

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

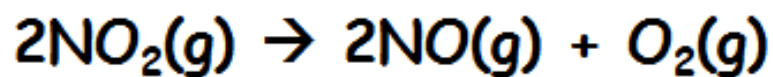
- Change in concentration over time

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

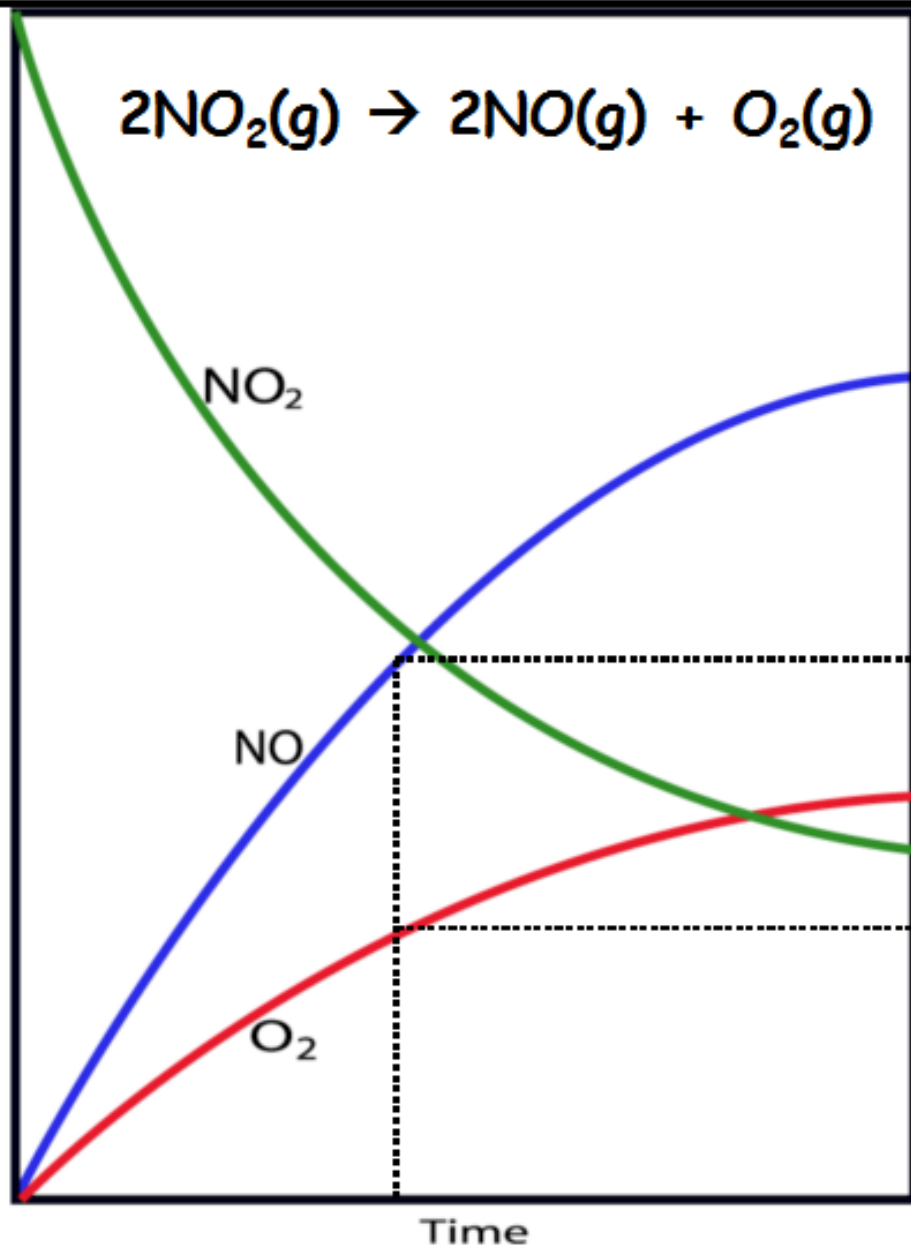
$$t_2 - t_1$$

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

$$\Delta t$$



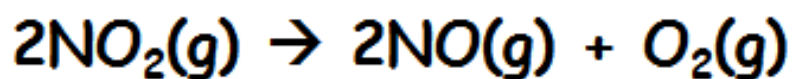
Concentration



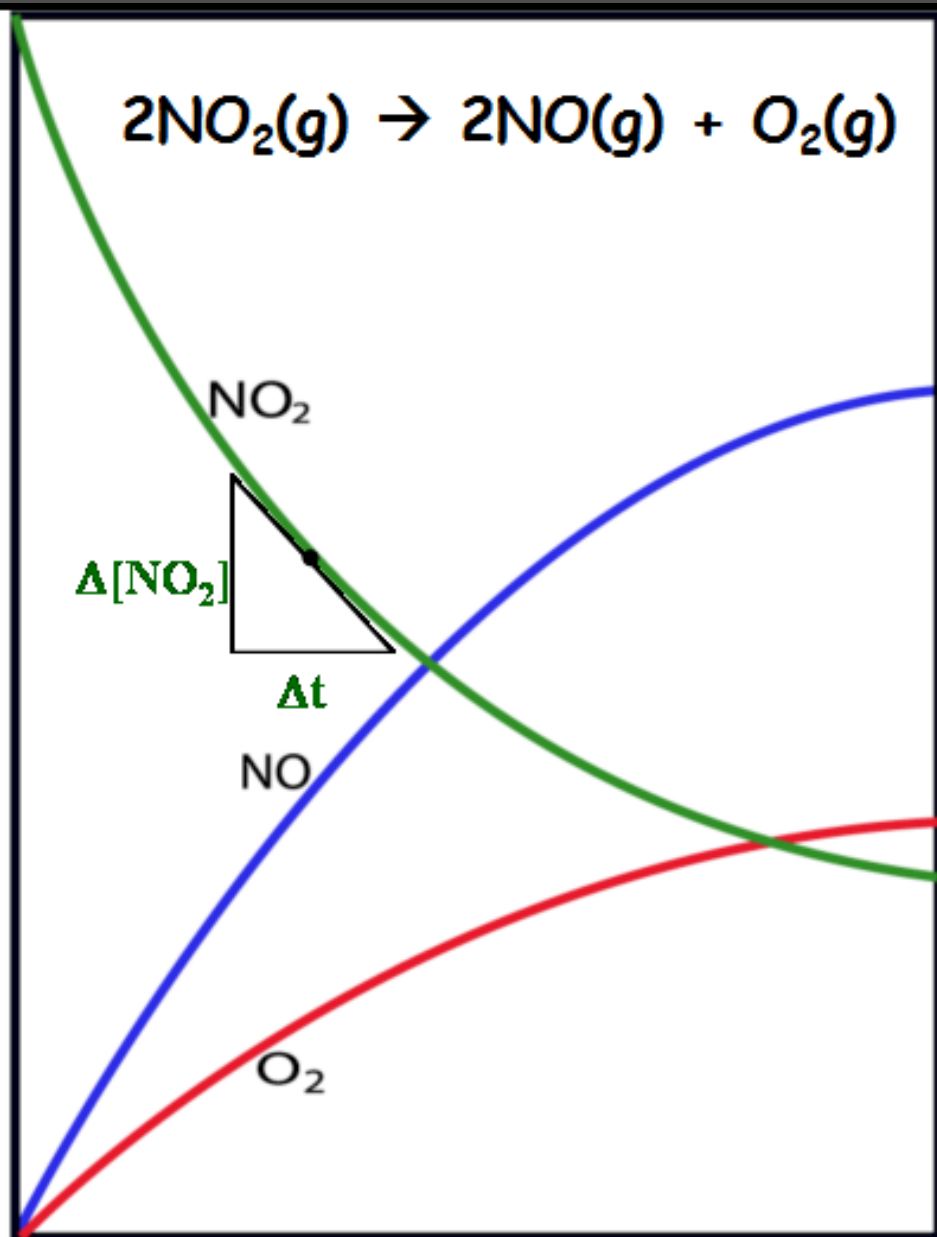
Time

Reaction Rates:

1. Can measure disappearance of reactants
2. Can measure appearance of products
3. Are proportional stoichiometrically



Concentration



Time

Reaction Rates:

- Are equal to the slope tangent to that point
- Change as the reaction proceeds, if the rate is dependent upon concentration

$$\frac{\Delta[\text{NO}_2]}{\Delta t} \neq \text{constant}$$

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

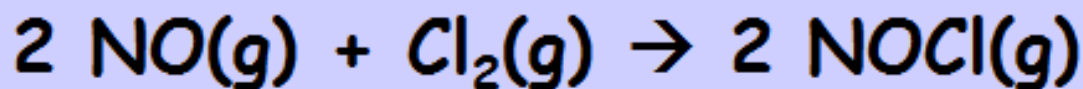
- Zero order
 - Rate = $k [A]^0$
- 1st order
 - Rate = $k [A]^1$
- 2nd order
 - Rate = $k[A]^2$

Rate Laws

- More than 1 reactant
- $\text{Rate} = k[\text{A}]^m[\text{B}]^n$
- 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:



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: $R = k[\text{NO}]^x[\text{Cl}_2]^y$

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 1 and 2, [Cl₂] is constant while [NO] doubles. The rate quadruples, so the reaction is second order with respect to [NO] $\therefore R = k[\text{NO}]^2[\text{Cl}_2]^y$

Initial concentrations

- Find a pair of experiments in which the initial concentrations are double.
- 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: $R = k[\text{NO}]^2[\text{Cl}_2]^y$

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 [Cl₂] doubles. The rate doubles, so the reaction is first order with respect to [Cl₂]. $\therefore R = k[\text{NO}]^2[\text{Cl}_2]$

Initial conditions method

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



Experiment	[NO] (mol/L)	[Cl ₂] (mol/L)	Rate Mol/L · s
1	0.250	0.250	1.43×10^{-6}

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

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

Writing a rate law

- After the exponents of the rate law are known
- Solve for k
- $\text{Rate} = k [\text{NO}]^2 [\text{Cl}]$
- 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.




$$2 + 1 = 3$$

∴ 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 = $k[A]^2$



$[\text{NH}_4^+]$	$[\text{NO}_2^-]$	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}

$$\text{Rate} = k[\text{NH}_4^+]^n [\text{NO}_2^-]^m$$

Example

- Experiment 2 to 3
- $[\text{NH}_4^+] = 2x$ and Rate = 2 or 2^m
- Experiment 1 to 2
- $[\text{NO}_2^-] = 2$ and Rate = 2 or 2^n

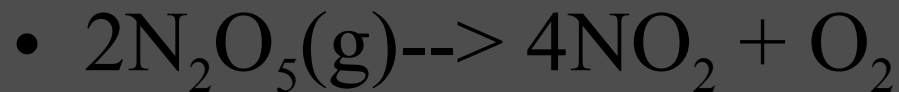
Example

- Rate Law
- $\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$
- $1.35 \times 10^7 = k(0.100)(0.0050)$
- $k = 2.7 \times 10^{-4} \text{ L/mol}\cdot\text{s}$

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 $1/\text{concentration}$** linear

Integrated Rate Law



- T (s) [N₂O₅]

- 0 0.100 M

- 50 0.0707 M

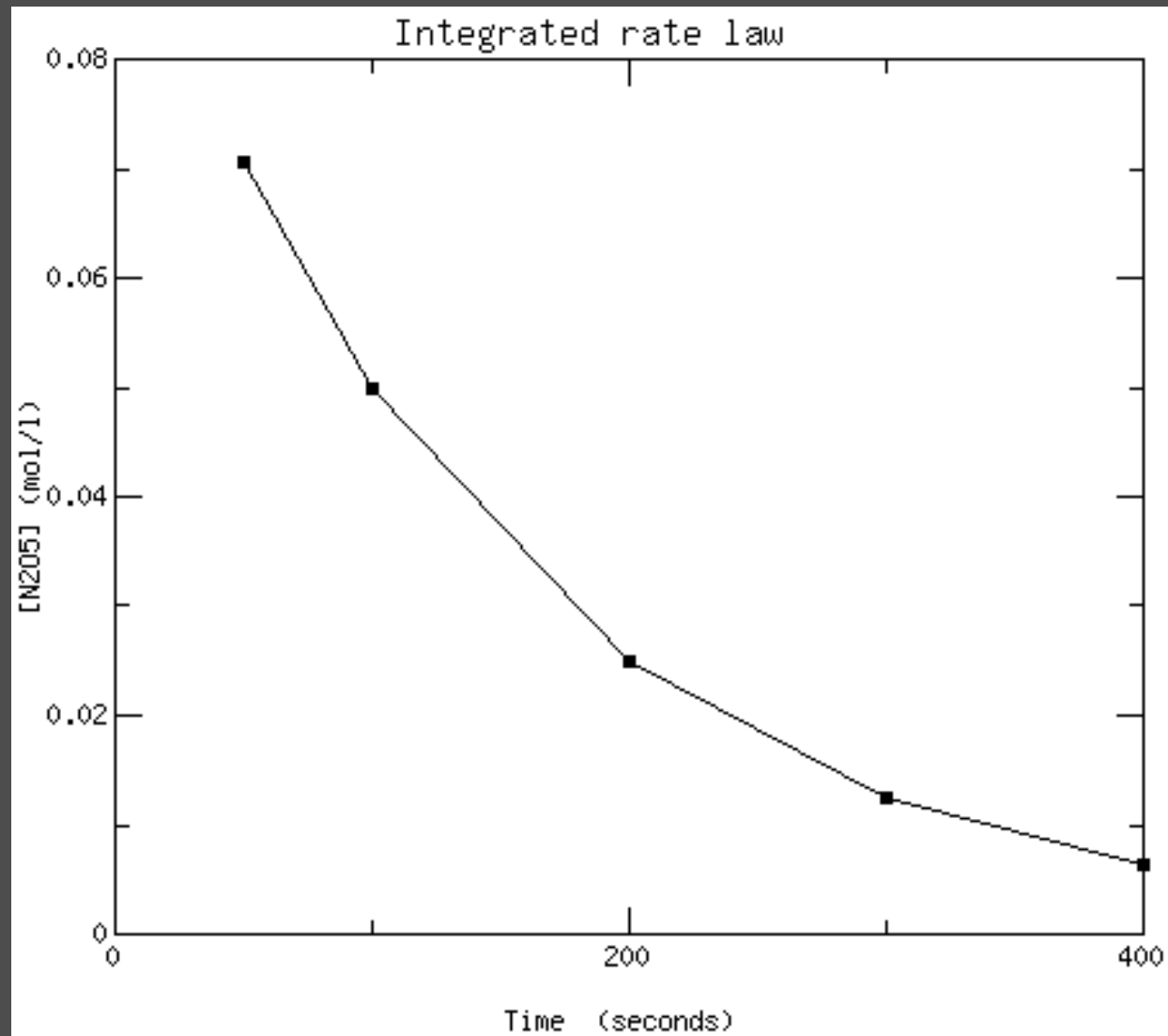
- 100 0.0500 M

- 200 0.0250M

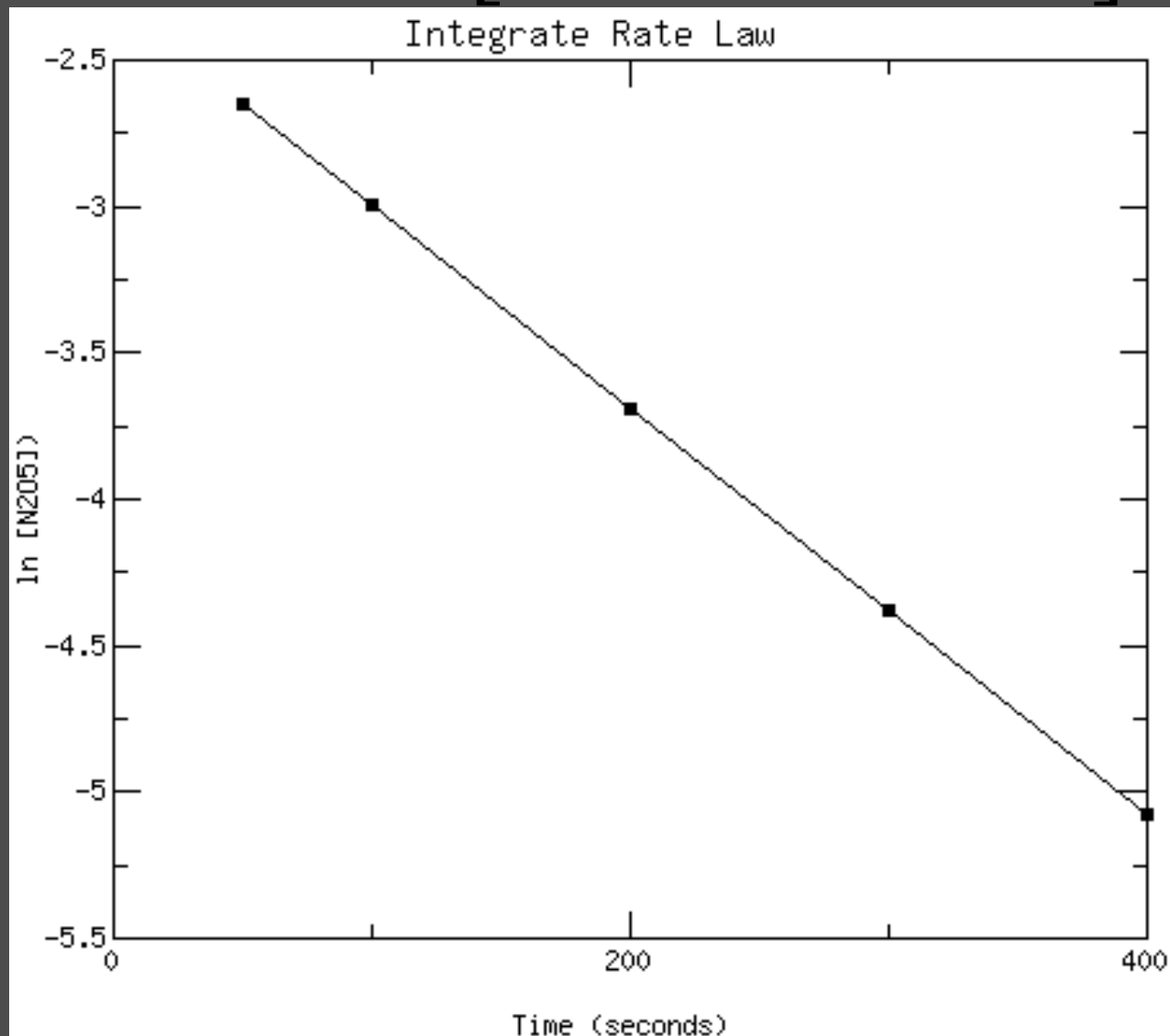
- 300 0.0125M

- 400 0.00625M

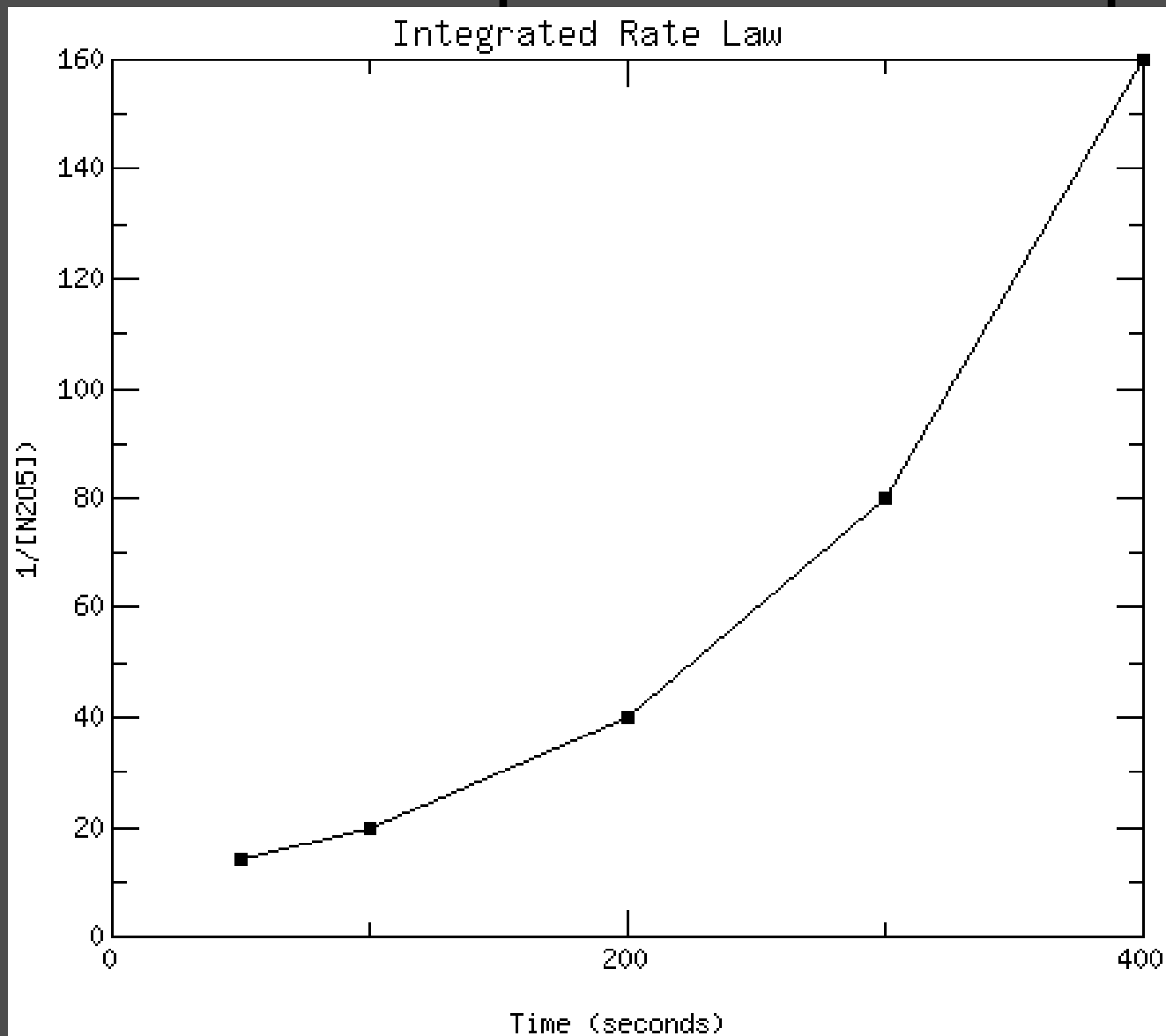
Time vs Concentration



Time vs $\ln[\text{concentration}]$



Time vs $1/[\text{concentration}]$



Integrated rate law

- $\ln[\text{N}_2\text{O}_5]$ is linear so... this is a 1st order reaction with respect to N_2O_5 !
- What is the value for k the reaction constant.
- Slope of line = $\frac{\Delta \ln[\text{N}_2\text{O}_5]}{\Delta t}$

Integrated Rate Law

- $\frac{-2.649 - -2.303}{50 - 0}$
- $\frac{-0.346}{50}$
- $k = 6.92 \times 10^{-3}/s$

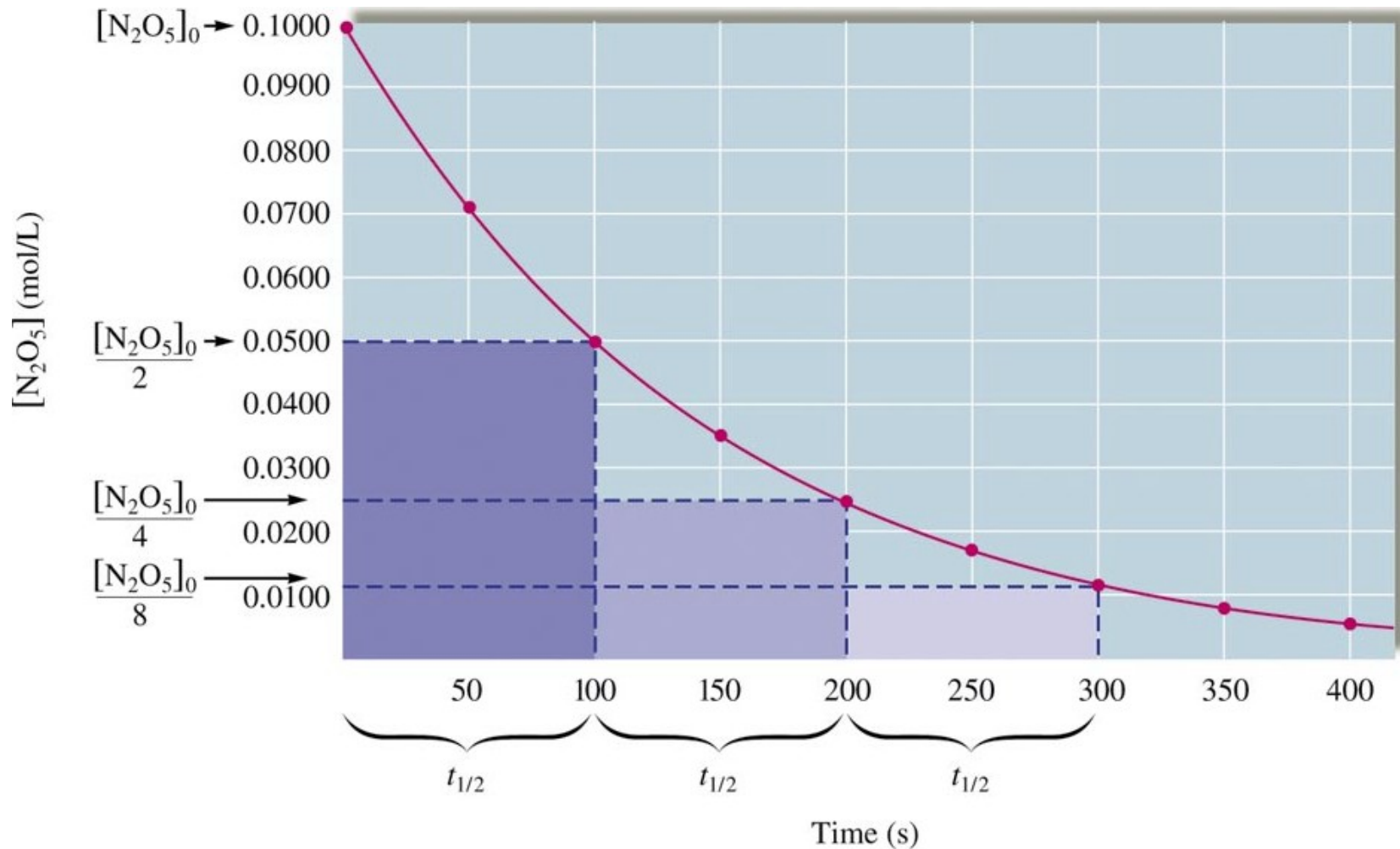
Half-lives of reaction

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

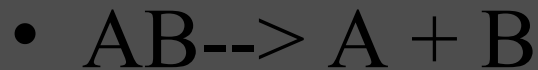
- The half-life of a reaction = time it takes for $[A] = [A]_0/2$



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	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot the produces a straight line	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to slope of straight line	Slope = -k	Slope = -k	Slope = k
Half-Life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Half-life example



- $[AB]_0$ Initial Rate mol/L·s

- 0.200 } $2 \times$ 3.2×10^{-3} } $4 \times$

- 0.400 } 1.28×10^{-2} }

- 0.600 2.88×10^{-2}

$$4 = 2^n$$

$$4 = 2^2$$

Since this is a 2nd order rxn

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

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)

- $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$ slow
- $\text{C}_4\text{H}_9^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH}_2^+$ fast
- $\text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+$ fast
- Write the rate law
- Identify intermediates
- Balance eqn

Example (51 Hmwk)

- $\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$ slow
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- $\text{C}_4\text{H}_9\text{OH}_2^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+$ fast
- Write the rate law
- This is the rate determining step it is unimolecular so $\text{Rate} = k[\text{C}_4\text{H}_9\text{Br}]$
- 1st order

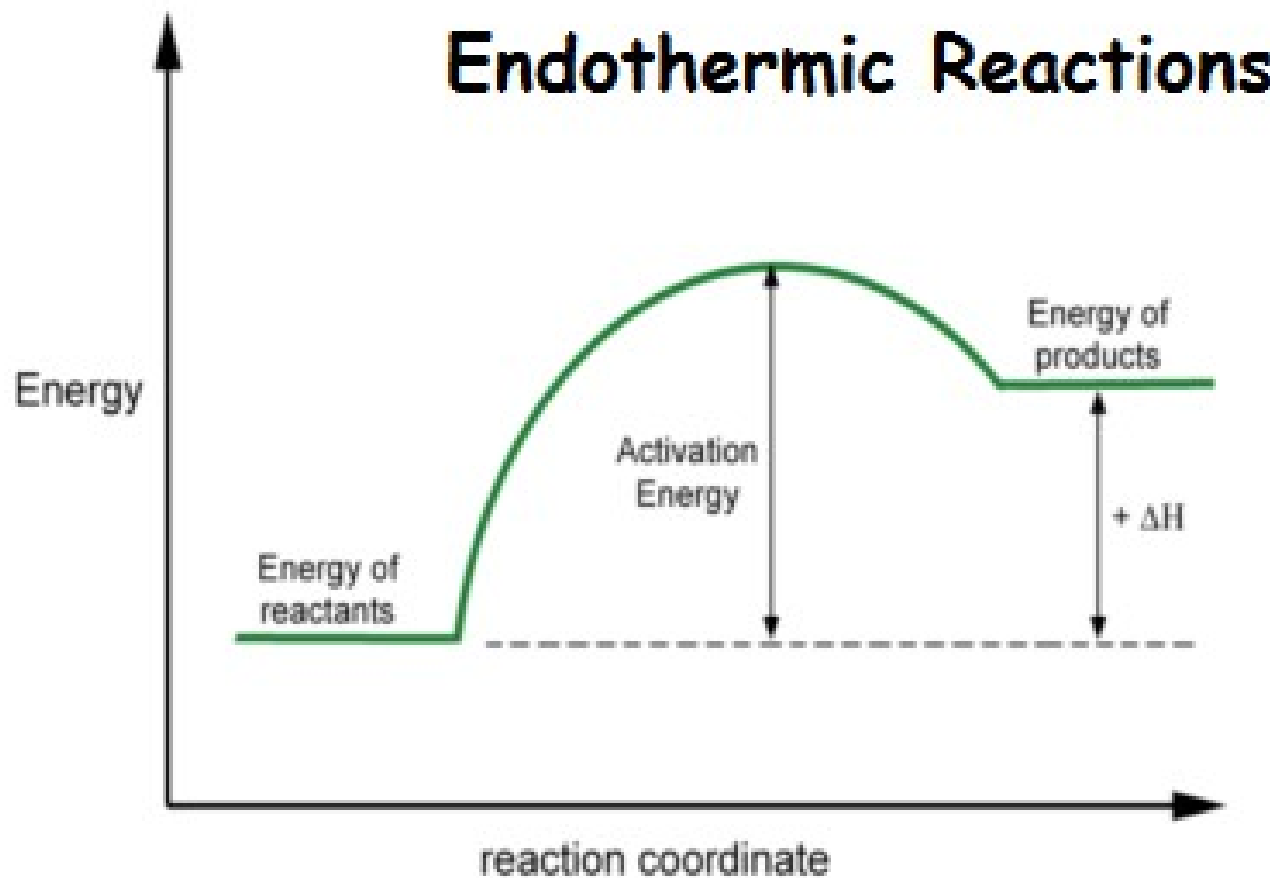
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- Identify intermediates
- ~~$\text{C}_4\text{H}_9\text{Br} \rightarrow \text{C}_4\text{H}_9^+ + \text{Br}^-$ slow~~
- ~~$\text{C}_4\text{H}_9^+ + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH}_2^+$ fast~~
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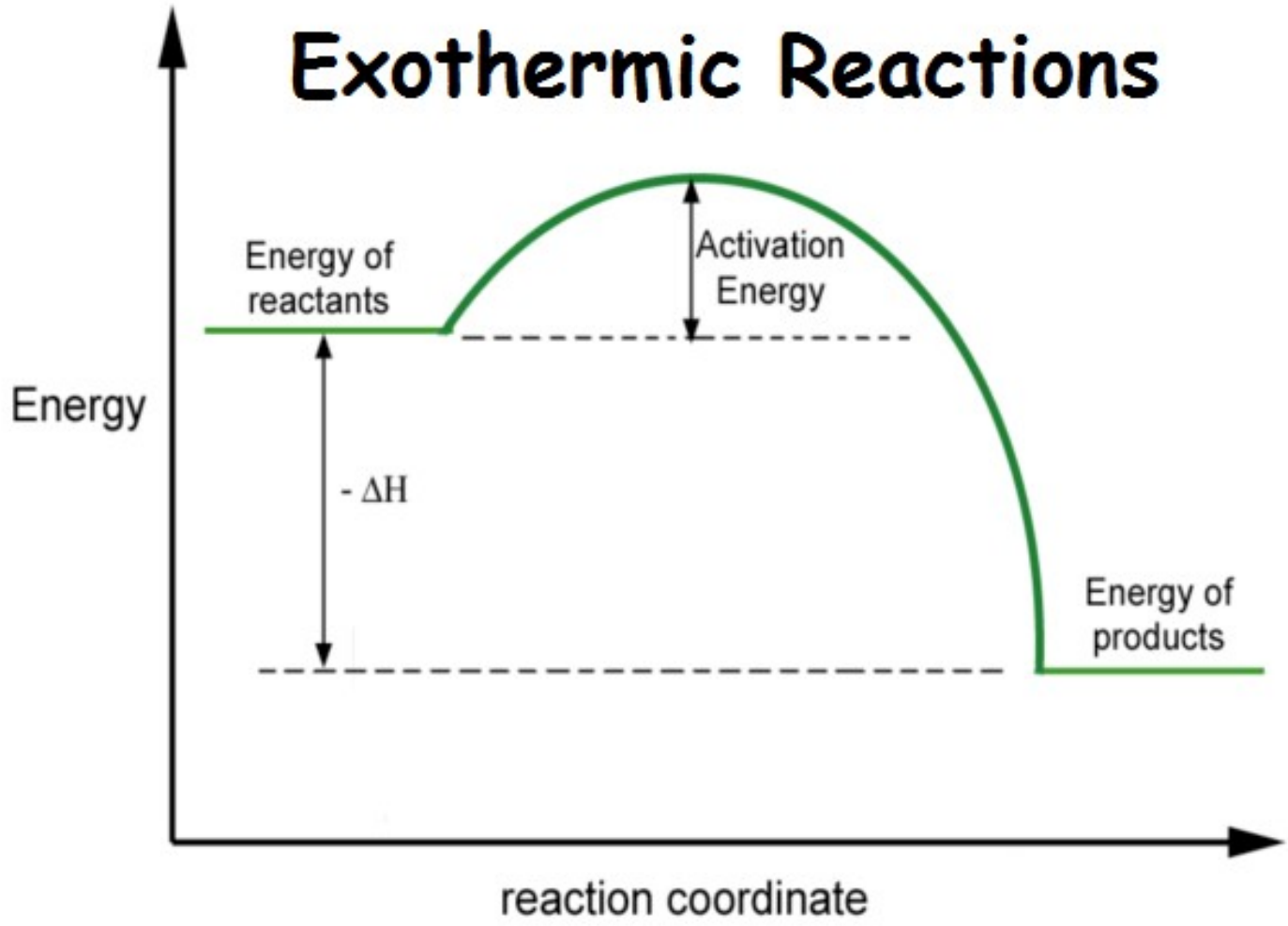
Example (51 Hmwk)

- Balance eqn
- $\text{C}_4\text{H}_9\text{Br} \rightarrow \cancel{\text{C}_4\text{H}_9^+} + \text{Br}^-$
- $\cancel{\text{C}_4\text{H}_9^+} + \text{H}_2\text{O} \rightarrow \cancel{\text{C}_4\text{H}_9\text{OH}_2^+}$
- $\underline{\cancel{\text{C}_4\text{H}_9\text{OH}_2^+} + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_9\text{OH} + \text{H}_3\text{O}^+}$
- $\text{C}_4\text{H}_9\text{Br} + 2\text{H}_2\text{O} \rightarrow \text{Br}^- + \text{C}_4\text{H}_9\text{OH}_2 + \text{H}_3\text{O}^+$

Energy Curves



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
- $E_a = -R(\text{slope})$

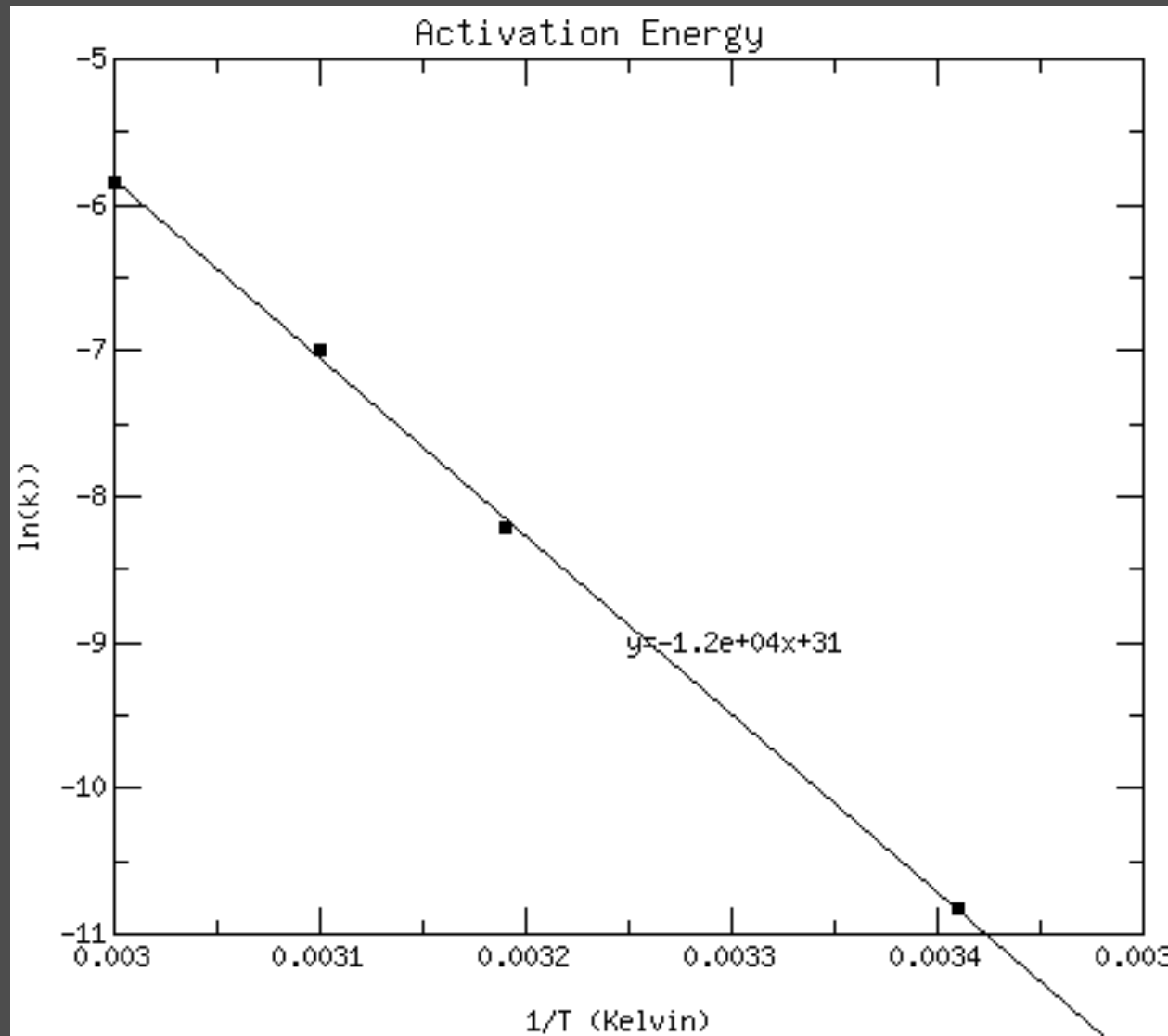


• $k(1/s)$	$T(^{\circ}\text{C})$	$1/T (\text{K})$	$\ln(k)$
• 2.0×10^{-5}	20		
• 7.3×10^{-5}	30		
• 2.7×10^{-4}	40		
• 9.1×10^{-4}	50		
• 2.9×10^{-3}	60		

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

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



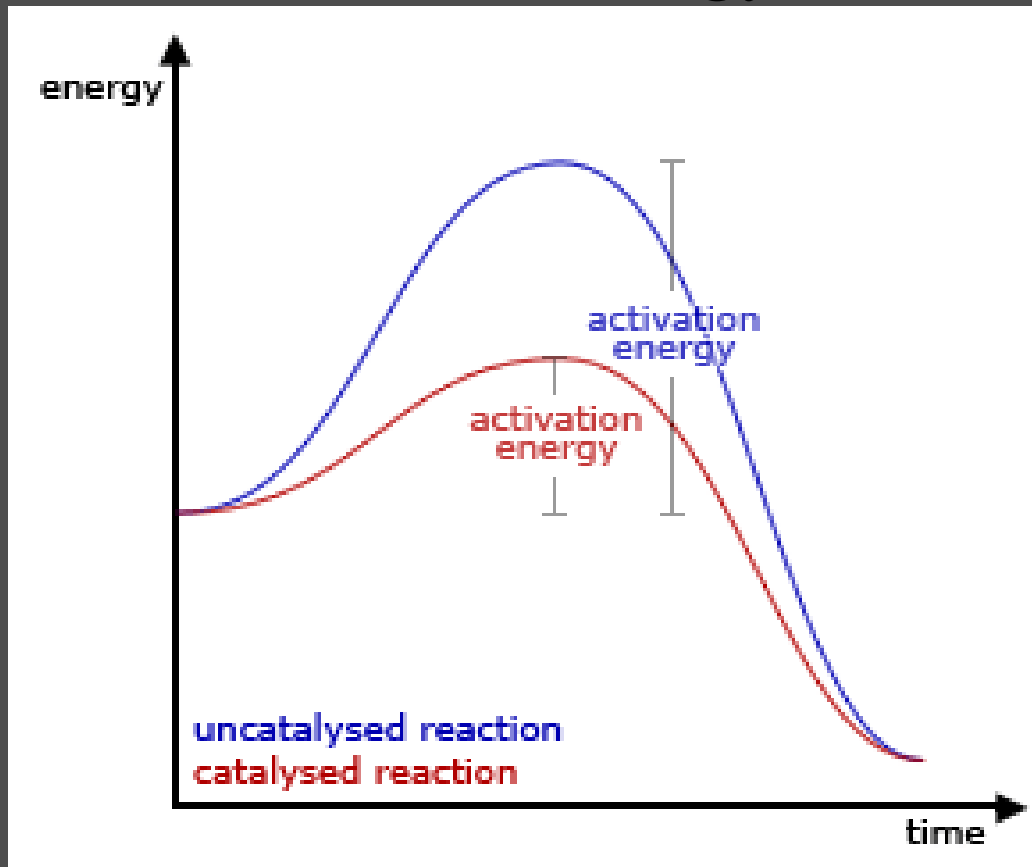
Slope = Regression line (if linear)

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

- $E_a = 1.0 \times 10^5 \text{ J/mol}$

Effects of catalysts

- Lower Activation energy



Effects of catalysts

- Increase effectiveness of collisions

