E_a/R) (1/T) + \ln(A)$

The larger E_a , the greater the temperature dependence.

This means that a catalyzed reaction will be less sensitive to temperature than its non-catalyzed version.

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16

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Half-life

First-order reactions have the **special property** that the time for reduction of the reactant by half, t_{half} , **does not change** as the amount of material present changes due to transformation into products..

Let's see why this is true.

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30

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Half-life

For process $A + \dots \rightarrow \dots$ that is **first order** in A,

$$\text{rate} = k[A] = -d[A]/dt \rightarrow d[A]/[A] = -k dt$$

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Half-life

Add successive time intervals of length dt covering the total elapsed time t ,

$$-k dt_0 - k dt_1 - \dots - k dt_n = -k(dt_0 + dt_1 + \dots + dt_n) = -k t,$$

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Half-life

Add corresponding successive ratios $d[A]/[A]$, covering to total elapsed time t ,

$$d[A]/[A]_0 + d[A]/[A]_1 + \dots + d[A]/[A]_n = \ln([A]_t/[A]_0)$$

This sum is the **definition of the natural logarithm**.

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Half-life

Therefore, the relation for a process $A + \dots \rightarrow \dots$ that is **first order** in A,

$$\text{rate} = k[A] = -d[A]/dt \rightarrow d[A]/[A] = -k dt$$

means that for the total elapsed time t ,

$$\ln([A]_t/[A]_0) = -k t$$

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Half-life

Since half-life is how long it takes for the amount to drop by half,

$$\ln([A]_{t_{\text{half}}}/[A]_0) = \ln(1/2) = -\ln(2) = -k t_{\text{half}}$$

the half life is

$$t_{\text{half}} = \ln(2) / k$$

That is, first-order reactions have the **special property** that the time for reduction of the reactant by half, t_{half} , **does not change** no matter the amount of material present.



35

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Half-life

Since half-life is the same no matter how much material we have, after n half-life $[A]_0$ is reduced to

$$\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} \times \dots \times \frac{1}{2} [A]_0 = \left(\frac{1}{2}\right)^n [A]_0 = [A]_n$$

and so, the **fraction remaining** tells us the number of half-lives n ,

$$\frac{[A]_n}{[A]_0} = \left(\frac{1}{2}\right)^n$$

This is true even if n is **not an integer!**



36

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Types of first-order decay calculations



37

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Types of first-order decay calculations

The essential equations of half-life are

$$\left(\frac{1}{2}\right)^n = \frac{[A]_n}{[A]_0}$$

$$\ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$nt_{\text{half}} = t$$

Let's see how to use these to carry out various kinds of half-life calculations.



38

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Types of first-order decay calculations

Given amount consumed in time t , how many half-lives have elapsed?

Given how many half-lives have elapsed in time t , what is t_{half} ?

Given t_{half} , how much remains after time t ?

Given amount consumed in time t , what is the rate constant k ?



39

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Types of first-order decay calculations

Given amount consumed in time t , how many half-lives have elapsed?

Given how many half-lives have elapsed in time t , what is t_{half} ?

Given t_{half} , how much remains after time t ?

Given amount consumed in time t , what is the rate constant k ?

In n half-lives, $[A]_0$ is reduced to $\frac{1}{2} \times \frac{1}{2} \times \dots \times \frac{1}{2} [A]_0 = \left(\frac{1}{2}\right)^n [A]_0 = [A]_n$

So, the **fraction remaining** tells us the number of half-lives n ,

$$\frac{[A]_n}{[A]_0} = \left(\frac{1}{2}\right)^n$$

This is true even if n is **not an integer**!



40

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Finding the half-lives elapsed, n

In a process, a **60%** of a substance has **decayed**. This means ...

$$\left(\frac{1}{2}\right)^n = [A]_n/[A]_0 = 0.40$$

The number of half-lives elapsed is ...

$$n = \log(0.40)/\log(1/2) = -\log(0.40)/\log(2) \approx 1.3$$



41