Chap. 10
April 11

Initial Rate Example (Chap. 10, Slide #20)

Example: Consider the reaction, $2A + B \rightarrow 2C$

$$R_o = k\,[A]_o^x\,[B]_o^y\,[C]_o^z$$

Use the experimental data below to determine x, y, z and the rate constant, k.

Expt.	$[A]_o$	$[B]_o$	$[C]_o$	R_o
#1	0.50 M	0.10 M	0.80 M	78 Ms^{-1}
#2	0.75	0.05	0.20	176
#3	0.75	0.10	0.80	176
#4	0.75	0.05	0.80	352

(1) 1 & 3

$$\frac{R_{o3}}{R_{o1}} = \left(\frac{0.75}{0.50}\right)^x \left(\frac{0.1}{0.1}\right)^y \left(\frac{0.8}{0.8}\right)^z = \frac{176}{78}$$

$$(1.5)^x = (2.25)$$

$$\ln(1.5)^x = \ln(2.25) =$$

$$x \ln(1.5) = \ln$$

$$x = \frac{\ln(2.25)}{\ln(1.5)} = \frac{0.81}{0.405} = 2.00 = x$$

(2) 2 & 4

$$\frac{R_{o4}}{R_{o2}} = \left(\frac{0.80}{0.2}\right)^z = \frac{352}{176} \rightarrow (4.0)^z = 2.0$$

$$z \ln(4.0) = \ln(4.0)^z = \ln(2.0) \rightarrow z = \frac{\ln(2.0)}{\ln(4.0)} = \frac{0.693}{1.386} = 0.50 = \frac{1}{2}$$

Find Rate (cont.)

(3) (24)

$$\frac{R_{0\,4}}{R_{0\,3}} = \left(\frac{[B_0]_4}{[B_0]_3}\right)^y$$

$$\frac{352}{176} = \left(\frac{0.05}{0.10}\right)^y$$

$$2.0 = 0.5^y$$

$$\ln(2.0) = \ln(0.5)^y = y\ln(0.5)$$

$$y = \frac{\ln(2)}{\ln(0.5)} = \frac{0.693}{-0.693} = -1.00 = -1$$

$x = 2$

$z = 0.5$

$y = -1$

$$\boxed{k}$$

$$R_0 = k[A_0]^2[B_0]^{-1}[C_0]^{0.5} = \frac{k[A_0]^2[C_0]^{0.5}}{[B_0]}$$

$$k = \frac{R_0[B_0]}{[A_0]^2[C_0]^{1/2}}$$

(A)

$$k = \frac{78\,M\,s^{-1}(0.1\,M)}{(0.5\,M)^2(0.8\,M)^{1/2}}$$

$$= 35.0\,\frac{M^2 s^{-1}}{M^{5/2}} = 35.0\,M^{-1/2}\,s^{-1}$$

Chap 10 Example: Kinetics of First Order Reaction
April 11 Slide #29

For a first order reaction, A $\rightarrow$ Products, the half-life is 150 s.

(a) What is the rate constant, k?

(b) If $[A]_o$ = 0.40 M, what is [A] after 240 s?

(c) If $[A]_o$ = 0.40 M, how long does it take for [A] to decrease to 0.08 M?

(a)

Assume, $[A_0] = 1.0\ M$ when $[A] = \frac{1}{2}[A_0] = \frac{1}{2}(1\,M) = 0.5\,M$

$t = t_{1/2}$

$\ln[A] = \ln[A_0] - kt$

$\ln[A] - \ln[A_0] = -kt$

$\ln(0.5) - \ln(1) = -k\, t_{1/2}$

$-0.693 - 0 = -k\, t_{1/2}$

$k = \dfrac{+0.693}{150\,s} = \boxed{4.62 \times 10^{-3}\ s^{-1}}$

(b) $[A_0] = 0.40\,M$ $t = 240\,s.$ $[A] = ?$

$\ln[A] = \ln[A_0] - kt = \ln(0.4) - 4.62 \times 10^{-3}\,s^{-1}(240\,s)$

$\ln[A] = -2.025$

$[A] = e^{-2.025} = 0.13\,M.$

1st Calc Dan (#59) Con'd.

(c) $[A_0] = 0.40\,M$ $[A] = 0.08\,M$ $t = ?$

$$\ln[A] - \ln[A_0] = -kt$$

$$t = -\frac{1}{k}\left(\ln[A] - \ln[A_0]\right)$$

$$= -\frac{1}{4.62 \times 10^{-3}\,s^{-1}}\left(\cancel{\ln(0.1)}\ \ln(0.08) - \ln(0.4)\right)$$

$$= t = 348\,s \simeq 350\,s$$

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Rxn Order Eqns. to Memorize

n = 0 $[A] = [A_0] - kt$

n = 1 $\ln[A] = \ln[A_0] - kt$

n = 2 $\frac{1}{[A]} = \frac{1}{[A_0]} + kt$

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Example: Kinetics of a Third Order Reaction
Slide #36

Example: The reaction, A $\rightarrow$ Products, is third order; i.e. $-d[A]/dt = k[A]^3$

$$\frac{1}{[A]^2} = \frac{1}{[A]_o^2} + 2kt$$

(a) When $[A]_o = 0.40$ M, it takes 75 s for the concentration to decrease to 0.10 M. What is the rate constant, k?

(b) When $[A]_o = 0.40$ M, what is the concentration of A after 315 s?

(a) $[A_o] = 0.4M$ $[A] = 0.1M$ $t = 75s.$

$$\frac{1}{[A]^2} - \frac{1}{[A_o]^2} = 2kt$$

$$k = \frac{1}{2t}\left[\frac{1}{[A]^2} - \frac{1}{[A_o]^2}\right] = \frac{1}{2(75s)}\left[\frac{1}{(0.1M)^2} - \frac{1}{(0.4M)^2}\right]$$

$$= 0.625\ \frac{1}{M^2}\frac{1}{s} = 0.625\ M^{-2}s^{-1}$$

(a) Alternative: when $[A_o] = 0.40$ M half life is 15 s.

$[A_o] = 0.4M$ $[A] = 0.2M$ $t = 15s$

$$k = \frac{1}{2 \times 15s}\left[\frac{1}{(0.2M)^2} - \frac{1}{(0.4M)^2}\right]$$

$$= 0.625\ M^{-2}s^{-1}$$

3rd order cont.

(b) $[A_0] = 0.4\,m$, what is $[A]$ at $t = 315\,s$

$$\frac{1}{[A]^2} = \frac{1}{[A_0]^2} + 2kt$$

$$= \frac{1}{(0.4\,m)^2} + 2\left(0.625\,m^{-2}s^{-1}\right)\left(315\,s\right)$$

$$\frac{1}{[A]^2} = 400\,\frac{1}{m^2}$$

$$\frac{1}{[A]} = \sqrt{400\,\frac{1}{M^2}} = 20\,\frac{1}{M}$$

$$[A] = \frac{1}{20\,{}^1\!/\!_M} = 0.05\,M$$

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Radiocarbon Dating: Slide #51

$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{5730\ yr} = 1.21 \times 10^{-4}\ yr^{-1}$

The half-life for ^{14}C decay is 5730 years.
The level of radioactivity of living objects is N_o = 15.4 counts/min per g C.

A wooden artifact has a level of N = 12.1 counts/min per g C.

What is the age of the artifact?

NOTE: ON A TEST, I WOULD GIVE YOU THE VALUE OF k.

$\ln[A] = \ln[A_0] - kt$

$\ln[A] - \ln[A_0] = -kt$

$t = -\frac{1}{k}\left(\ln(12.1) - \ln(15.4)\right)$

$k = 1.21 \times 10^{-4}\ yr^{-1}$

$t = 1.99 \times 10^{3}\ yr. = 1990\ yr \approx 2000\ yr.$

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Rock Dating: Slide #53

$t_{1/2}(^{40}K) = 1.25x10^9$ years.

Example: It was found that a rock had a ratio, $[^{40}K]/[^{40}Ar] = 1.50$. The age of the rock is:

(A) 0.9 by
(B) 1.4 by
(C) 2.7 by
(D) 3.9 by

t	[K]	[Ar]	[Ar]/[K]	[K]/[Ar]
0	100%	0%	0	∞
1 $t_{1/2}$ = 1.25 by	50%	50%	1.0	1.0
2 $t_{1/2}$ = 2.5 by	25%	75%	3.0	0.33
3 $t_{1/2}$ = 3.75 by	12.5%	87.5%	7.0	0.14

0 → 1.25 by

A 0.9 by

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Review: Reaction order by Half-Life Method

A given reaction is nth. order: Rate = $-d[A]/dt = k[A]^n$

When $[A_o]$ = 0.60 M, the half-life is 20 s.
When $[A_o]$ = 0.15 M, the half-life is 1280 s.

Calculate the reaction order, n

$$\frac{(t_{1/2})_2}{(t_{1/2})_1} = \left(\frac{[A_0]_1}{[A_0]_2}\right)^{n-1}$$

$$\frac{1280}{20} = \left(\frac{0.60}{0.15}\right)^{n-1}$$

$$64 = 4^{n-1}$$

$$\ln(64) = \ln 4^{n-1} = n-1 \ln(4)$$

$$n-1 = \frac{\ln(64)}{\ln(4)} = \frac{4.16}{1.39} = 3.00$$

$$n = 3+1 = \boxed{4}$$

Comparison of Rates

$$R_0 = k[A_0]^n$$

$$\frac{R_{0_2}}{R_{01}} = \frac{k[A_0]_2^n}{k[A_0]_1^n} = \left(\frac{[A_0]_2}{[A_0]_1}\right)^n$$

$[A_0]_1 = 0.1\,M \quad R_{01} = 1\,M s^{-1}$

$[A_0]_2 = 0.3\,M \quad R_{02} = 27\,M s^{-1}$

$$\frac{27}{1} = \left(\frac{0.3}{0.1}\right)^n$$

$$27 = 3^n$$

$$\ln(27) = \ln 3^n = n \ln 3$$

$$n = \frac{\ln(27)}{\ln(3)} = \frac{3.30}{1.10} = 3.00$$

Chap 10 **Arrhenius Example 1: Slide #61**
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$T_1 = 298\,K$ $T_2 = 308$

For a first order reaction, the measured rate constant was 5. s^{-1} at 25 °C and 15. s^{-1} at 35 °C.

Calculate A and E_a for this reaction.

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$E_a = -\frac{R\ln\left(\frac{k_2}{k_1}\right)}{\frac{1}{T_2}-\frac{1}{T_1}} = \frac{-8.31\ln\left(\frac{15}{5}\right)}{\frac{1}{308}-\frac{1}{298}} = 8.38\times10^4\ J/mol$$

$\times 10^3$

$$E_a = 83.8\ kJ/mol$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

$$\ln A = \ln k_1 + \frac{E_a}{RT_1} = \ln(5) + \frac{8.38\times10^4}{(8.314)(298)}$$

$$\ln A = 35.4$$

$$A = e^{35.4} = 2.4\times10^{15}\ s^{-1}$$

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Arrhenius Example 2: Slide #62

$T_1 = 298\,K \quad T_2 = 323\,K$

A second order reaction has an activation energy of 60 kJ/mol.
The rate constant is 3.0 $M^{-1}s^{-1}$ at 25 °C.
What is the value of k at 50 °C?

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln \frac{k_2}{3.0\,M^{-1}s^{-1}} = \frac{-60 \times 10^3\,J}{8.31\,J/K} \left(\frac{1}{298\,K} - \frac{1}{323\,K}\right)$$

$$= 1.87$$

$$\frac{k_2}{3.0} = e^{1.87} = 6.5$$

$$k_2 = 6.5\,(3.0\,M^{-1}s^{-1}) = 19.5\,M^{-1}s^{-1}$$

Chap 10 **Arrhenius Example 3: Slide #62**
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A first order reaction has an activation energy of 45 kJ/mol.
The rate constant is 50 s^{-1} at 225 °C.
At what temperature (in °C) is the rate constant equal to 10 s^{-1}?

$E_a = 4.5 \times 10^4$ J/mol.

$k_1 = 50 s^{-1}$ $\qquad$ $k_2 = 10 s^{-1}$

$T_1 = 225°C = 498 K$ $\qquad$ $T_2 = ?$

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$-\frac{R}{E_a}\ln\left(\frac{k_2}{k_1}\right) = \frac{1}{T_2} - \frac{1}{T_1}$$

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{E_a}\ln\left(\frac{k_2}{k_1}\right)$$

$$= \frac{1}{498 K} - \frac{8.31}{4.5 \times 10^4}\ln\left(\frac{10}{50}\right)$$

$$\frac{1}{T_2} = 2.305 \times 10^{-3} K^{-1}$$

$$T_2 = \frac{1}{2.305 \times 10^{-3} K^{-1}} = 434 K - 273 = 161°C$$