Kinetics

Chapter 12, Zumdahl and Zumdahl

Kinetics

- The study of reaction rates
  - The factors that determine the speed of a reaction

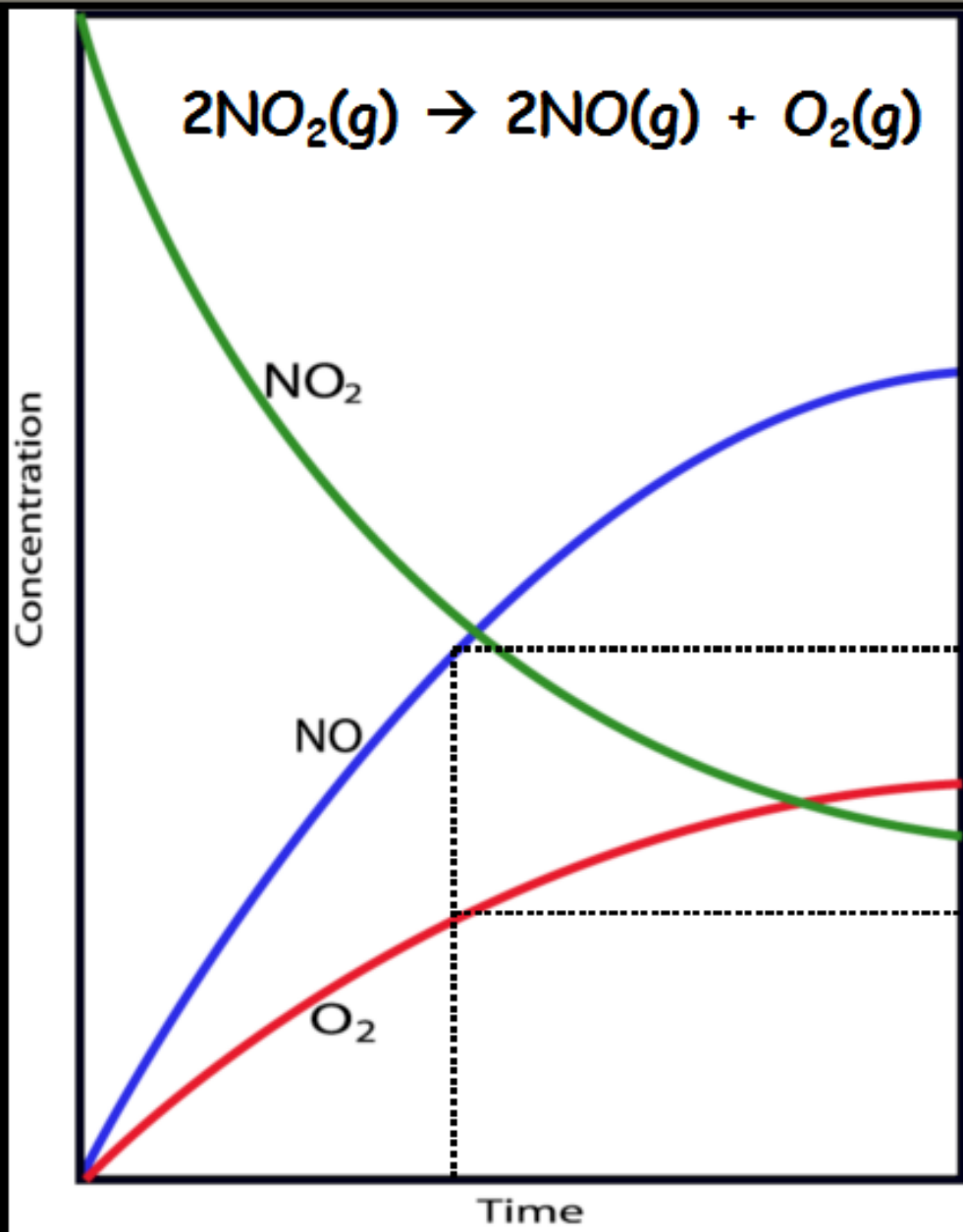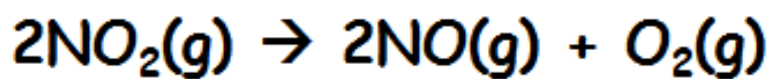- Reaction mechanisms

Reaction Rate

- Change in concentration over time

  - $\dfrac{[A]_2 - [A]_1}{t_2 - t_1}$

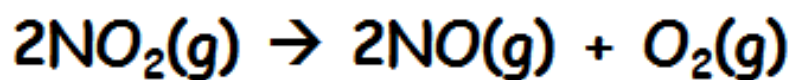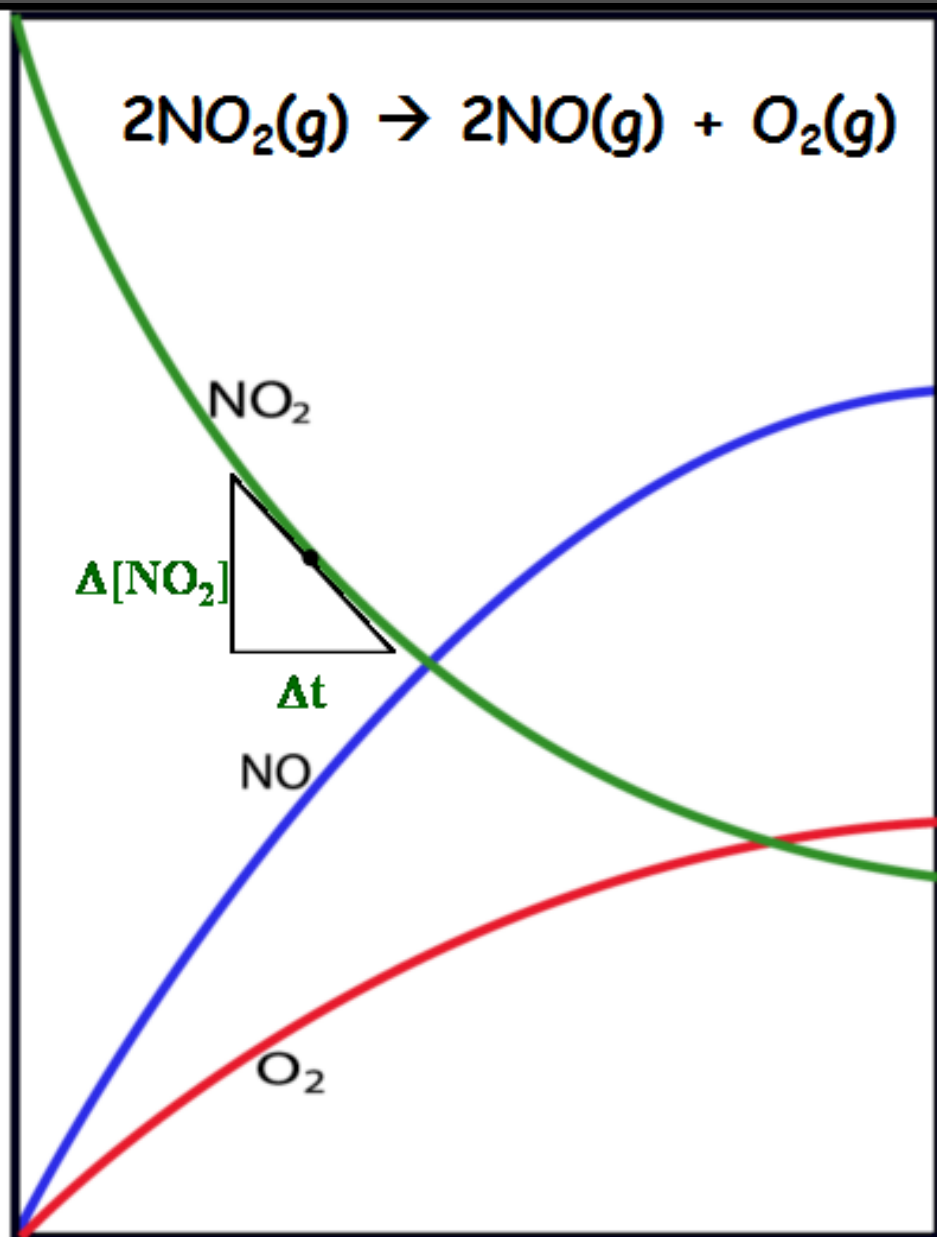 - Or $\dfrac{\Delta[A]}{\Delta t}$

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

Reaction Rates:

1. Can measure disappearance of reactants

2. Can measure appearance of products

3. Are proportional stoichiometrically

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

Concentration

$\Delta[NO_2]$

Δt

NO$_2$

NO

O$_2$

Time

Reaction Rates:

4. Are equal to the slope tangent to that point

5. Change as the reaction proceeds, if the rate is dependent upon concentration

$$\frac{\Delta[NO_2]}{\Delta t} \neq \text{constant}$$

Rate Laws

- **Differential Rate Law**
  - Used to show the relationship between the reaction rate and the concentrations of the reactants
  - Referred to as "The Rate Law" in problems

- **Integrated Rate Law**
  - Shows the relationship of concentration of reactants to time.

Determining Rate Laws

- Initial conditions

  – concentration of products so small that it can be ignored.

- Need multiple sets of experimental data showing different concentrations and the measured or observed rates of reaction

- Determine the relationship between concentration and rate.

Rate Laws

- Zero order
  - Rate = k $[A]^0$
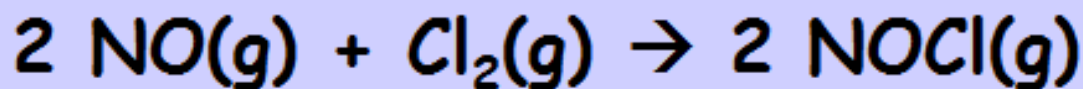- 1st order
  - Rate = k $[A]^1$
- 2nd order
  - Rate = k$[A]^2$

Rate Laws

- More than 1 reactant
- Rate = $k[A]^m[B]^n$
- Overall reaction order
- Order WRT A = m
- Order WRT B = n
- Overall order = m+n

Initial conditions method

Problem - Write the rate law, determine the value of the rate constant, k, and the overall order for the following reaction:

$$2 \text{ NO}(g) + \text{Cl}_2(g) \rightarrow 2 \text{ NOCl}(g)$$

Experiment	[NO] (mol/L)	[Cl$_2$] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	11.4×10^{-6}

Initial conditions method

Part 1 – Determine the values for the exponents in the rate law: $R = k[NO]^x[Cl_2]^y$

Experiment	[NO] (mol/L)	[Cl₂] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	1.14×10^{-5}

In experiment 1 and 2, $[Cl_2]$ is constant while $[NO]$ doubles. The rate quadruples, so the reaction is second order with respect to $[NO]$ $\therefore R = k[NO]^2[Cl_2]^y$

Initial concentrations

- Find a pair of experiments in which the initial concentrations are <u>double</u>.

- Then see how the rate varies

- Look for 2^n

- Where n is the order of that reactant

Initial conditions method

Part 1 – Determine the values for the exponents in the rate law: $R = k[NO]^2[Cl_2]^y$

Experiment	[NO] (mol/L)	$[Cl_2]$ (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}
2	0.500	0.250	5.72×10^{-6}
3	0.250	0.500	2.86×10^{-6}
4	0.500	0.500	1.14×10^{-5}

In experiment 2 and 4, [NO] is constant while $[Cl_2]$ doubles. The rate doubles, so the reaction is first order with respect to $[Cl_2]$ ∴ $R = k[NO]^2[Cl_2]$

Initial conditions method

Part 2 – Determine the value for k, the rate constant, by using any set of experimental data:

$$R = k[NO]^2[Cl_2]$$

Experiment	[NO] (mol/L)	[Cl₂] (mol/L)	Rate Mol/L·s
1	0.250	0.250	1.43×10^{-6}

$$1.43 \times 10^{-6} \frac{mol}{L \cdot s} = k \left(0.250 \frac{mol}{L} \right)^2 \left(0.250 \frac{mol}{L} \right)$$

$$k = \left(\frac{1.43 \times 10^{-6}}{0.250^3} \right) \left(\frac{mol}{L \cdot s} \right) \left(\frac{L^3}{mol^3} \right) = 9.15 \times 10^{-5} \frac{L^2}{mol^2 \cdot s}$$

Writing a rate law

- After the exponents of the rate law are known
- Solve for k
- Rate = k [NO]^2 [Cl]
- Pick any rate from the table
- Everything is known except the rate constant.

Writing a rate law

Part 3 – Determine the overall order for the reaction.

$$R = k[NO]^2[Cl_2]$$

2 + 1 = 3

∴ The reaction is 3rd order

Overall order is the sum of the exponents, or orders, of the reactants

3 orders are common

- Zero order
  - Rate = k $[A]^0$
  - Rate = k
- 1st order
  - Rate = k$[A]^1$
- 2nd order
  - Rate = k$[A]^2$

Example: $NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$

$[NH_4^+]$	$[NO_2^-]$	Rate
0.100M	0.0050M	1.35×10^{-7}
0.100M	0.0100M	2.70×10^{-7}
0.200M	0.0100M	5.40×10^{-7}

Rate $= k[NH_4^+]^n [NO_2^-]^m$

Example

- Experiment 2 to 3
- $[NH_4^+] = 2x$ and Rate $= 2$ or 2^m

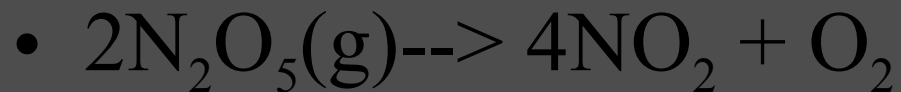- Experiment 1 to 2
- $[NO2-] = 2$ and Rate $= 2$ or 2^n

Example

- Rate Law
- Rate = $k[NH_4^+] [NO_2^-]$
- $1.35 \times 10^7 = k\ (0.100)(0.0050)$
- $k = 2.7 \times 10^{-4}$ L/mol·s

Time vs Concentration

- Graph changes in concentration over time
- Determine the order of reaction directly from graph.
- Zero Order: Time vs concentration linear
- 1st Order: Time vs ln concentration linear
- 2nd Order: Time vs 1/concentration linear

Integrated Rate Law

- $2N_2O_5(g) \rightarrow 4NO_2 + O_2$
- T (s)   [N2O5]
- 0   0.100 M
- 50   0.0707 M
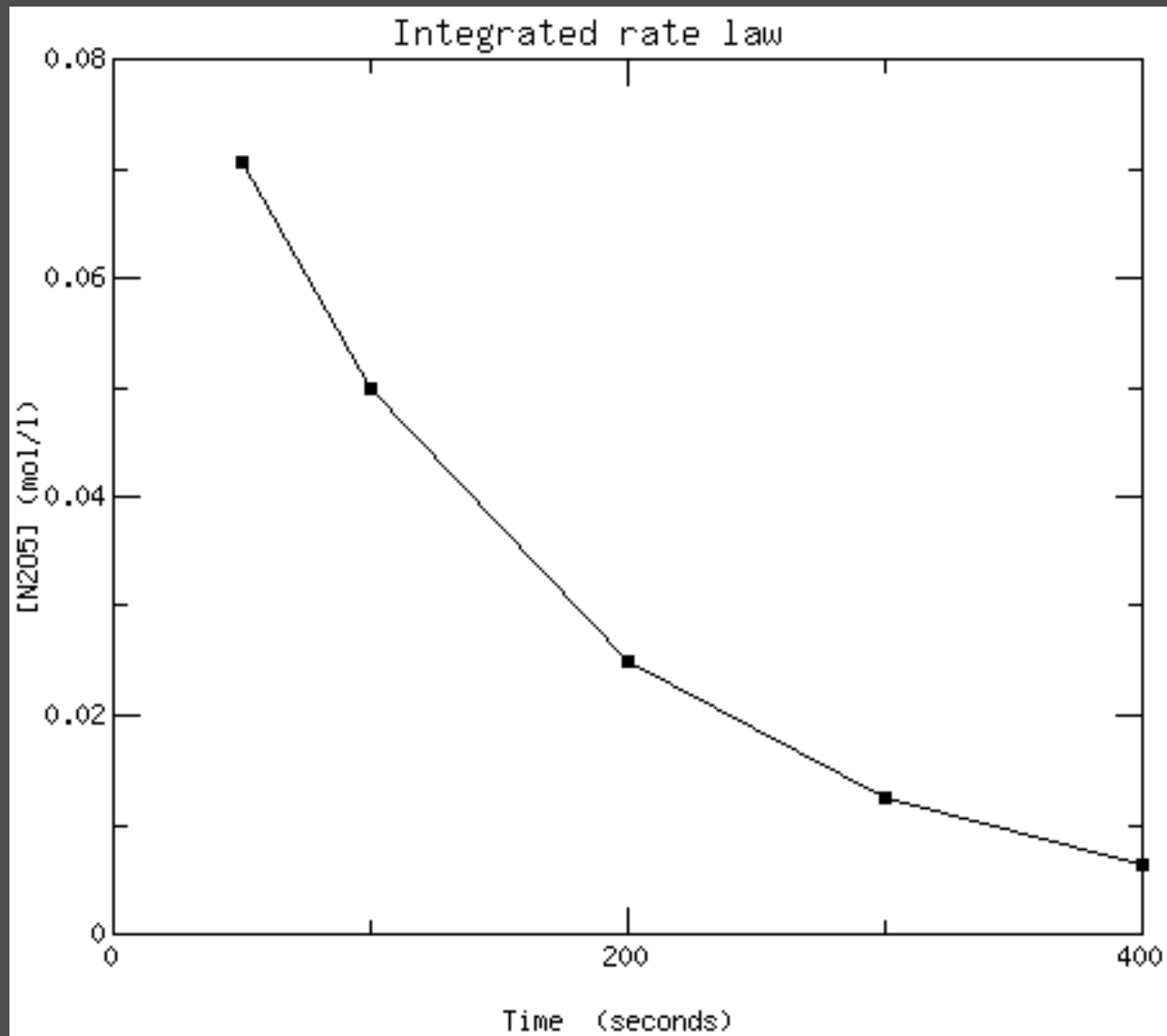- 100   0.0500 M
- 200   0.0250M
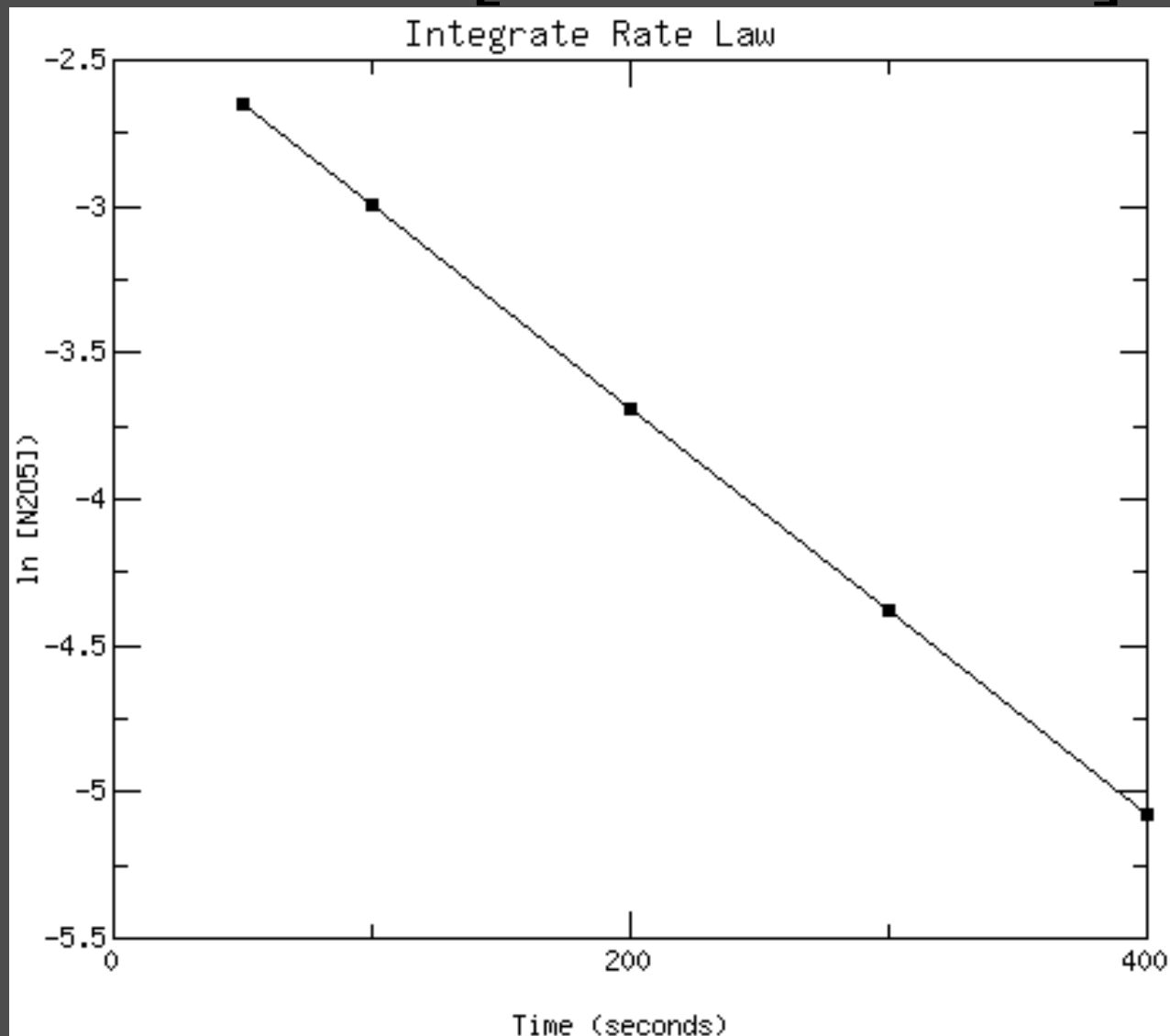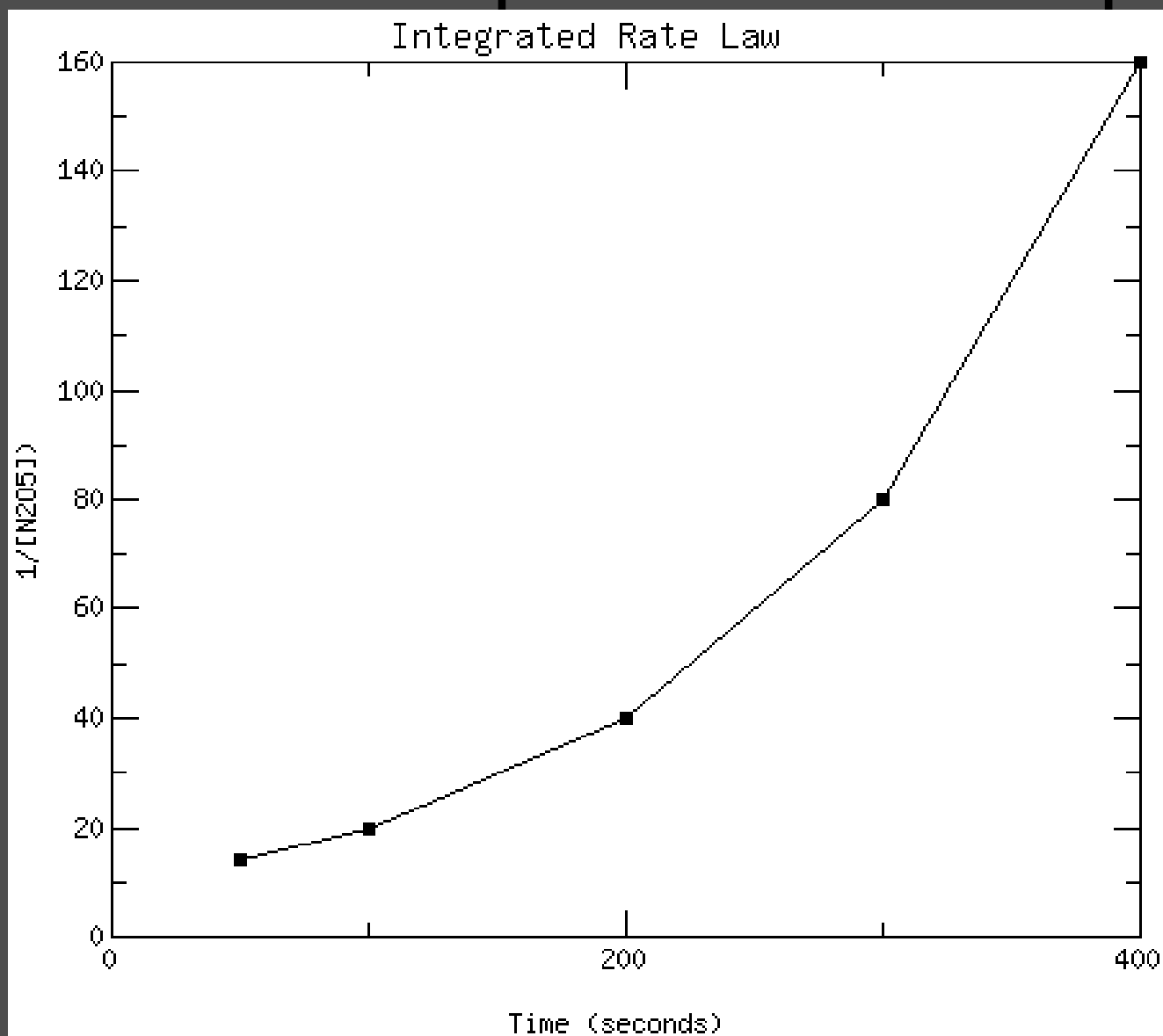- 300   0.0125M
- 400   0.00625M

Time vs Concentration

Time vs ln[concentration]

Time vs 1/[concentration]

Integrated Rate Law

Integrated rate law

- Ln[N2O5] is linear so… this is a 1st order reaction with respect to N2O5 !

- What is the value for k the reaction constant.

- Slope of line = $\underline{\Delta ln[N2O5]}$
Δ t

Integrated Rate Law

- $\dfrac{-2.649 - -2.303}{50 - 0}$
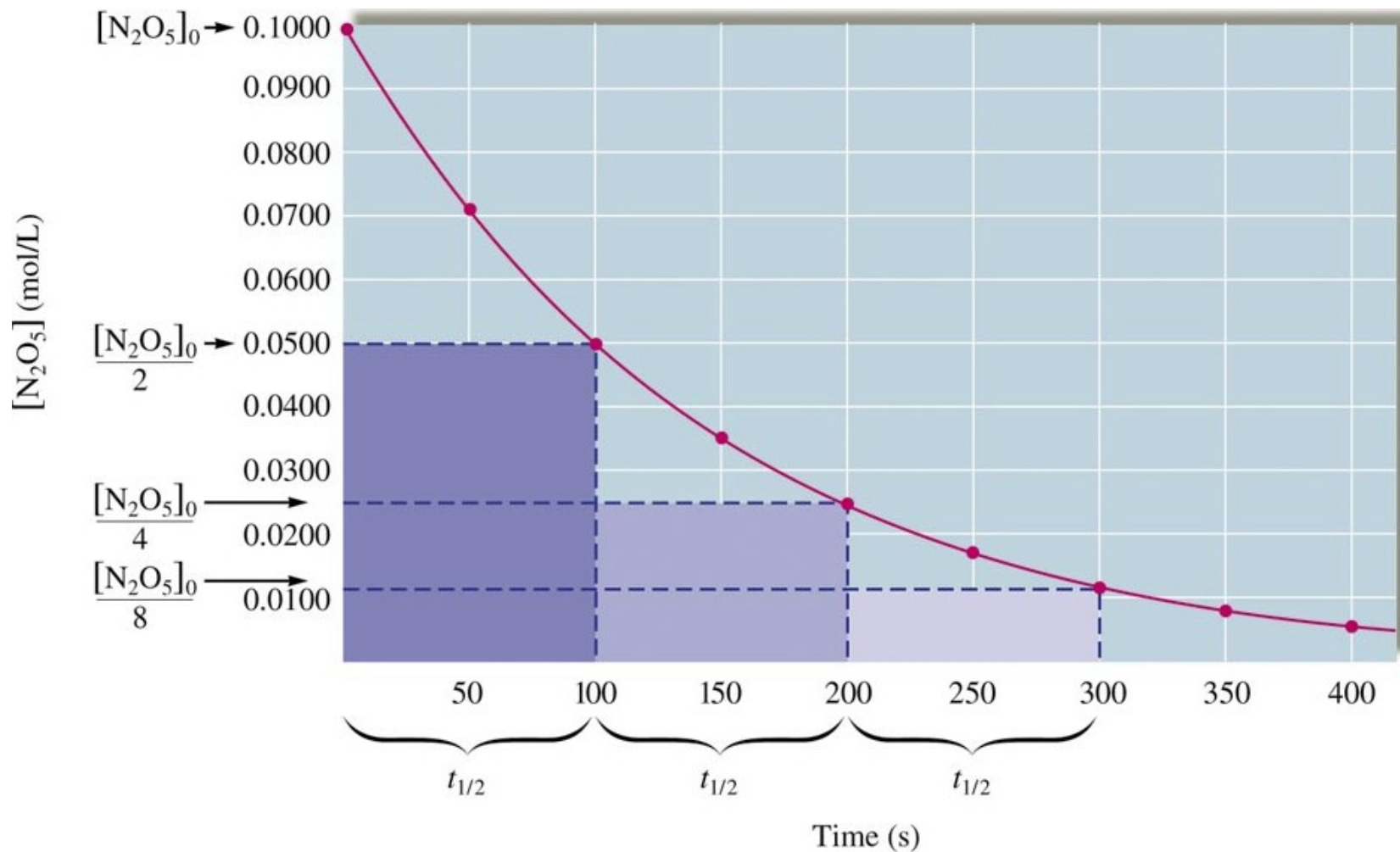
- $\dfrac{-0.346}{50}$

- k= 6.92 x 10^{-3}/s

Half-lives of reaction

- Time required for reactant(s) to be reduced by 1/2 .

- Half-life of a first order reaction
  - The integrated first order rate law can be rewritten as: $\ln\left(\dfrac{[A]_0}{[A]}\right) = kt$

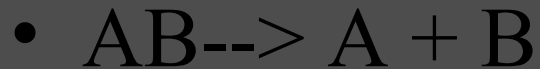 - The half-life of a reaction = time it takes for $[A] = [A]_0/2$

$[N_2O_5]_0 \rightarrow 0.1000$

$\dfrac{[N_2O_5]_0}{2} \rightarrow 0.0500$

$\dfrac{[N_2O_5]_0}{4} \rightarrow 0.0200$

$\dfrac{[N_2O_5]_0}{8} \rightarrow 0.0100$

$[N_2O_5]$ (mol/L)

50   100   150   200   250   300   350   400

$t_{1/2}$ $t_{1/2}$ $t_{1/2}$

Time (s)

Rate Laws Summary

	Zero Order	First Order	Second Order
Rate Law	Rate = k	Rate = k[A]	Rate = k[A]^2
Integrated Rate Law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$
Plot the produces a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\dfrac{1}{[A]}$ versus t
Relationship of rate constant to slope of straight line	Slope = -k	Slope = -k	Slope = k
Half-Life	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

Half-life example

- AB--> A + B
- [AB]0   Initial Rate mol/L·s
- 0.200 3.2×10^{-3}
- 0.400 1.28×10^{-2}
- 0.600 2.88×10^{-2}

Half-life example

- AB--> A + B
- [AB]0   Initial Rate mol/L·s
- 0.200 3.2×10^{-3}
- 0.400 1.28×10^{-2}
- 0.600 2.88×10^{-2}

2 x   4 x

$4 = 2^{n}$ $4 = 2^{2}$

Since this is a 2nd order rxn

- Half life = $t_{1/2}$ = 1/k[AB]$_0$
- Now we have to determine k
- Rate = k[AB]^2
- 3.20 x 10^{-3} =k(0.200)^2
- k= 8.00 x 10-2
- t 1/2 = 1/(8.00 x10-2)(1.00) = 12.5 s

Reaction mechanisms

- Elementary steps that lead to a rxn
- Rate law can be written from the molecularity of the reaction
- Rate determining step. Slowest elementary step
- Steps must sum to balanced equation
- Agree with experimentally determined rate law

Example (51 Hmwk)

- $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ slow
- $C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ fast
- $C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ fast
- Write the rate law
- Identify intermediates
- Balance eqn

Example (51 Hmwk)

- $C_4H_9Br \longrightarrow C_4H_9^+ + Br^-$ slow
- $C_4H_9^+ + H_2O \longrightarrow C_4H_9OH_2^+$ fast
- $C_4H_9OH_2^+ + H_2O \longrightarrow C_4H_9OH + H_3O^+$ fast
- Write the rate law
- This is the rate determining step it is unimolecular so Rate = $k[C_4H_9Br]$
- 1st order

Example (51 Hmwk)

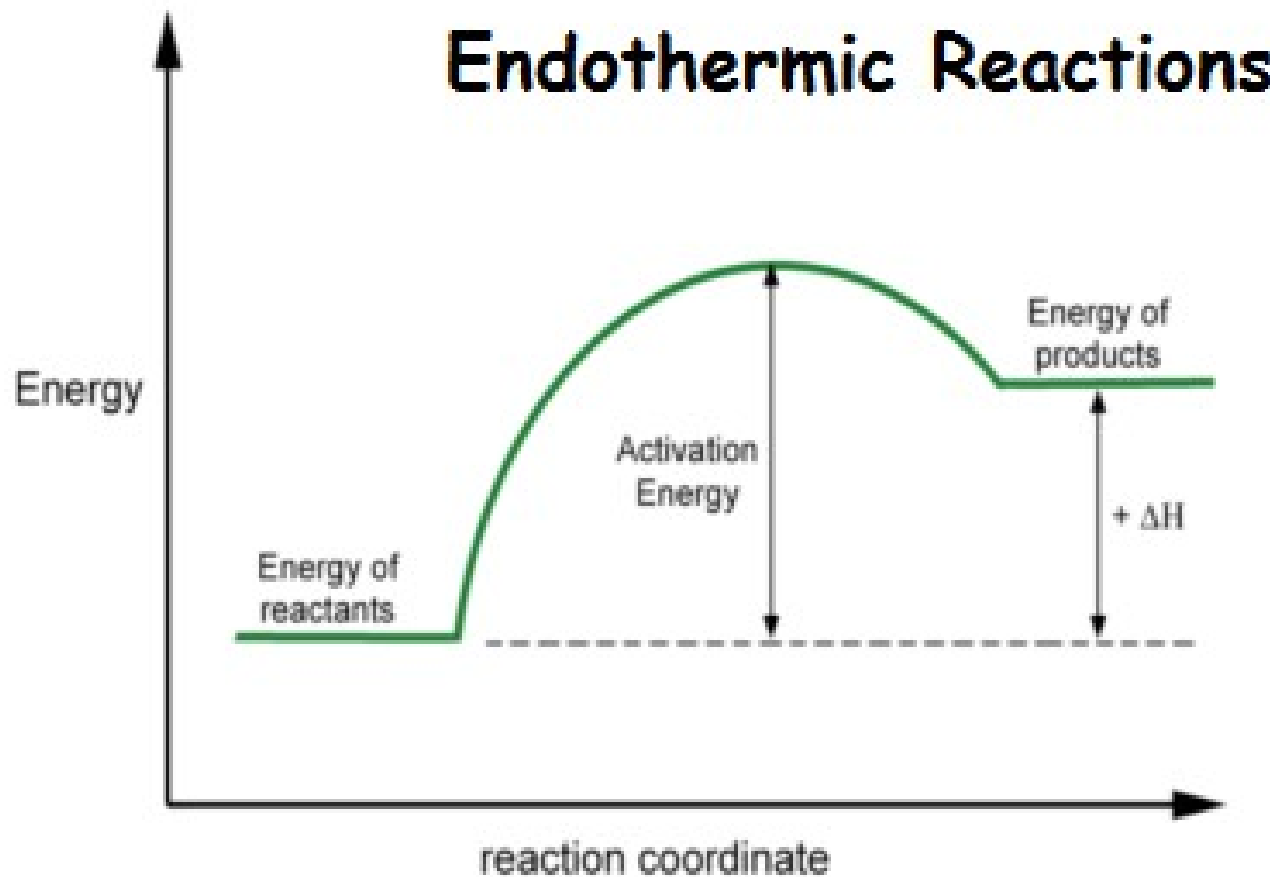- $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ slow

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- $C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ fast

- Identify intermediates

- $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$ slow

- $C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ fast
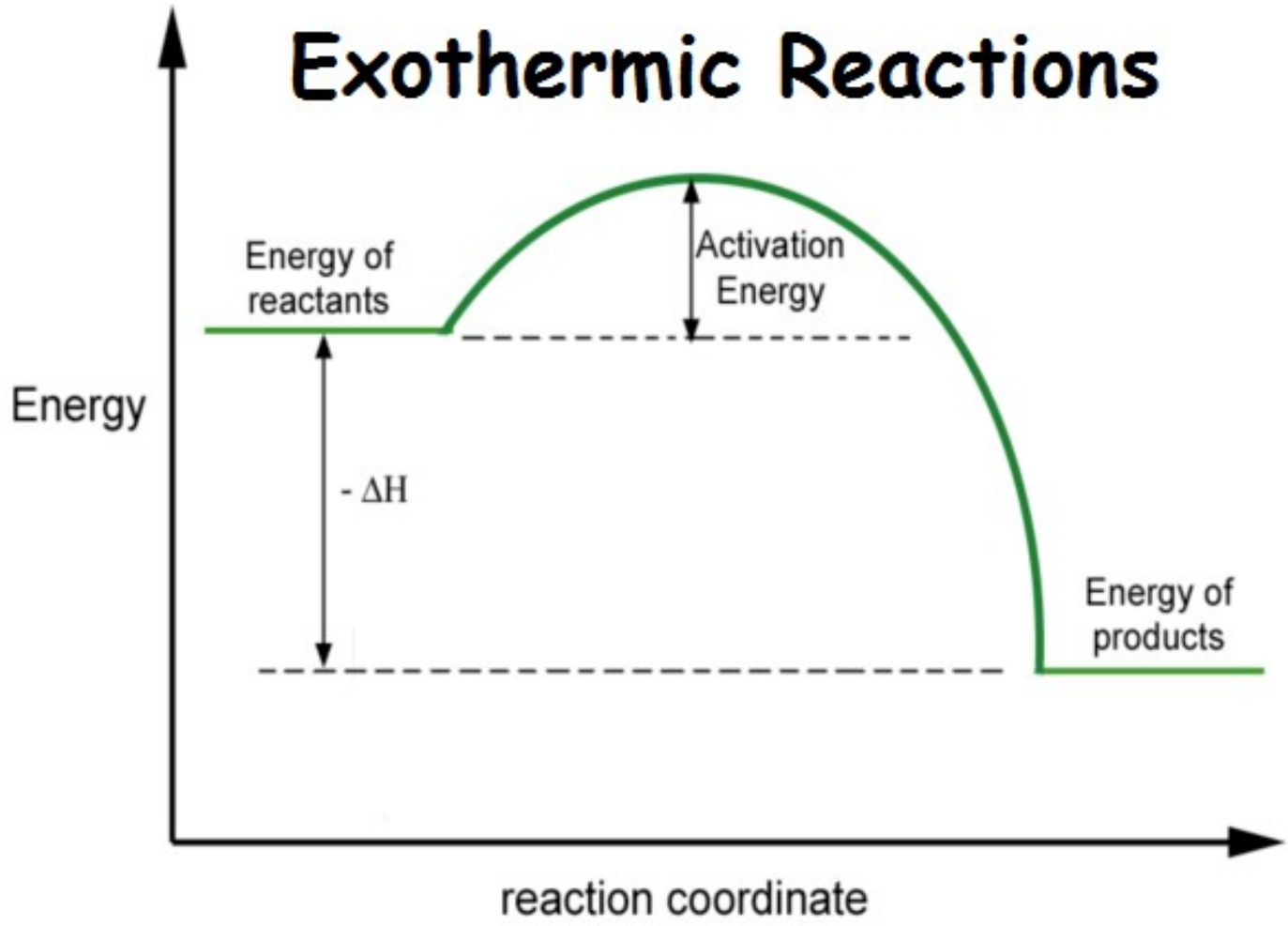
- $C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ fast

Example (51 Hmwk)

- Balance eqn
- $C_4H_9Br \rightarrow C_4H_9^+ + Br^-$
- $C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$
- $\underline{C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+}$
- $C_4H_9Br + 2H_2O \rightarrow Br^- + C_4H_9OH_2 + H_3O^+$

Energy Curves

Endothermic Reactions

Energy Curves

The Arrhenius Equation

$$k = Ae^{-E_a/RT}$$

- k = rate constant at temperature T
- A = frequency factor
- E_a = activation energy
- R = Gas constant, 8.31451 J/K·mol

The Arrhenius Equation, Rearranged

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

➢ Simplifies solving for E_a

➢ $-E_a/R$ is the slope when $(1/T)$ is plotted against $\ln(k)$

➢ $\ln(A)$ is the y-intercept

➢ Linear regression analysis of a table of $(1/T)$ vs. $\ln(k)$ can quickly yield a slope

➢ $E_a = -R(slope)$

Example: $2N_2O_5 \rightarrow 4NO_2 + O_2$
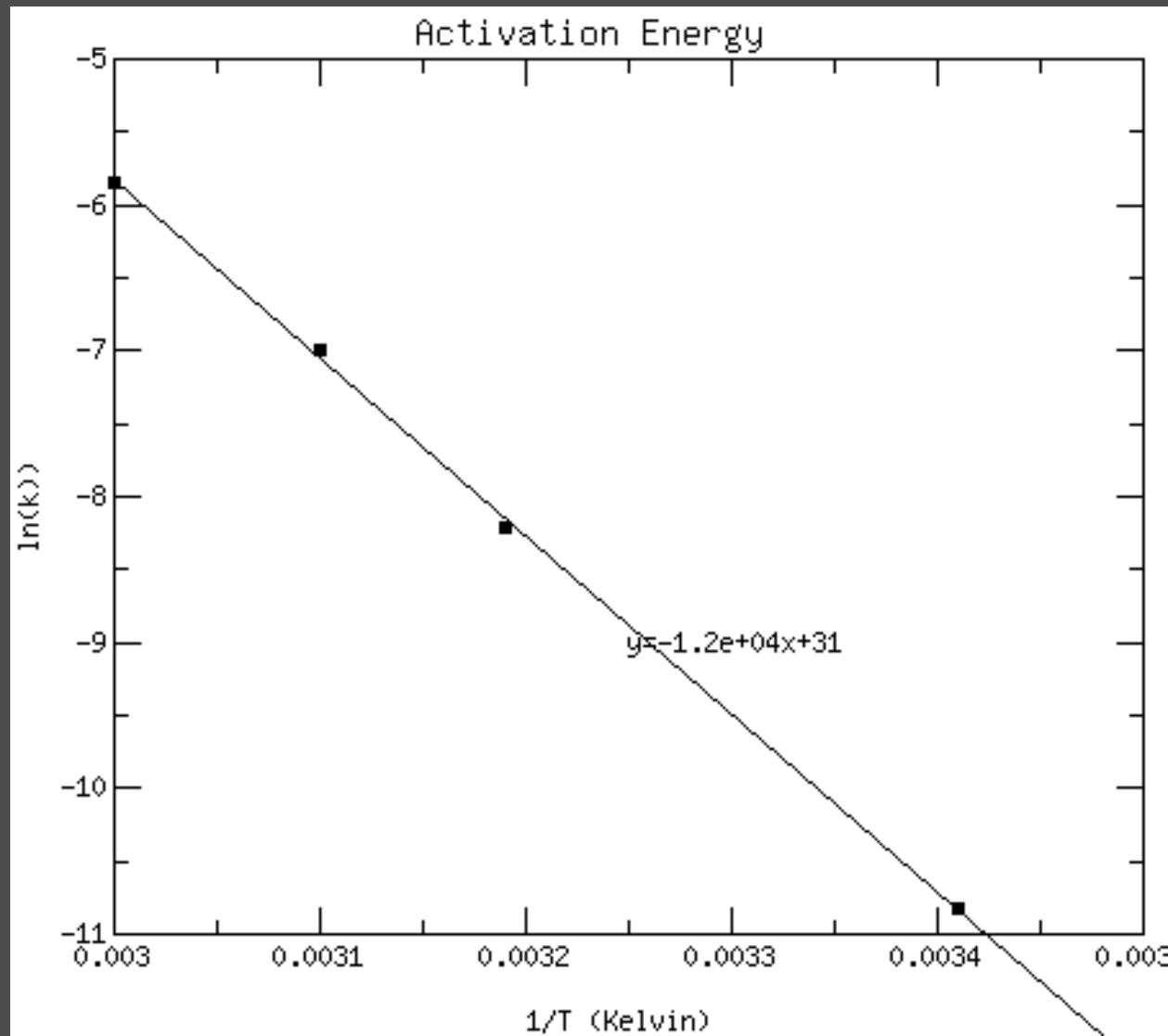
- K(1/s)   T(C)   1/T (K)   ln (k)
- 2.0×10^{-5} 20
- 7.3×10^{-5} 30
- 2.7×10^{-4} 40
- 9.1×10^{-4} 50
- 2.9×10^{-3} 60

Plot ln(k) vs 1/T get slope

- 1/T (K)   ln (k)
- 3.41×10^{-3} -10.82
- 3.30×10^{-3} -9.53
- 3.19×10^{-3} -8.22
- 3.10×10^{-3} -7.00
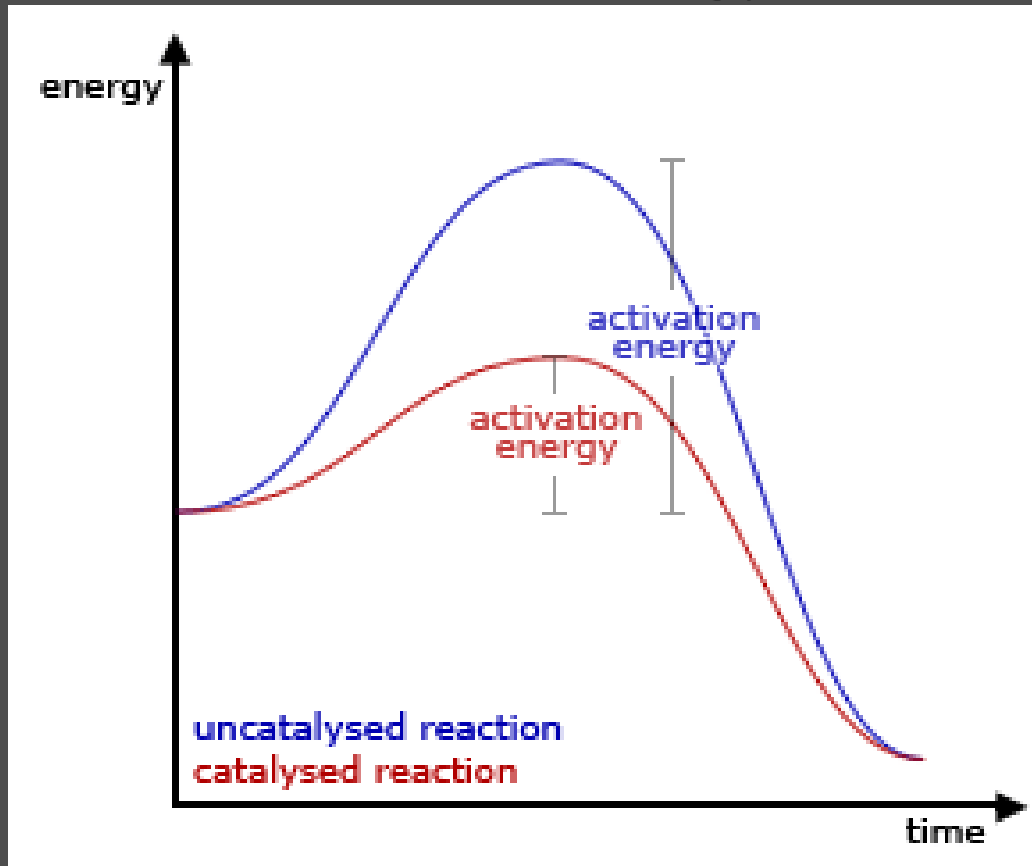- 3.00×10^{-3} -5.84

Slope = -E$_a$/R

Slope = Regression line (if linear)

- $-1.2 \times 10^4 = -E_a/8.3145$

- Ea = 1.0×10^5 J/mol

Effects of catalysts

- Lower Activation energy

Effects of catalysts

- Increase effectiveness of collisions