

CHEM 102

General Chemistry II

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SPRING 08/09
TERM 082

We ak	Lec.		Date	Chapt er	Sec.	Lab.	Homework
1	01	Sat	Feb. 28	12	1,2	No Lab	
	02	Mo n	March 02	12	3,4		
	03	We d	04	12	5,6,7		
	04	Thu	05	12	7,8		
2	05	Sat	07	13	1,2	<u>Introuction to Lab:</u> Check in, Safety rules etc. Network system introduction	.Chapter 12: 18,24,30,40,48,56,61,64. Mar. 10, Dropping course(s) without permanent record
	06	Mo n	09	13	3,4		
	07	We d	11	13	5,6		
3	09	Sat	14	13	7	<u>Lab # 1</u> Exp # 22: Factors Affecting Reaction Rates (p. 257).	Chapter 13: 22,30,38,42,46,52,62,66
	08	Mo n	16	14	1,2		
	10	We d	18	14	3,4,5		

4	11	Sat	21	14	6,7,8	<u>Lab # 2 *</u> Exp # 23: Determination of a Rate Law (p.267).	Chapter 14: 30,36,48,54,58,66,82,94,100, 104,110,122,124.
	12	Mon	23	14	8,9		
5	14	Sat	28	15	1,2	<u>Lab # 3 *</u> Exp # 25: An Equilibrium Constant (p. 293)	Chapter 15: 24,28,46,58,60,78,82,88,108.
	15	Mon	30	15	3,4		
	16	Wed	April 01	15	5,6		

6	17	Sat	04	15	7,8	Lab # 4 Exp # 29: Acids, Bases and Salts; pH (p. 169)	Maj. I-Old Exams April 12, Dropping with "W" any course
	18	Mon	06	12-15	Review		
	19	Wed	08	16	1,2,3		
	Maj 1 (Ch 12 -15) Wed. April 08, 7:00 p.m.						
7	20	Sat	11	16	4,5	Lab # 5 Exp # 29: Molar Solubility: Common-Ion Effect (p. 331)	Chapter 16: 26,40,46,50,56,66,70.
	21	Mon	13	16	6,7		
	22	Wed	15	16	8,9		
8	23	Sat	18	17	1,2	Lab # 6 Exp # 15: Bleach Analysis (p. 191)	Chapter 17: 16,30,40,48,58,64,84,86,88.
	24	Mon	20	17	3		
	25	Wed	22	17	4,5		

Midterm Vacation April 25-29

9	26	Sat	May 02	17	5,6	Lab # 7 Exp #32: Galvanic Cells (p.357)	Chapter 18: 10,12,22,36,38,42. May 10, withdrawal from all courses with grade of "W"
	27	Mon	04	17	7,8		
	28	Wed	06	18	1,2		
10	29	Sat	09	18	3,4	Lab # 8 Exp # 26: Antacid Analysis (p. 305).	Chapter 19: 2,14,18,30,32,42,46.
	30	Mon	11	18	5,6		
	31	Wed	13	18	6,7		
11	32	Sat	16	16-18	Review	Lab # 9 * Exp # 16: Vitamin C Analysis (p. 201).	Maj. II-Old Exams
	Maj 2 (Ch 16-18) Sat. May 16, 7:00 p.m.						
	33	Mon	18	19	1 to 6		
	34	Wed	20	19-20	1 to 6		

12	35	Sat	23	20	1 to 6	Lab # 10 * Exp # 28: Aspirin Synthesis & Analysis (p. 323).	Chapter 20: 8,12,14,34,38,42.
	36	Mon	25	21	1,2		
	37	Wed	27	21	3		
13	38	Sat	30	21	4,5	Lab # 11 Exp # 38: Transition Metal Chemistry (p. 423).	Chapter 21: 14,16,26,32,36,40,50,54. June 6, withdrawal with grade of "WP/WF"
	39	Mon	June 01	21	5,6		
	40	Wed	03	22	1		
14	41	Sat	06	22	2	Lab Test	Chapter 22: 25,32,42,52,62,25,32,42,52,62,72.
	42	Mon	08	22	3		
	43	Wed	10	22	4		
15	44	Sat	13	22	5	No Lab	Final-Old Exams
	45	Mon	15	12-22	Review		

CHEPTER 12

Chemical Kinetics

Chemistry of reaction rates

Main Topics

- Introduction
- Reaction rates
- Rate Laws
- Determining the form of the rate law
- The integrated rate law
- Reaction mechanisms
- A model for chemical kinetics
- Catalysis

Kinetics

Introduction

- **KINETICS** — the study of **REACTION RATES** and their relation to the way the reaction proceeds, i.e., its **MECHANISM**.
- **Spontaneous** reactions are reactions that will happen - but we can't tell how fast.
- Diamond will spontaneously turn to graphite – eventually but very slow
- Reaction **mechanism**- the steps by which a reaction takes place.

12.1 Reaction Rates

- **Change in concentration (Δconc) of a reactant or product per unit time**

$$\text{Rate} = \frac{\text{conc of A at time } t_2 - \text{conc of A at time } t_1}{t_2 - t_1}$$
$$= \frac{\Delta[A]}{\Delta t}$$

- The rate could be **positive or negative** whether the material being produced or consumed
- The rate is **usually expressed as positive** thus we use the negative sign for materials to be consumed $-\Delta[A]/\Delta t$

Reaction rate and stoichiometry of chemical reaction



- $\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{3\Delta[\text{N}_2]}{\Delta t}$
- $\frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{-2\Delta[\text{N}_2]}{\Delta t}$
- $\frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{-2\Delta[\text{H}_2]}{3\Delta t}$
- $\text{Rate} = -\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{NH}_3]}{2\Delta t}$
-

- For this reaction



$$\text{Rate} = -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = \frac{\Delta[\text{NO}_2]}{2\Delta t} = \frac{\Delta[\text{O}_2]}{\frac{1}{2}\Delta t}$$

For the reaction

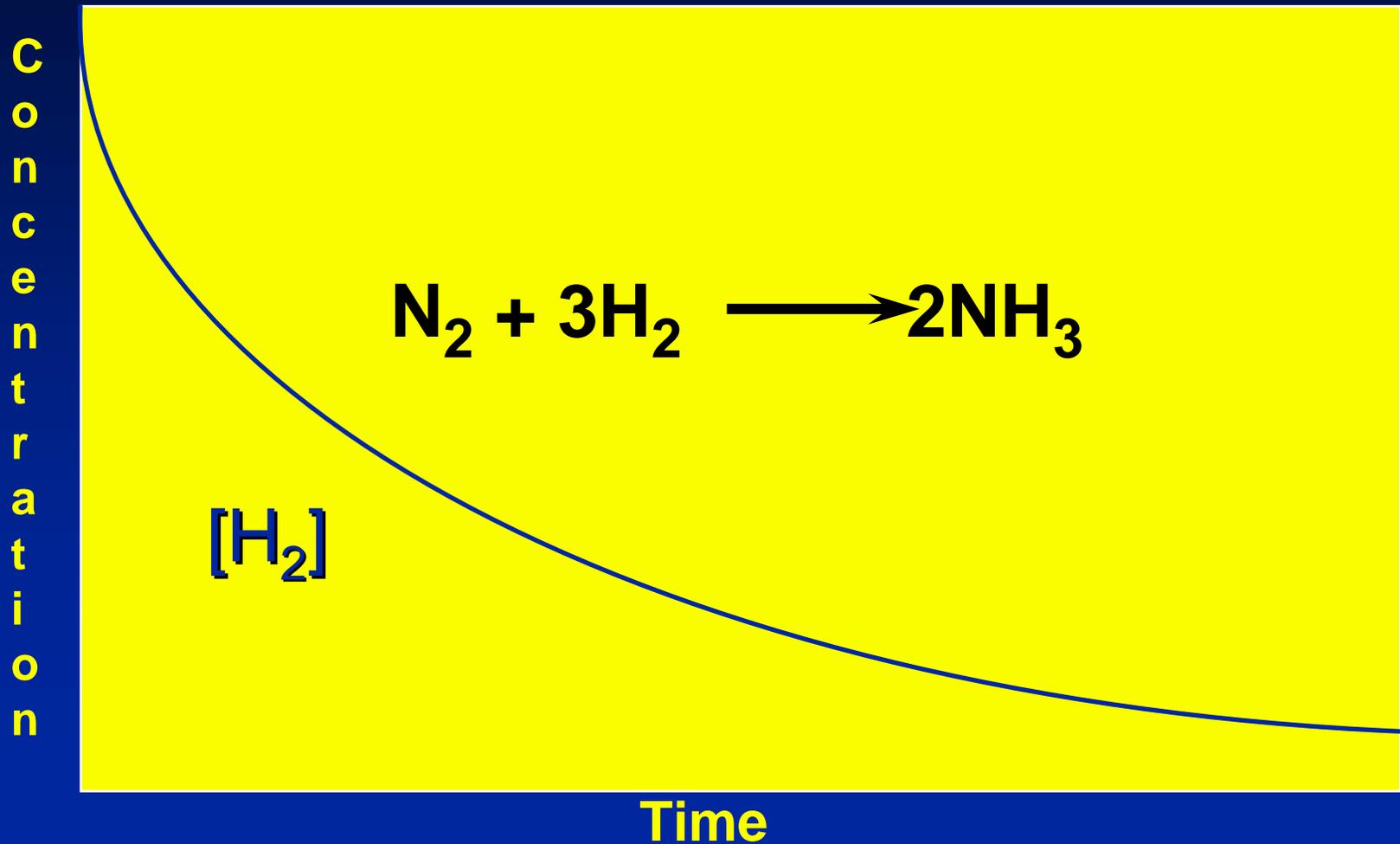


$$\text{Rate} = \frac{-1}{a} \frac{\Delta[\text{A}]}{\Delta t} = \frac{-1}{b} \frac{\Delta[\text{B}]}{\Delta t} = \frac{1}{c} \frac{\Delta[\text{C}]}{\Delta t} = \frac{1}{d} \frac{\Delta[\text{D}]}{\Delta t}$$

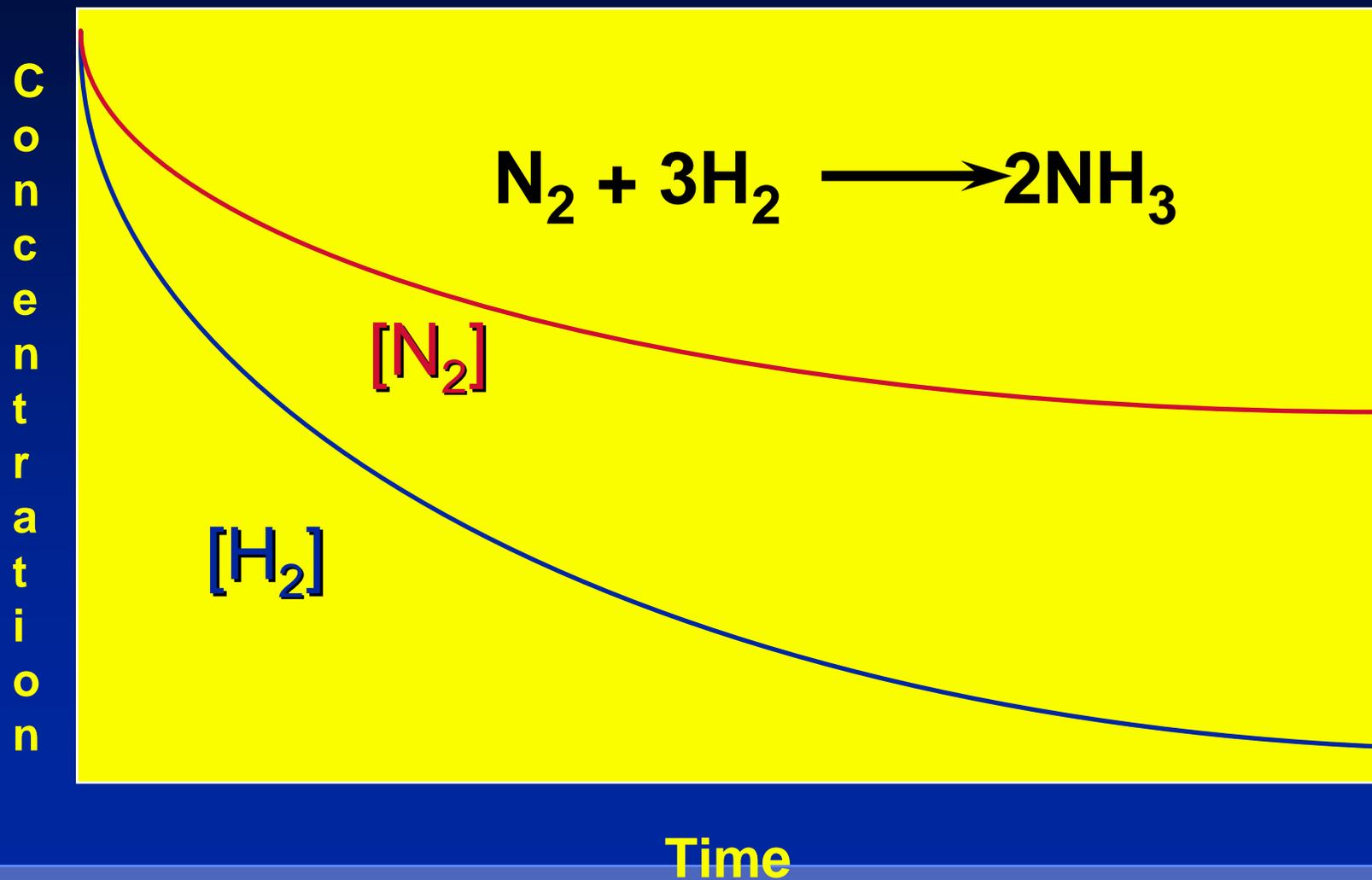
- Consider the reaction



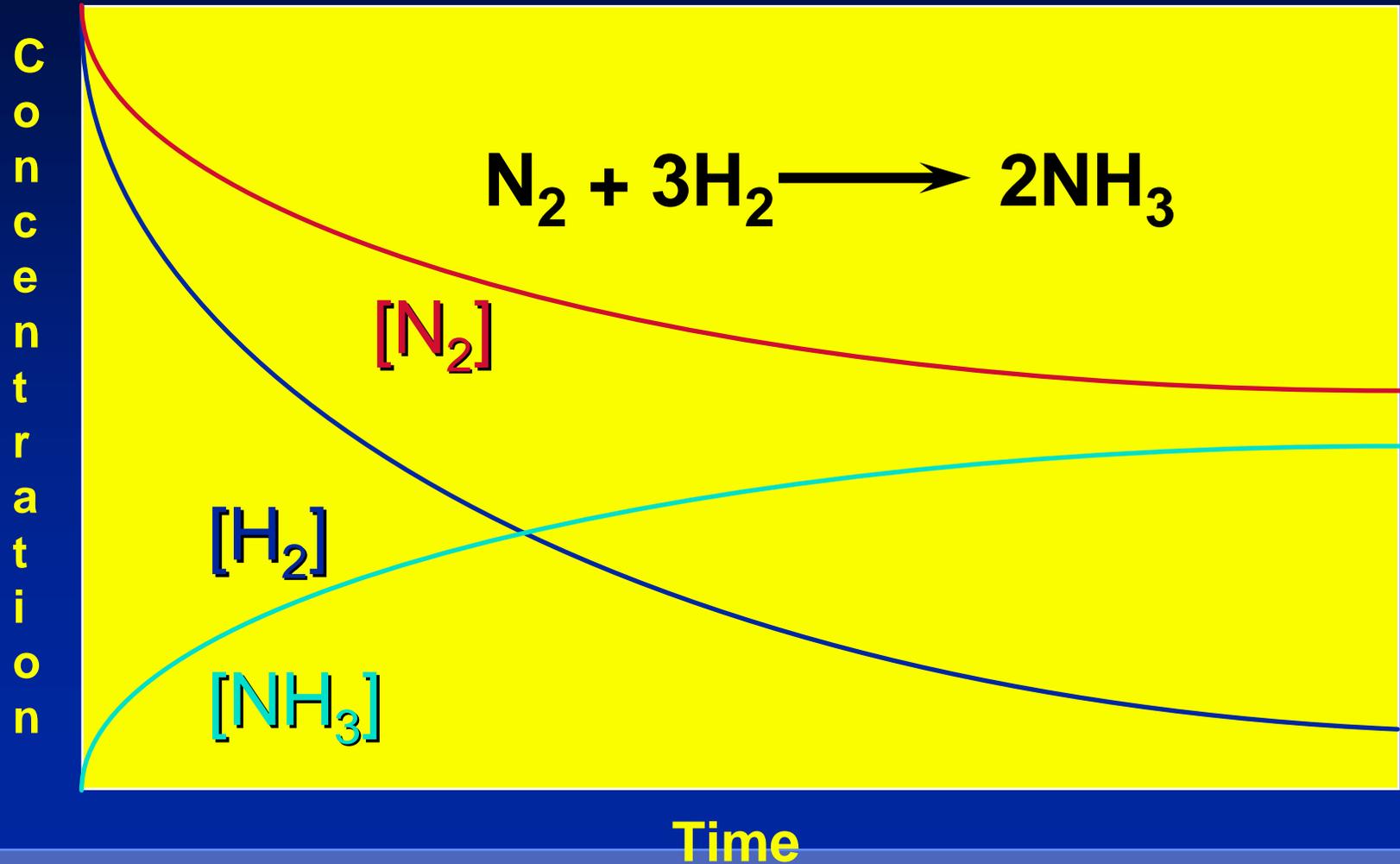
- As the reaction progresses the concentration H_2 decreases



- As the reaction progresses the concentration of N_2 decreases 1/3 as fast



- As the reaction progresses the concentration NH_3 goes up 2/3 times

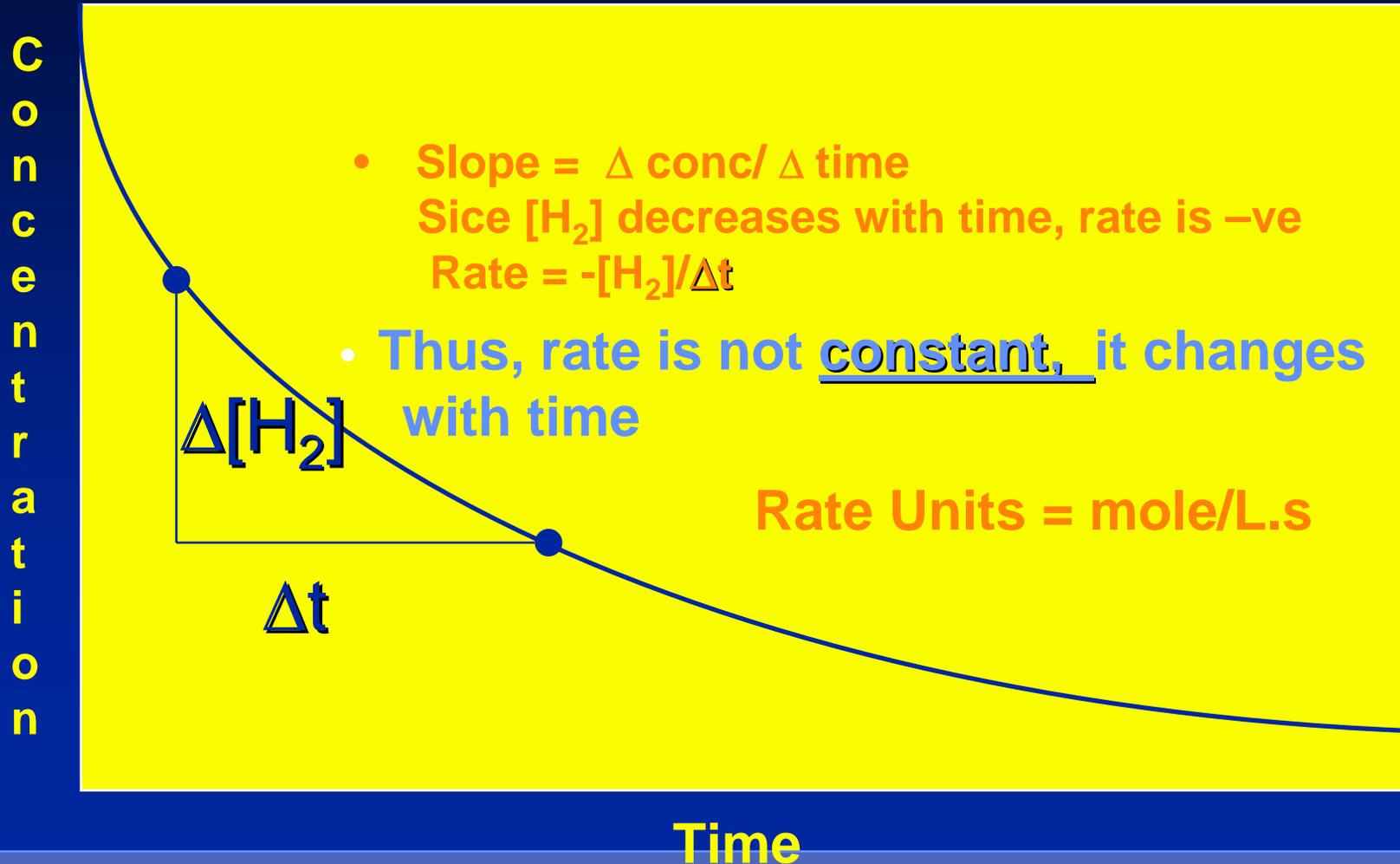


Calculating Rates

From the curves of concentration VS time

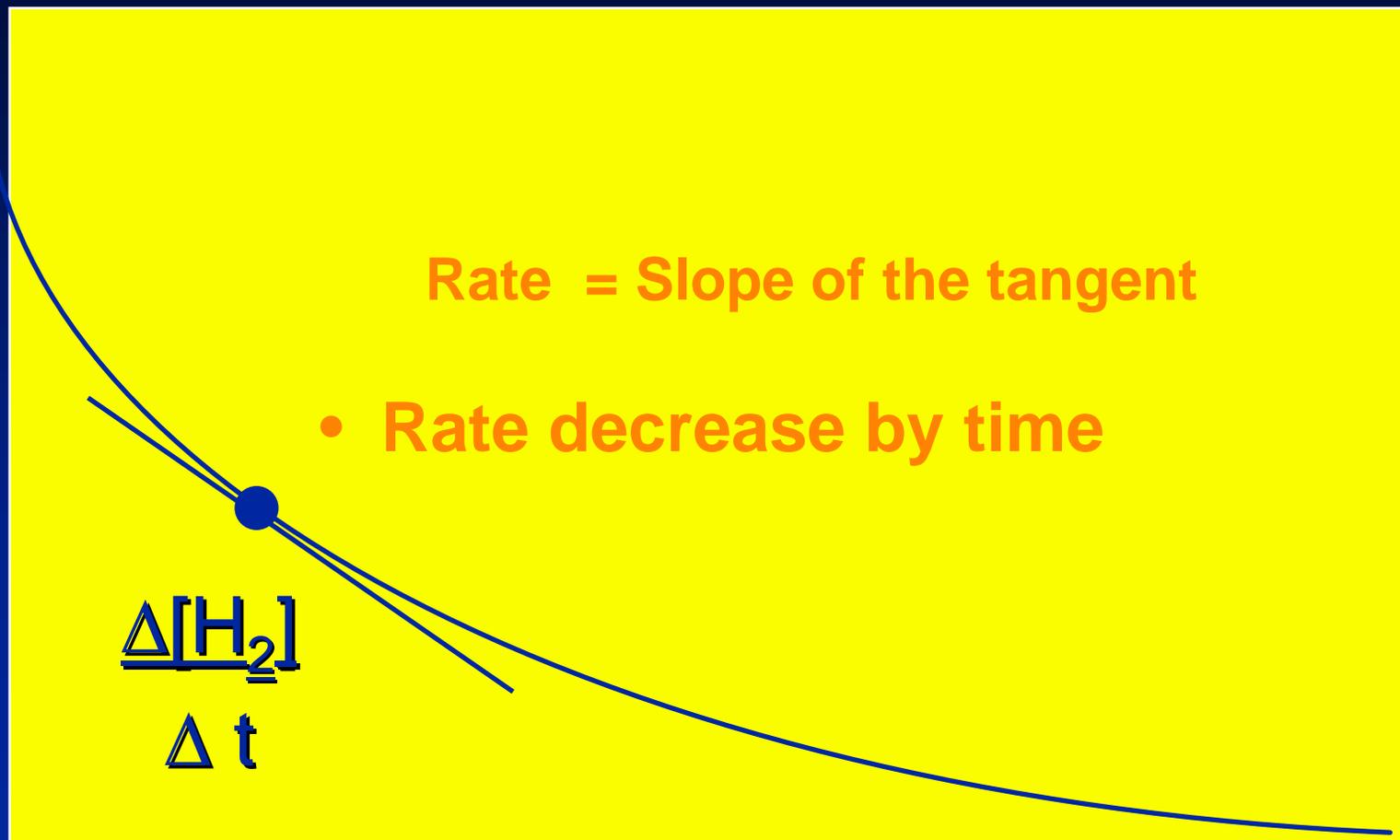
- Average rates are taken over long intervals
- Instantaneous rates are determined by finding the slope of a line tangent to the curve at any given point because the rate can change over time

- Average rate (slope) method

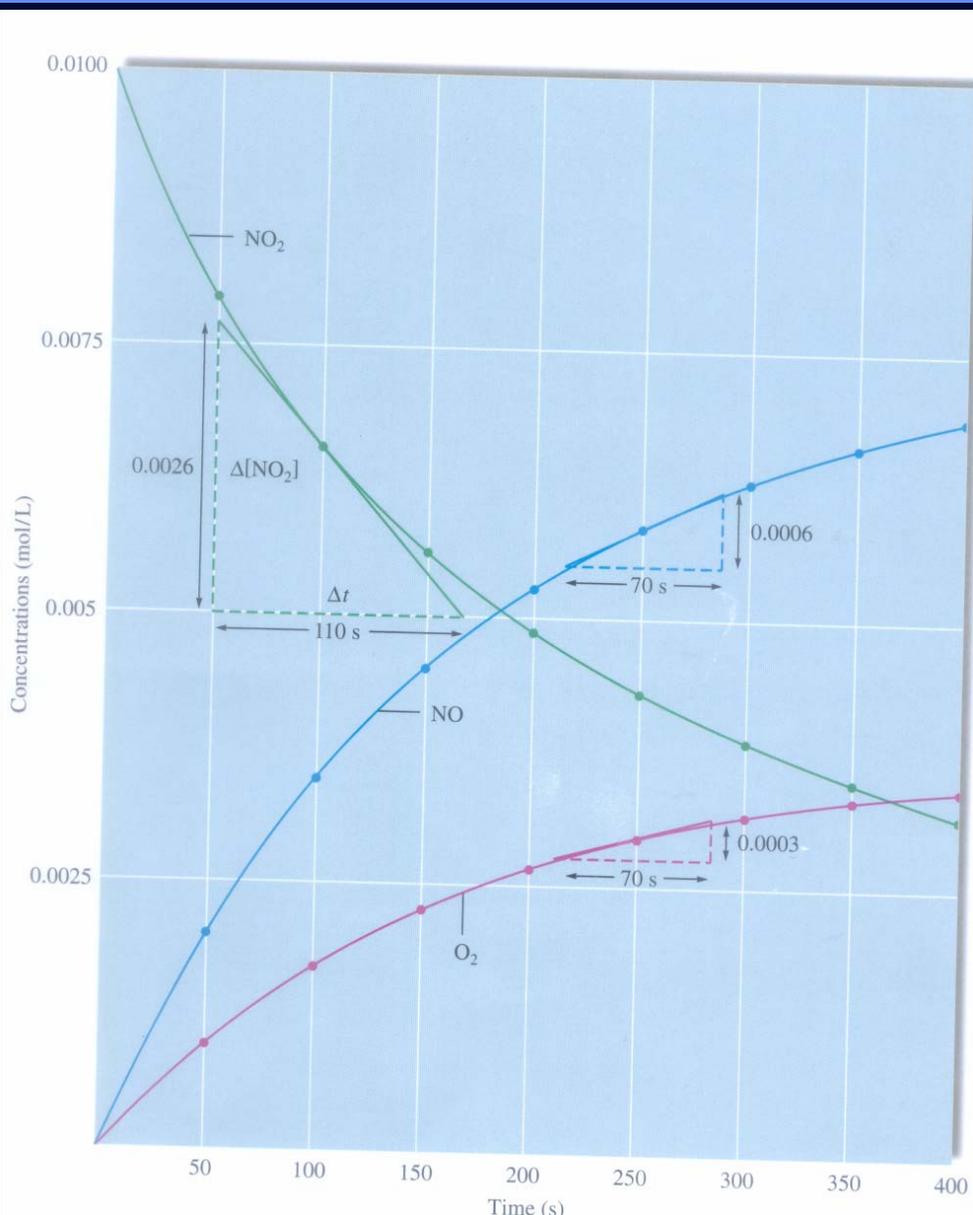


- Instantaneous rate (slope) method.

C
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Time



Measurement of Rate

- Start at a certain initial conc of reactant
- Measure the conc. of reactant and the conc. of product/s at certain time intervals (1 min for example)
- Plot conc VS. time

Reaction rate and concentration

- Reaction rate is \propto Concentration
- The higher the conc of starting material the more rapidly the reaction takes place
- H_2O_2 (l) \longrightarrow H_2O + $\frac{1}{2} \text{O}_2$
40 mol/L (pure hydrogen peroxide) decomposes vigorously. **Why does the rate increase with conc?**
- Reactions occur as a result of collisions between reactant molecules
- Reaction rate drops off with time. It becomes zero when the reactant is consumed

12.2 Rate Laws: an introduction

Reactions reversibility and Rate:

- As products accumulate the direction of reaction starts shifting backward
- Thus, reverse reaction becomes important
- $\Delta[\text{Reactant}]$ will depend on the $R_{\text{Forward}} - R_{\text{revers}}$
- **Early on the reaction**, the rate will depend on **only the amount of reactants** present.
- We should measure the reactants as soon as they are mixed.
- Thus, we avoid the reverse reaction
- This is called the **Initial rate method**.

In the initial rate method, Two key points should be considered:

- The concentration of the products do not appear in the rate law because this is an initial rate.
- The order (exponent) must be determined experimentally,
- **can't** be obtained from the equation



- The rate will only depend on the conc. of the reactants.
- Rate = $k[\text{NO}_2]^n$
- This is called a **rate law expression**.
- **k** is called the **rate constant**.
- **n** is the rate **order** -usually a positive integer but **could be a fraction**.
- **In the initial rate method**, Two key points should be considered:
 - ☞ The concentration of the products do not appear in the rate law because this is an initial rate.
 - ☞ The order (exponent) must be determined experimentally,
 - ☞ **It can't** be obtained from the balanced equation



$$\text{Rate} = \frac{\Delta[\text{NO}_2]}{\Delta t} = k[\text{NO}_2]^n$$

- The rate of appearance of O_2 can be

$$\text{Rate}' = \frac{\Delta[\text{O}_2]}{\Delta t} = k'[\text{NO}_2]^n$$

- Because there are 2 NO_2 for each O_2
- $\text{Rate} = 2 \times \text{Rate}'$
- So $k[\text{NO}_2]^n = 2 \times k'[\text{NO}_2]^n$
- So $k = 2 \times k'$
- Thus, the value of K depends on how the rate is defined

Types of Rate Laws

- **Differential** Rate law - describes how rate depends on concentration (Rate/Conc). (It is the usual known **rate law**)
- **Integrated** Rate Law - Describes how **concentration** depends on **time (conc/time)**.
- For each type of differential rate law there is an integrated rate law and vice versa.
- Rate laws can help us better understand reaction mechanisms (steps by which the reaction occurs).

12.3 Determining the Rate Law

- The first step is to determine the **form of the rate law (especially its order)**.
- Rate law must be determined from experimental data.

- For this reaction



The reverse reaction won't play a role

[N₂O₅] (mol/L)

Time (s)

1.00

0

0.88

200

0.78

400

0.69

600

0.61

800

0.54

1000

0.48

1200

0.43

1400

0.38

1600

0.34

1800

0.30

2000

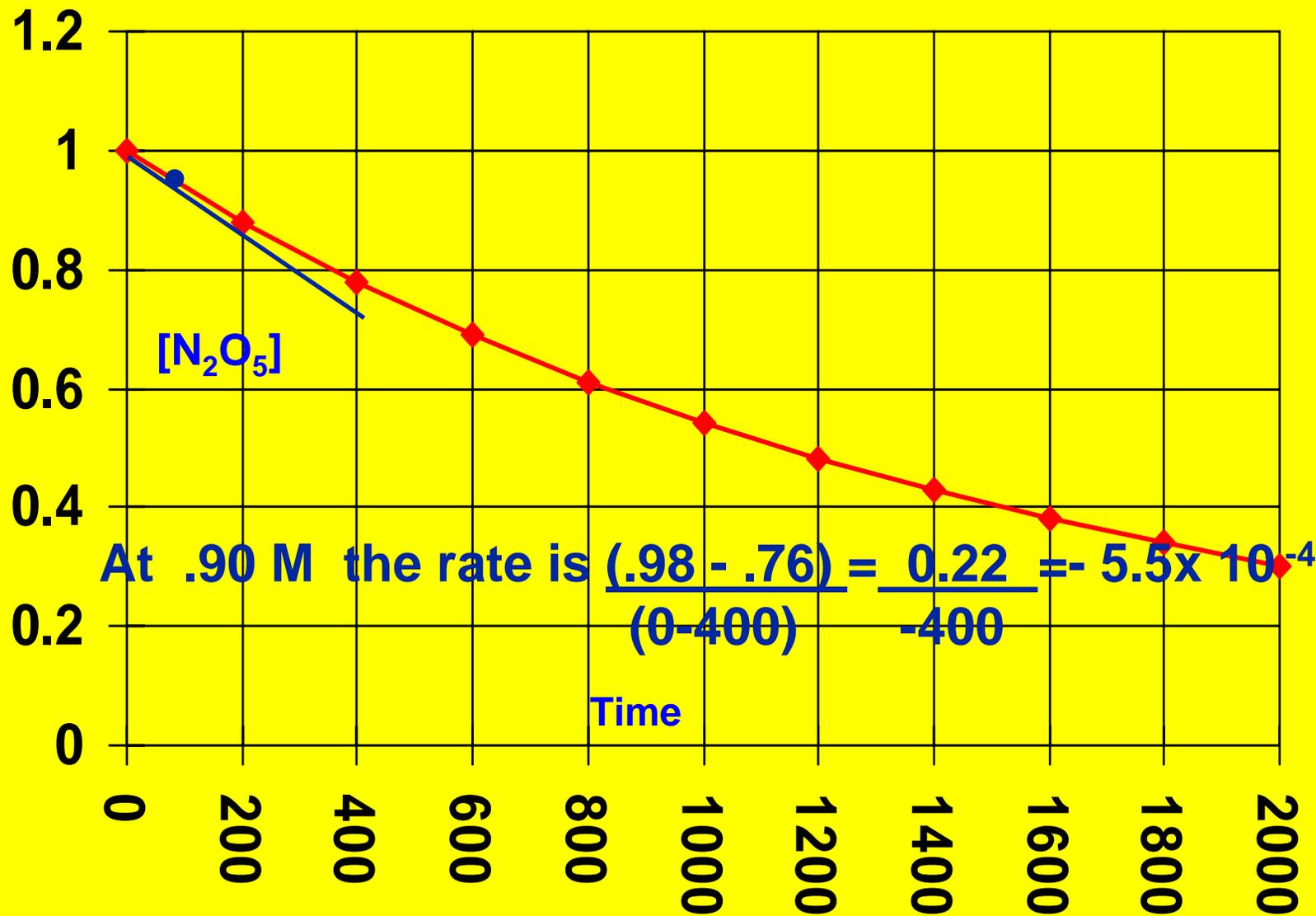
Now plot the data, []/t

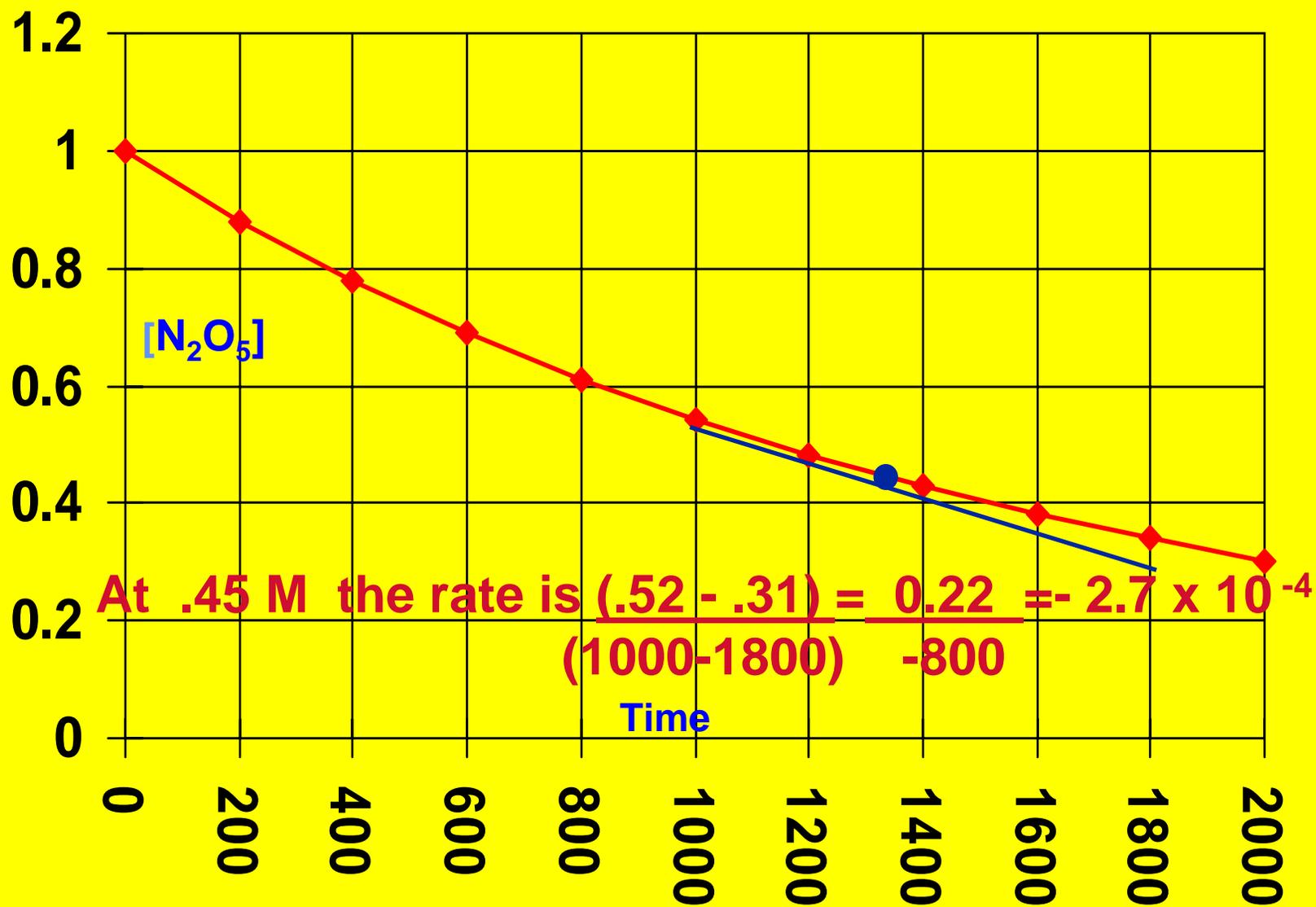


$[\text{N}_2\text{O}_5]$

To find the rate we have to find the slope of tangents at two points.

Time





- Rate_1 at 0.90 M = -5.5×10^{-4}

- Rate_2 at 0.45 M = -2.7×10^{-4}

- $\text{Rate}_1 = 2 \times \text{Rate}_2$

- $\text{Rate}_1 = k'' (\text{Rate}_2)^1$

- $\text{Rate}_1 \propto \text{Rate}_2$

- This means that the rate depends on conc of N_2O_5 to the first power
- **Doubling conc will double rate**
- Rate = $-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1 = k[\text{N}_2\text{O}_5]$
- We say this reaction is first order in N_2O_5
- The only way to determine the order is to run the experiment.

Determination of Rate law by Method of Initial Rates

- This method requires that a reaction be run several times.
- The initial concentrations of the reactants are varied.
- The reaction rate is measured just after the reactants are mixed (just after $t = 0$) (**Instantaneous rate**)
- Eliminates the effect of the reverse reaction.

Order of reactions having one reactant only



- $\text{Rate} = k [A]^m$

Determination the rate of reaction by initial rate method

- $A \longrightarrow$ Products
- Initial rate = Rate at $t=0$
- Initial rates are measured at different initial concentrations
- Assume rate of decomposition of A is measured at two different concentrations 1 and 2

$$\rightarrow \text{Rate}_2 = k[A]_2^m$$

$$\text{Rate}_1 = k[A]_1^m$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{[A]_2^m}{[A]_1^m} = \left(\frac{[A]_2}{[A]_1} \right)^m$$

$$\ln \frac{\text{Rate}_2}{\text{Rate}_1} = m \ln \left(\frac{[A]_2}{[A]_1} \right)$$

$$m = \left(\ln \frac{R_2}{R_1} \right) / \ln \frac{[A]_2}{[A]_1}$$

ORDER OF REACTION



Conc. CH_3CHO (mol/l)	: 0.10	0.20	0.30	0.40
Initial rate (mol/l.s)	: 0.085	0.34	0.76	1.4

(a) Determine the reaction order

$$\text{Rate} = k [\text{CH}_3\text{CHO}]^m$$

$$\frac{R_2}{R_1} = \left(\frac{[\text{CH}_3\text{CHO}]_2}{[\text{CH}_3\text{CHO}]_1} \right)^m \Rightarrow \frac{0.34}{0.085} = \left(\frac{0.20}{0.10} \right)^m$$

$$\therefore \ln \left(\frac{0.34}{0.085} \right) = m \ln \left(\frac{0.20}{0.10} \right)$$

$$\ln 4 = m \ln 2$$

$$\ln 4 = m \ln 2$$

$$m = \frac{\ln 4}{\ln 2} = 2 \quad ; \text{ i.e., it is a } \boxed{\text{2nd order reaction}}$$

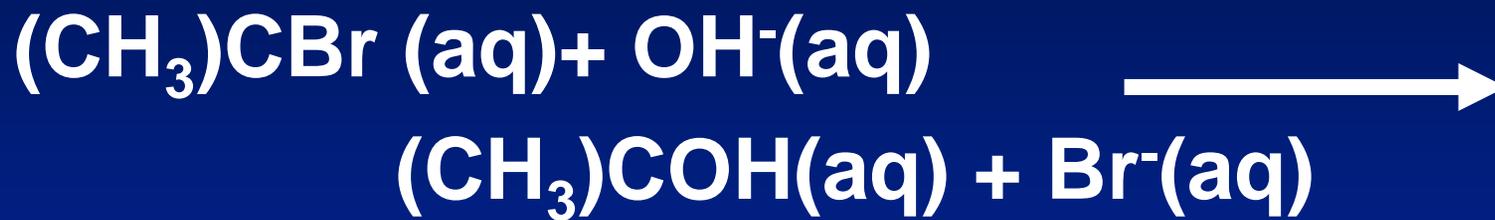
* (b) Determine k

$$\begin{aligned} \text{Rate} &= k \times [\text{CH}_3\text{CHO}]^2 \\ 0.085 \text{ mol/l.s} &= k (0.10 \text{ mol/l})^2 \\ k &= 8.5 \text{ l/mol.s} \end{aligned}$$

* (c) Determine the rate when conc. $\text{CH}_3\text{CHO} = 0.50 \text{ mol/l}$

$$\begin{aligned} \text{Rate} &= 8.50 \text{ l/mol.s} \times (0.50 \text{ mol/l})^2 \\ &= 2.1 \text{ mol/l.s} \end{aligned}$$

Example of more than one reactant



Experimental determination of reaction order for A process involving more than one reactant



- 1. Hold the initial conc. of OH⁻ constant (0.05M) and vary that of (CH₃)₃CBr**
- 2. Hold the initial conc of (CH₃)₃CBr constant (1.0M) and vary that of OH⁻**

	(1)	(2)	(3)	(4)	(5)
Conc. $(\text{CH}_3)_3\text{CBr}$	0.50	1.0	1.5	1.0	1.0
Conc. OH^-	0.050	0.050	0.050	0.10	0.20
Rate (mol/l.s)	0.0050	0.010	0.015	0.010	0.010

$$\frac{R_3}{R_1} = \left(\frac{[\text{CH}_3)_3\text{CBr}]_3}{[\text{CH}_3)_3\text{CBr}]_1} \right)^m \left(\frac{[\text{OH}]_3}{[\text{OH}]_1} \right)^n$$

$$\frac{0.015}{0.0050} = \left(\frac{1.5}{0.50} \right)^m \Rightarrow \ln \frac{0.015}{0.0050} = m \ln \left(\frac{1.5}{0.5} \right) \Rightarrow \underline{\underline{m=1}}$$

$$\frac{\text{Rate}_5}{\text{Rate}_2} = \left(\frac{[\text{OH}^-]_5}{[\text{OH}^-]_2} \right)^n \left(\frac{[\text{CH}_3\text{CBr}]_5}{[\text{CH}_3\text{CBr}]_2} \right)^m$$

$$\frac{0.010}{0.010} = \left(\frac{0.20}{0.050} \right)^n \Rightarrow \ln \frac{0.010}{0.010} = n \ln \frac{0.20}{0.05} \Rightarrow n = 0$$

Example of more than two reactants

- For the reaction
- $\text{BrO}_3^- + 5 \text{Br}^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + 3 \text{H}_2\text{O}$
- The general form of the Rate Law is $\text{Rate} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$
- We use experimental data to determine the values of n,m,and p

Initial concentrations (M)



BrO_3^-	Br^-	H^+	Rate (M/s)
0.10	0.10	0.10	8.0×10^{-4}
0.20	0.10	0.10	1.6×10^{-3}
0.20	0.20	0.10	3.2×10^{-3}
0.10	0.10	0.20	3.2×10^{-3}

**Now we have to see how the rate changes
with concentration**

12.4 Integrated Rate Law

Reactant conc. & time

- The rate law so far expressed rate in terms of concentration
- Now the reactant concentration will be expressed as a function of time.
- It is called differential rate law for the reaction
- Changes $Rate = \frac{\Delta[A]^n}{\Delta t}$
- We will only work with n=0, 1, and 2

First Order

- For the reaction $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
- We found the Rate = $-\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} = k[\text{N}_2\text{O}_5]^1$
- If concentration doubles rate doubles.
- If we integrate (using calculus) this equation with respect to time we get the Integrated Rate Law

$$\ln \frac{[\text{N}_2\text{O}_5]_0}{[\text{N}_2\text{O}_5]} = kt$$

- $\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0$
- \ln is the natural log
- $[\text{N}_2\text{O}_5]_0$ is the initial concentration.

First Order

- General form: $\text{Rate} = \Delta[A] / \Delta t = k[A]$

- $\ln[A] = -kt + \ln[A]_0$

$$y = mx + b$$


Slope intercept

- A graph of $\ln[A]$ vs time is a straight line.

$$\ln \frac{[A_0]}{[A]} = kt$$

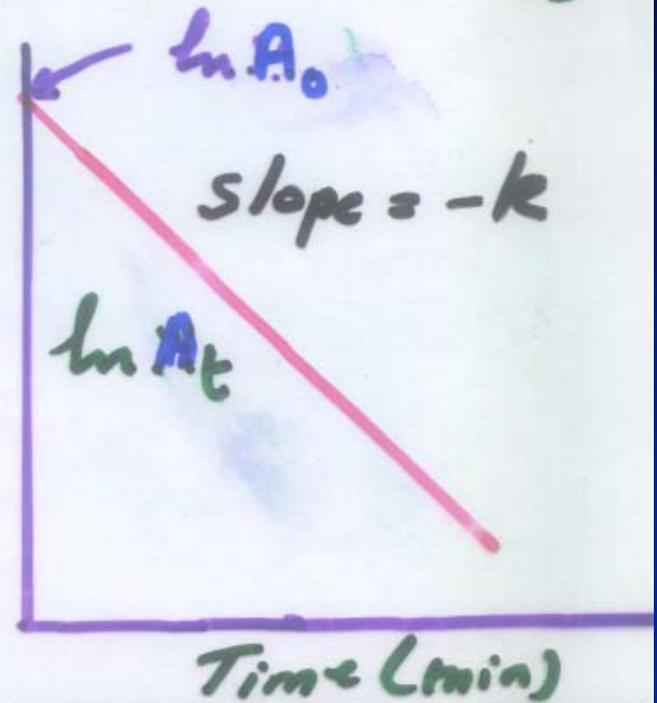
$$\ln[A_0] - \ln[A] = kt$$

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

$$y = b + mx$$

↑ ↑
intercept slope

(First-order only)



First order rate laws

- By getting the straight line you can prove it is first order
- Often expressed in a ratio

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

Half Life of a reaction, $t_{1/2}$

- The time required to reach half the original concentration.
- Time required for one half of the reactant to disappear
- If the reaction is first order
- $[A] = [A]_0/2$ when $t = t_{1/2}$

$$\ln \left(\frac{[A]_0}{[A]_0/2} \right) = kt_{1/2}$$

Constant independent of conc.

$$\bullet \ln(2) = kt_{1/2} \Rightarrow kt_{1/2} = 0.693 \Rightarrow t_{1/2} = \frac{0.693}{k}$$

Half-Life of a Reaction, $t_{1/2}$

14

$t_{1/2}$ is the time required for ^{one} half of the reactant to disappear.

$$[A] = \frac{1}{2}[A]_0 \quad \text{--- (at } t_{1/2}\text{)}$$

$$\ln \frac{[A]_0}{[A]} = k t_{1/2}$$

$$\ln 2 = k t_{1/2} \quad \Rightarrow \quad k t_{1/2} = 0.693$$

✓ \therefore $t_{1/2} = \frac{0.693}{k}$; $t_{1/2}$ is constant, independent of conc.

Given k for decomposition of N_2O_5

to be 0.35 min^{-1} .

(a) Calculate conc. N_2O_5 after 4.0 min . Starting with 0.160 mol/l $[A]_0$.

$$\ln \frac{[A]_0}{[A]} = kt$$

$$\ln \frac{0.160}{[A]} = 0.35 \times 4 = 1.4$$

$$\therefore \frac{0.160}{[A]} = e^{1.4} = 4.0$$

$$\therefore [A] = \frac{0.160}{4.0} = 0.040 \text{ mol/l}$$

(b) The time required for the conc. to drop from 0.16 to 0.100 M .

$$\ln \frac{0.16}{0.10} = 0.35 \times t \Rightarrow t = 1.3 \text{ min}$$

(c) The time required for half of the sample to decompose:

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{0.35} = 2 \text{ min}$$

Example $\frac{11.3}{297}$. Given k for decomposition of N_2O_5 to be 0.35 min^{-1} .

(a) Calculate conc. N_2O_5 after 4.0 min . Starting with 0.160 mol/l $[A]_0$.

$$\ln \frac{[A]_0}{[A]} = kt$$

$$\ln \frac{0.160}{[A]} = 0.35 \times 4 = 1.4$$

$$\therefore \frac{0.160}{[A]} = e^{1.4} = 4.0$$

$$\therefore [A] = \frac{0.160}{4.0} = 0.040 \text{ mol/l}$$

(b) The time required for the conc. to drop from 0.16 to 0.100 M .

$$\ln \frac{0.16}{0.10} = 0.35 \times t \Rightarrow t = 1.3 \text{ min}$$

(c) The time required for half of the sample to decompose:

$$t_{\frac{1}{2}} = \frac{0.693}{k} = \frac{0.693}{0.35} = 2 \text{ min}$$

Half Life

- $t_{1/2} = 0.693/k$
- The time to reach half the original concentration does not depend on the starting concentration.
- An easy way to find k

Second-Order Reaction

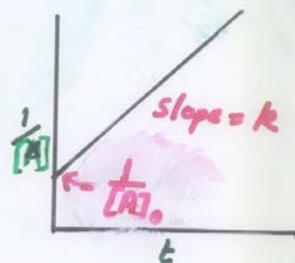
a $A_2 \rightarrow$ products

$$\text{Rate} = k[A]^2$$

From Calculus,

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$$



$t_{1/2}$

$$[A] = \frac{[A]_0}{2}$$

$$\frac{1}{\frac{1}{2}[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$t_{1/2} \propto \frac{1}{\text{orig. conc.}}$$

Second order rate laws

- $aA \longrightarrow$ Products
- Rate = $-\Delta[A] / \Delta t = k[A]^2$
- integrated rate law
- $1/[A] = kt + 1/[A]_0$
- $y = 1/[A]$ $m = k$ $Y = mX + b$
- $x = t$ $b = 1/[A]_0$
- A straight line of $1/[A]$ vs t is graphed
- Knowing k and $[A]_0$ you can calculate $[A]$ at any time t

Second Order Half Life

- $[A] = \frac{[A]_0}{2}$ at $t = t_{1/2}$

$$\frac{1}{\frac{[A]_0}{2}} = kt_{1/2} + \frac{1}{[A]_0}$$

$$\frac{2}{[A]_0} - \frac{1}{[A]_0} = kt_{1/2}$$

$$\frac{1}{[A]_0} = kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

* Zero Order

a A \rightarrow Products

$$\text{rate} = k [A]^0 = k$$

i.e., Rate is independent of conc.

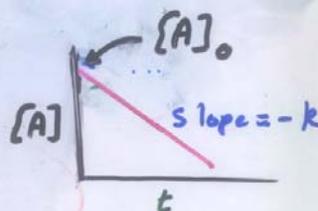
$$\text{Rate} = - \frac{\Delta[A]}{\Delta t} = k$$

$$\Delta t = t - 0 = t ; \Delta [A] = [A] - [A]_0$$

$$- \frac{\Delta[A]}{\Delta t} = \frac{[A]_0 - [A]}{t} = k$$

$$[A]_0 - [A] = kt$$

$$\boxed{[A] = [A]_0 - kt}$$



* $t_{1/2}$

$$\text{When } t = t_{1/2} \Rightarrow [A] = [A]_0 / 2$$

$$\therefore \frac{[A]_0}{2} = [A]_0 - kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{[A]_0}{2k}}$$

* $t_{1/2} \propto$ original concentration

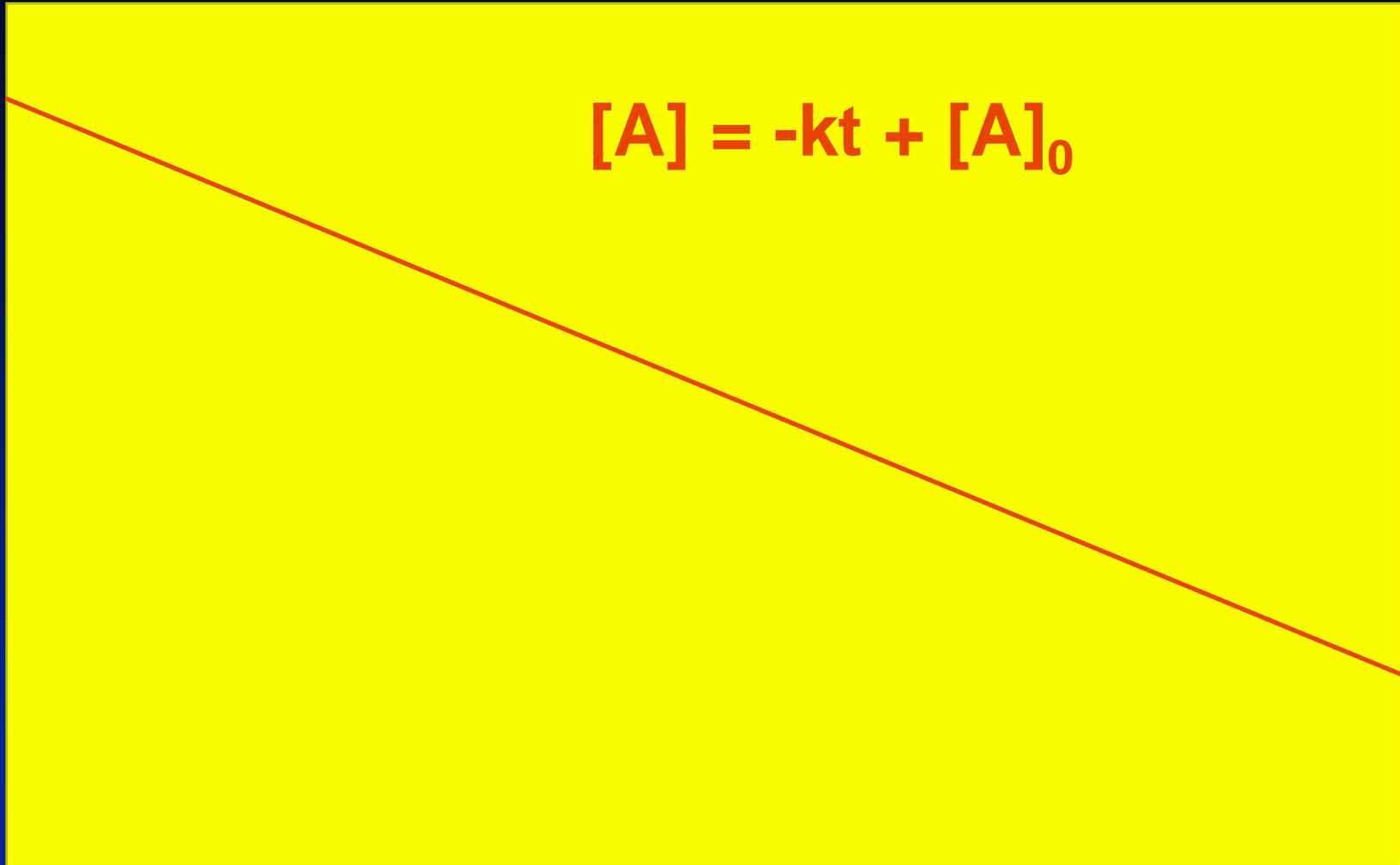
Zero order rate laws

- $aA \longrightarrow$ Products
- Rate = $k[A]^0 = k$
- Rate does not change with Conc.
- Integrated rate law: $[A] = -kt + [A]_0$
- When $[A] = \frac{[A]_0}{2}$ $t = t_{1/2}$
- $t_{1/2} = \frac{[A]_0}{2k}$

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$$[A] = -kt + [A]_0$$

Time



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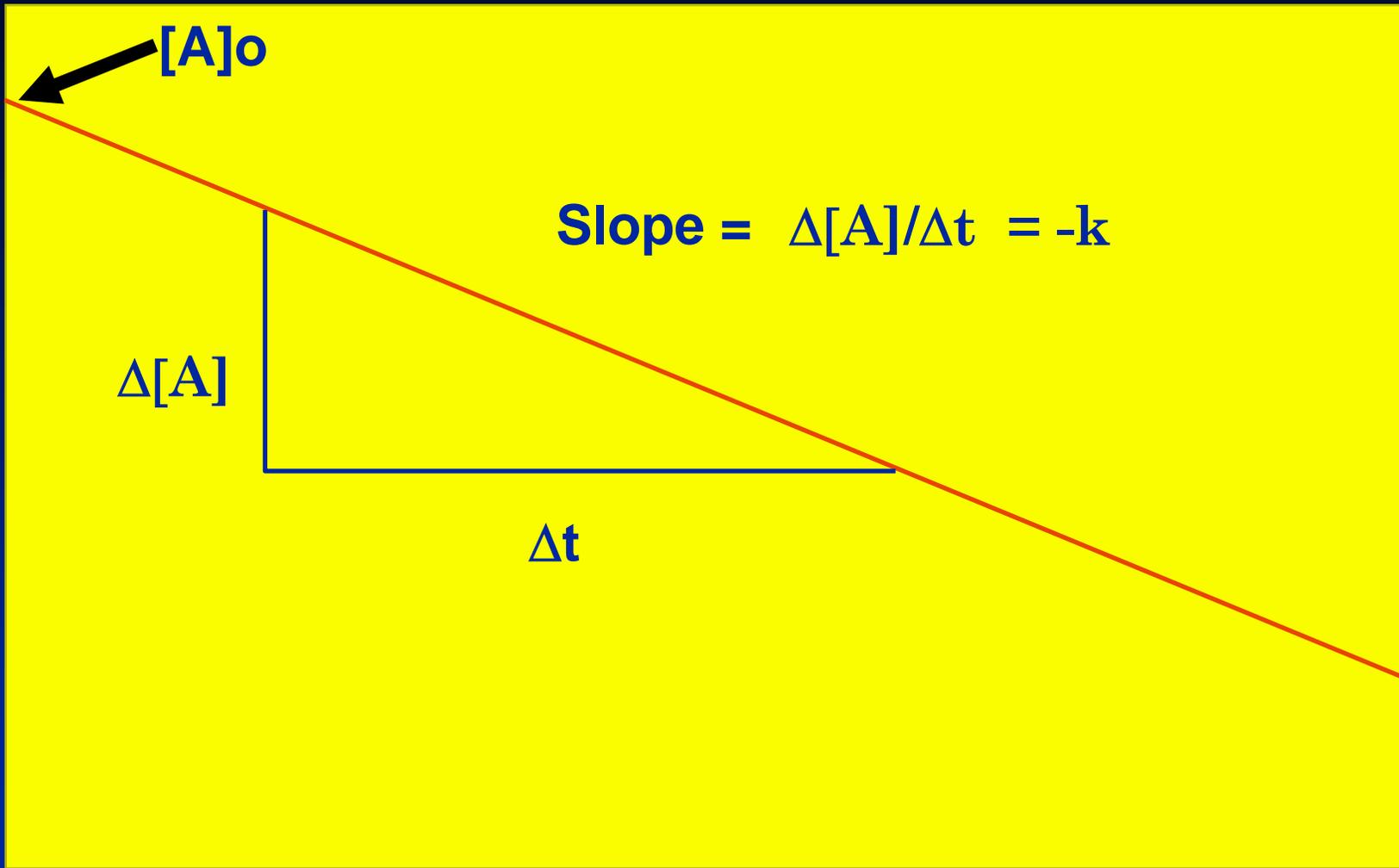
$[A]_0$

Slope = $\Delta[A]/\Delta t = -k$

$\Delta[A]$

Δt

Time



Examples of zero order rate law

- reactions take place on a surface because the surface area stays constant.
- Enzyme chemistry

Integrated rate laws for reactions with more than one reactant

- $\text{BrO}_3^- + 5 \text{Br}^- + 6\text{H}^+ \longrightarrow 3\text{Br}_2 + 3 \text{H}_2\text{O}$
- The rate law for this reaction was found to be
- $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$
- To investigate this reaction rate conditions need to be controlled

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

- The experiment is set so that two of the reactants are in large excess.
- $[\text{BrO}_3^-]_0 = 1.0 \times 10^{-3} \text{ M}$
- $[\text{Br}^-]_0 = 1.0 \text{ M}$
- $[\text{H}^+]_0 = 1.0 \text{ M}$
- As the reaction proceeds $[\text{BrO}_3^-]$ changes significantly
- $[\text{Br}^-]$ and $[\text{H}^+]$ don't

$$\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$$

- This rate law can be rewritten

- $\text{Rate} = k[\text{BrO}_3^-][\text{Br}^-]_0[\text{H}^+]_0^2$ 0 = initial conc.

- $\text{Rate} = k[\text{Br}^-]_0[\text{H}^+]_0^2[\text{BrO}_3^-]$

- $\text{Rate} = k'[\text{BrO}_3^-]$

- This is called a pseudo first order rate law.

- $k = \frac{k'}{[\text{Br}^-]_0[\text{H}^+]_0^2}$

12.5 Summary of Rate Laws

TABLE 12.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order in $[A]$

	Order		
	Zero	First	Second
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 Needed to Give a Straight Line:	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Linearity Relationship

- Order Linear relationship
- 0-order $[A] \propto t$
- 1-order $\ln [A] \propto t$
- 2-order $\frac{1}{[A]} \propto t$

Example



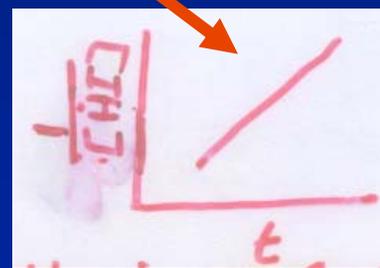
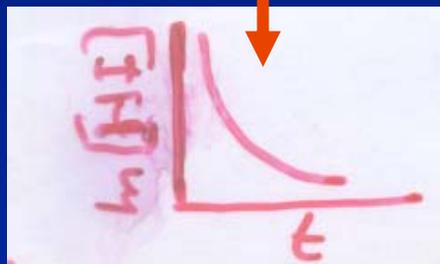
The following data were obtained

for the gas-phase decomposition of HI. Is this reaction 0-, first-, or second-order in HI?

t (h)	:	0	2	4	6
[A] Conc. HI (mol/l)	:	1.00	0.50	0.33	0.25

Prepare a Table:

t (h)	$[HI]$	$\ln[HI]$	$\frac{1}{[HI]}$
0	1.00	0	1.0
2	0.500	-0.69	2
4	0.33	-1.10	3
6	0.25	-1.39	4.0



Since $\frac{1}{[HI]}$ vs t is linear, the reaction is a Second-order

Example

In the first order decomposition of N_2H_4 at 740 K, it is found that 30% of a sample

has decomposed in 13.2 min. How long will

it take 50.0% of the sample to decompose?

$$\ln \frac{[A]_0}{[A]} = kt$$

$$\ln \frac{100}{70} = \frac{kt \times 13.2}{3} \Rightarrow \ln \frac{10}{7} = \frac{13.2kt}{3} \dots \textcircled{1}$$

$$\ln \frac{100}{50} = \frac{kt}{1} \Rightarrow \ln \frac{2}{1} = \frac{kt}{1} \dots \textcircled{2}$$

$$\frac{\ln \frac{10}{7}}{\ln \frac{2}{1}} = \frac{13.2kt}{kt}$$

$$0.51 = \frac{13.2}{t}$$

$$t = 25.9 \text{ min}$$

12.6 Reaction Mechanisms

- **The series of steps that actually occur in a chemical reaction.**
- **Kinetics can tell us something about the mechanism**
- **A balanced equation does not tell us how the reactants become products.**

Reaction Mechanisms

- $2\text{NO}_2 + \text{F}_2 \longrightarrow 2\text{NO}_2\text{F}$
- Rate = $k[\text{NO}_2][\text{F}_2]$ (known from experiment)
- The **proposed** mechanism is
- $\text{NO}_2 + \text{F}_2 \xrightarrow{k_1} \text{NO}_2\text{F} + \text{F}$ (slow)
- $\text{F} + \text{NO}_2 \xrightarrow{k_2} \text{NO}_2\text{F}$ (fast)
- F is called an **intermediate**. It is formed then consumed in the reaction

Reaction Mechanisms

- Each of the two reactions given above is called an elementary step (steps that constitute a reaction mechanism)
- The rate law for an elementary step reaction can be written from its molecularity .
- **Molecularity** is the number of species that must collide (come together) to produce the reaction given in the step.

- **Unimolecular** step involves one molecule - Rate is first order.
- **Bimolecular** step - requires two molecules - Rate is second order
- **Termolecular** step- requires three molecules - Rate is third order
 - **Termolecular** steps are almost never heard of because the chances of three molecules coming into contact at the same time are very small
- Elementary steps involve: decomposition of a single molecule or collisions between molecules

- $A \rightarrow \text{prod.}$ **Unimol** Rate = $k[A]$
- $A+A \rightarrow \text{prod.}$ **Bimol** Rate = $k[A]^2$
- $2A \rightarrow \text{prod.}$
- $A+B \rightarrow \text{prod.}$ **Bimol** Rate = $k[A][B]$
- $A+A+B \rightarrow \text{Prod.}$ **Termol** Rate = $k[A]^2[B]$
- $2A+B \rightarrow \text{Prod.}$
- $A+B+C \rightarrow \text{Prod.}$ **Termol** Rate = $k[A][B][C]$

- It is obvious that the rate law for an elementary step is derived directly from the molecularity of the elementary step.

Precisely, what is the reaction mechanism?

- It is a series of elementary steps that must satisfy two requirements
 1. The sum of the elementary steps must give the overall balanced equation for the reaction
 2. The mechanism must agree with the experimentally determined rate law.

How to make sure that a proposed mechanism is acceptable?

The balanced equation for the reaction:



The experimentally determined rate law is

$$\text{Rate} = k [\text{NO}_2][\text{F}_2]$$

The suggested mechanism is:



Is the suggested mechanism acceptable?

Is the suggested mechanism acceptable?

1. Make sure that the sum of the two steps give the overall equation (requirement 1 above)



➤ Yes this requirement is met

2. To check requirement 2 we need to introduce the term : “ Rate determining step” that is usually the slow step

A reaction cannot be faster than the slowest step!!

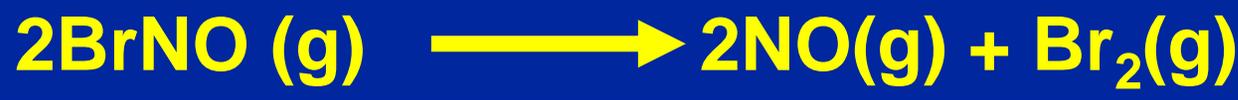
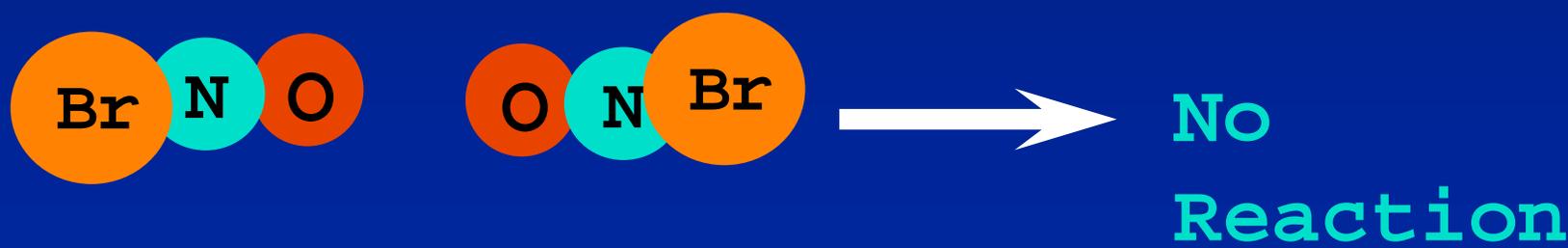
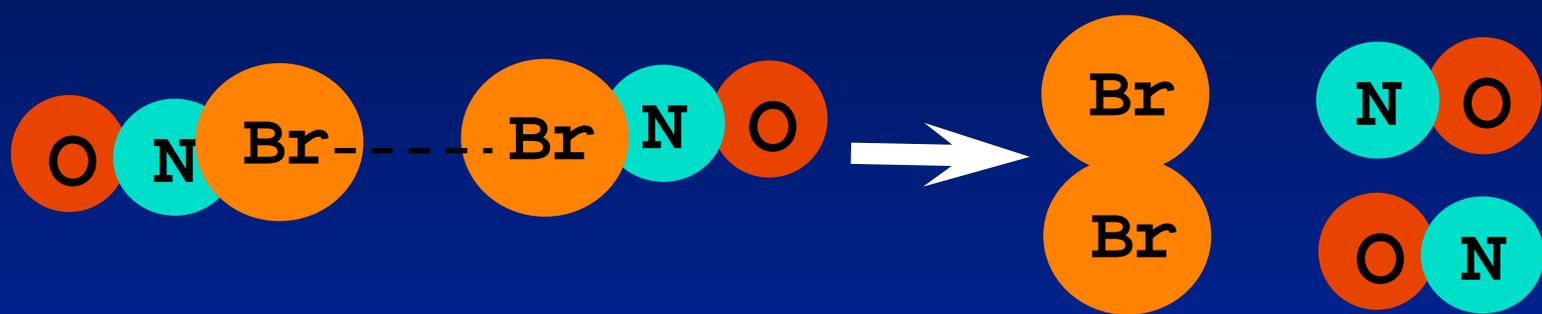
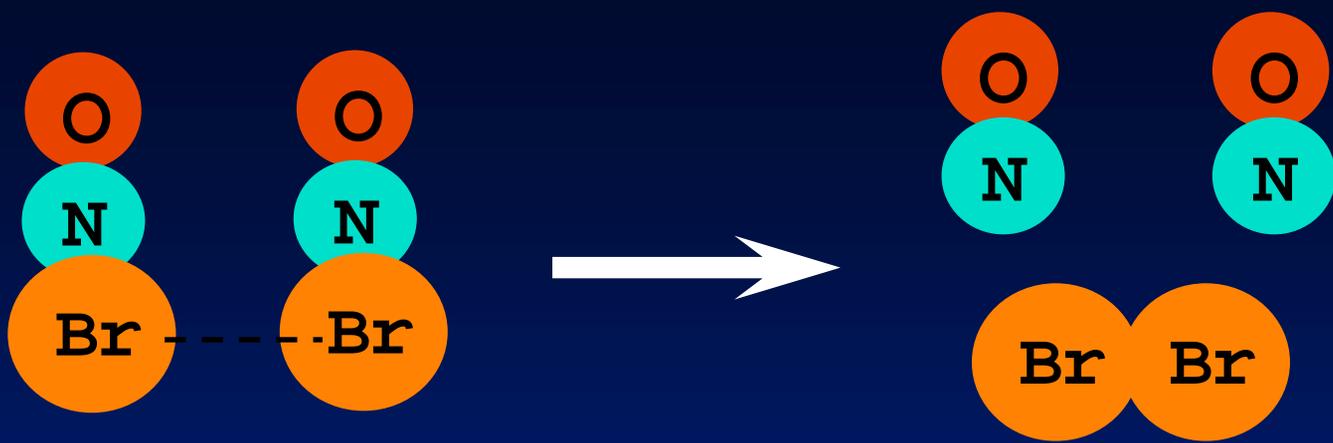
- The rate of the forward reaction is controlled by the rate of formation of NO_2F in the first step
- Since this is an elementary step, the rate law for the whole reaction can be written from the molecularity of this step
- **Rate law for slow step = $k_1 [\text{NO}_2][\text{F}_2]$**
- Since the overall reaction cannot be faster than this step, then the overall rate = $k_1 [\text{NO}_2][\text{F}_2]$
- This rate law agrees with that suggested from experiment as mentioned above

12.7 A model for Chemical Kinetics (Collision Theory)

- Molecules must collide to react.
- Concentration affects rates because collisions are more likely depends upon concentration
- Molecules must collide hard enough.
- Only a small number of collisions (active collisions) produce reactions.
- Temperature and rate are related.
- Arrhenius: An activation energy must be overcome.

What are the requirements for a collision to be active?

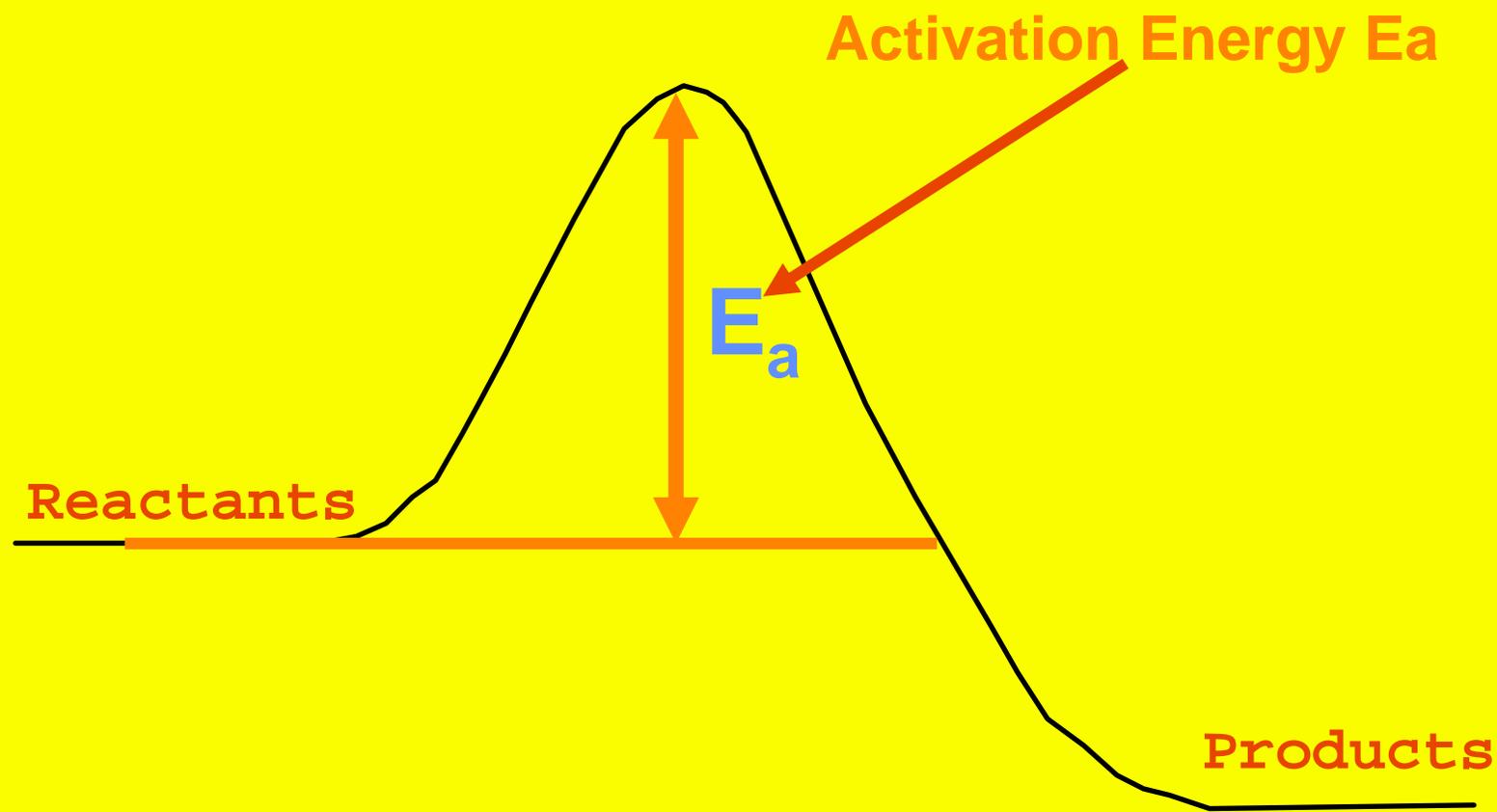
1. Molecules should be energetic enough (possess enough kinetic energy)
 - That is: molecules should possess energy equal or above a certain value known as **activation energy, E_a**
2. Molecules should be properly oriented
Rate \propto Effective (active) collisions



Activation Energy, E_a

- It is the minimum energy required for an effective collision to take place, i.e., for reactants to produce products

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Reaction Coordinate

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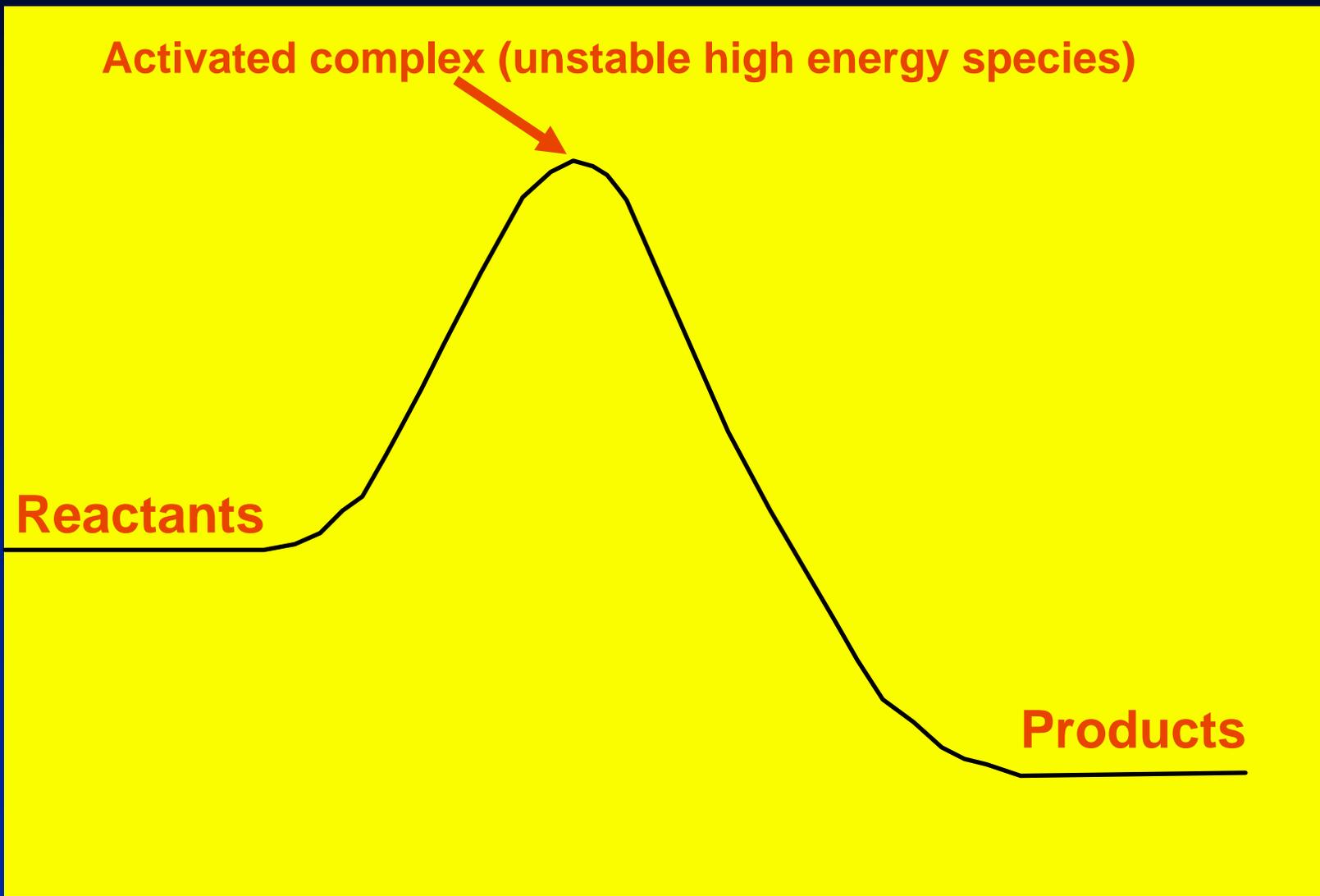
Activated complex (unstable high energy species)



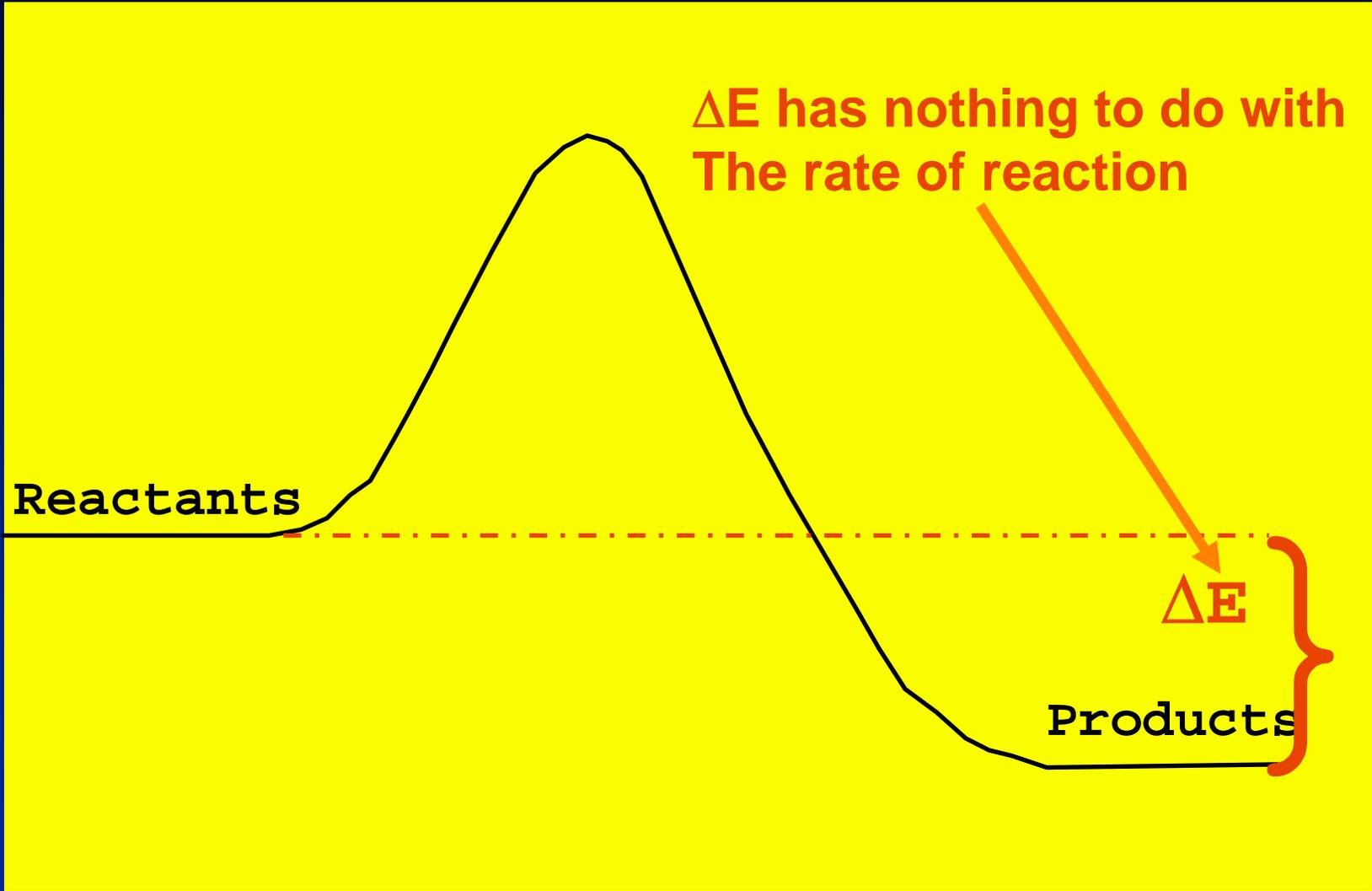
Reactants

Products

Reaction Coordinate



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ΔE has nothing to do with
The rate of reaction

Reactants

ΔE

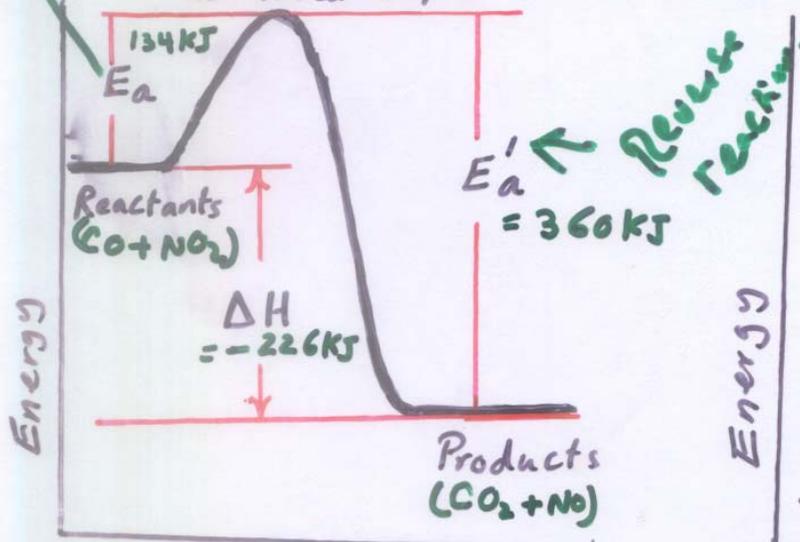
Products

Reaction Coordinate

Forward Reaction

Activation Energy Diagrams

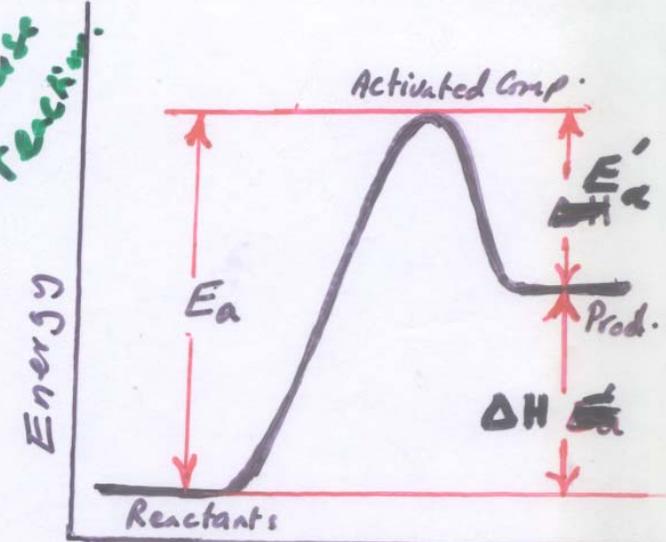
(unstable high energy species)
Activated Complex



Path of reaction
(Exothermic React.)

$$\Delta H = E_a - E_a'$$

$$\Delta H = -ve; E_a < E_a'$$



Path of reaction
(Endothermic React.)

$$\Delta H = E_a - E_a'$$

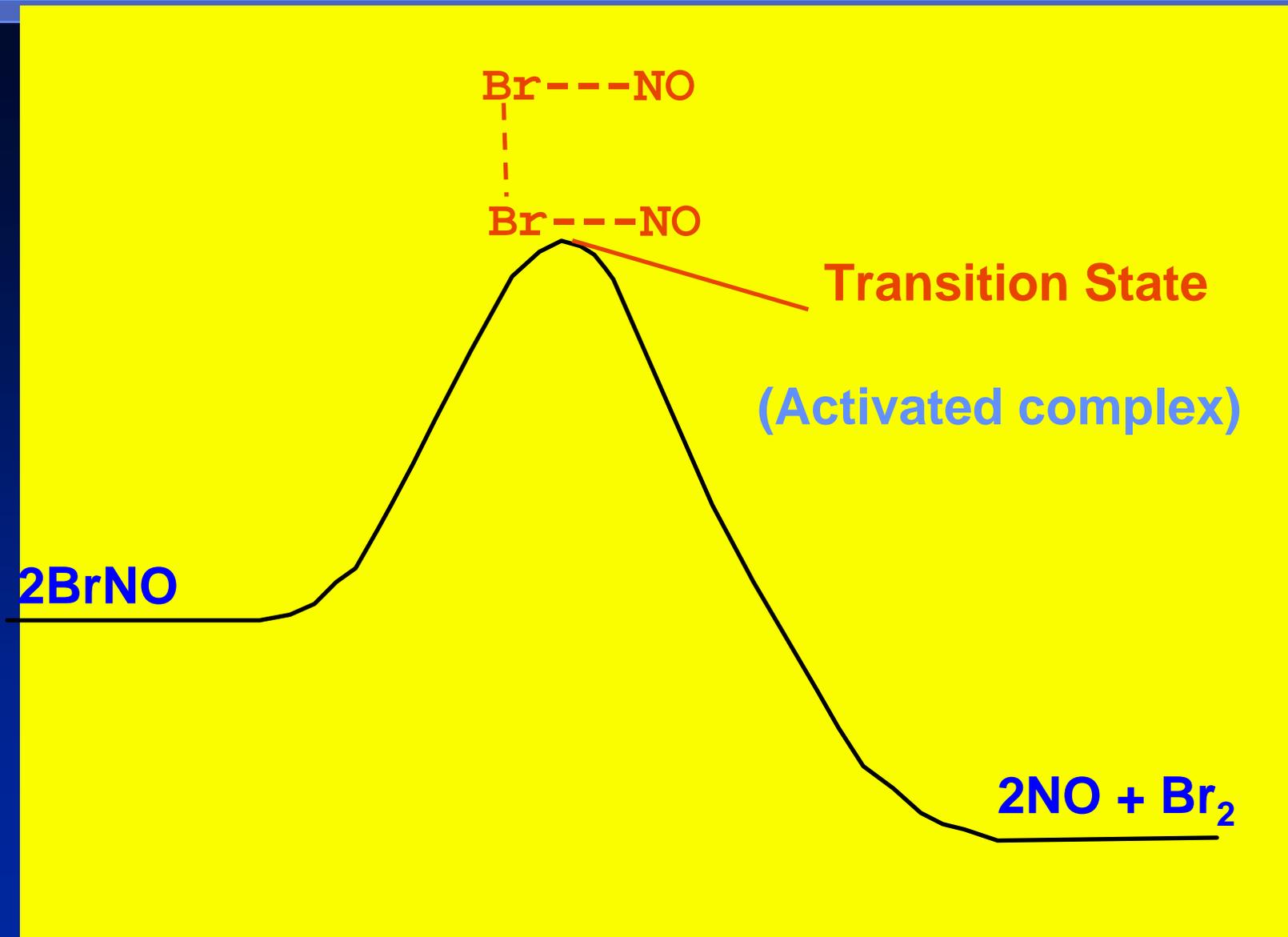
$$\Delta H = +ve; E_a > E_a'$$

- Consider the reaction

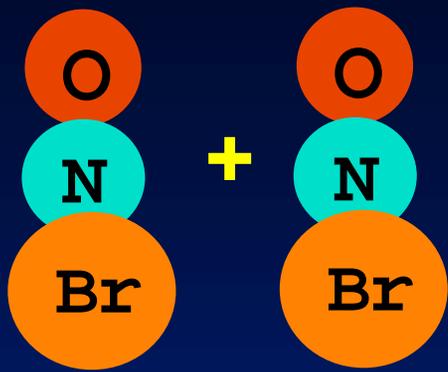


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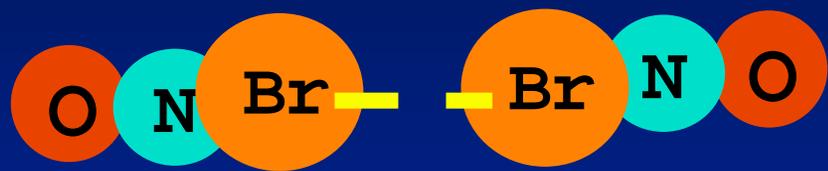
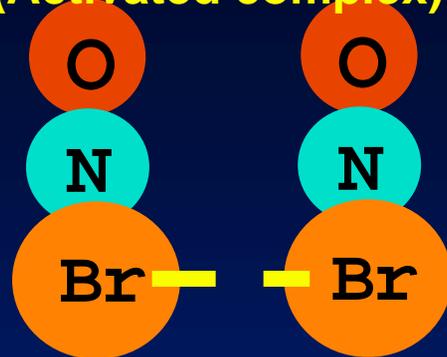
Reaction Coordinate



+



(Activated complex)



(Activated complex)

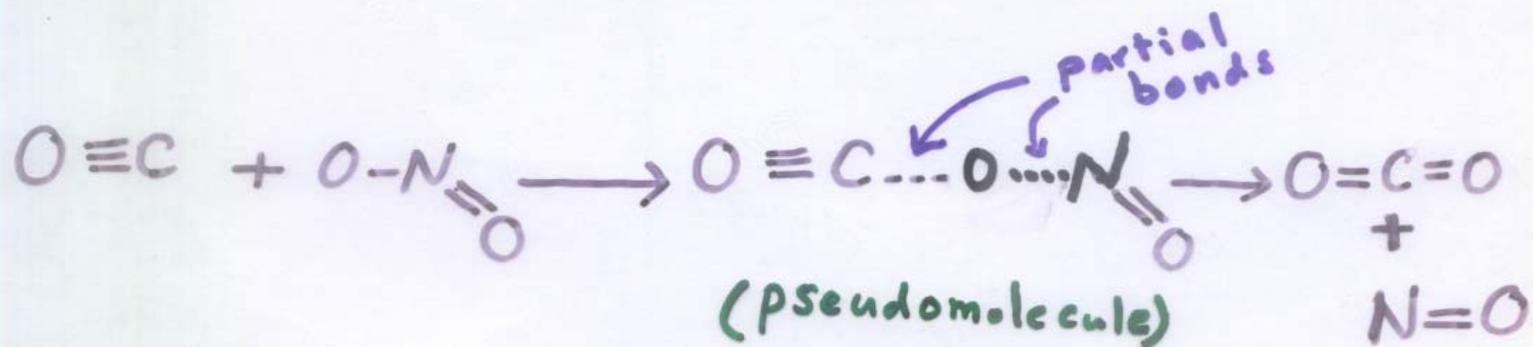


Br₂



2NO

Mechanism of the path of reaction



Reactants

$$E_a = +134 \text{ kJ}$$

Activated
Complex

$$\Delta H = 134 - 360 \\ = -226 \text{ kJ}$$

Products

$$E_a' = +360 \text{ kJ}$$

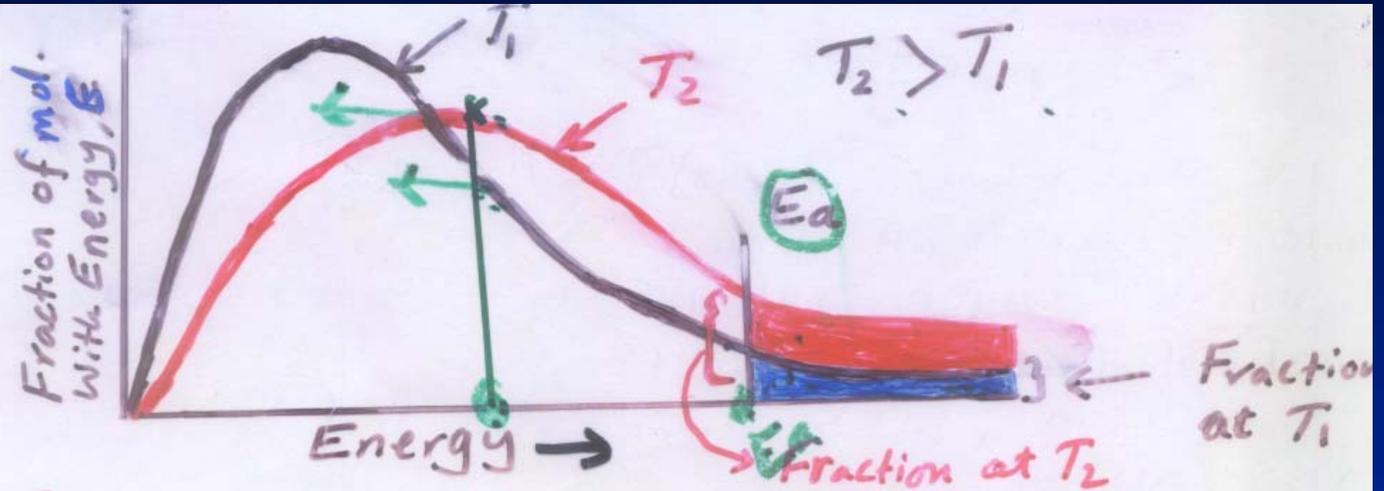
Characteristics of E_a

- E_a is independent of temperature
- E_a is a positive quantity, i.e., $E_a > 0$
- E_a depends upon the nature of reaction. That is :
 - **Fast reactions have small E_a**
 - **Slow reactions have large E_a**

Arrhenius Equation

- According to Arrhenius:
Reaction rate should increase with temperature.
- At high temperature more molecules have the energy required to get over the E_a barrier.
- The number of collisions with the necessary energy increases exponentially with temperature

Number of collisions



Generally : Rate is doubled For each 10°C increase in T

Reaction Rate and Temperature

- Rate of reaction is α Temperature (endo- and exothermic reactions)
- Pressure cooker is used to cook fast. High temp. is achieved
- Refrigerator is used to store food. Chemical reactions responsible for food spoilage are slowed down
- In general an increase of 10°C doubles the reaction rate

Arrhenius Equation

- ☞ Collisions must have enough energy to produce the reaction (must equal or exceed the activation energy).
- ☞ Orientation of reactants must allow formation of new bonds.

Arrhenius Equation

- Number of collisions with the required energy = $zpe^{-E_a/RT}$

- z = collision frequency (total # of collisions)
- p = steric factor that reflects the fraction of collisions with effective orientations
- E_a = activation energy
- R = ideal gas constant
- T is temperature in Kelvin

Problems

- Observed rate is less than the number of collisions that have the minimum energy?
- There are many inactive collisions; why?
- **Due to Molecular orientation**

Arrhenius Equation (continued)

$$k = A e^{-E_a / RT}$$

- A = *frequency factor (replaces zp factor)*
- k = rate constant
- E_a = activation energy
- T = temperature
- R = gas constant

Arrhenius equation

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

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

y  **b**  **slope**  **x** 

R : gas constant =
8.31 j/mol.K

$E_a = -R$ (slope)

To determine E_a :
Plot $\ln k$ versus $1/T$

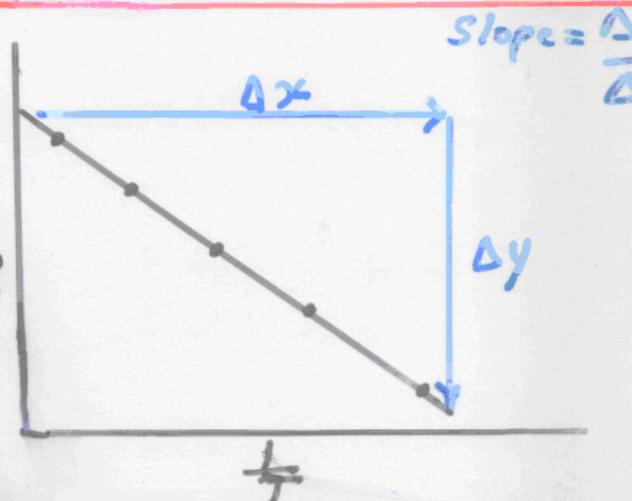
$$k = A e^{-E_a/RT}$$

$$\ln k = \ln A - \frac{E_a}{RT}$$

8.31 J/mol.K

Arrhenius equation

$\ln k$



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

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

Two point equation relating k and T

- Consider k_1 and k_2 at two temperatures T_2 and T_1

$$\ln k_2 = \ln A - \frac{Ea}{RT_2} \quad (1)$$

$$\ln k_1 = \ln A - \frac{Ea}{RT_1} \quad (2)$$

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

Subtract eq 2
from eq 1

$$\ln \frac{k_2}{k_1} = \frac{Ea}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] = \ln \frac{Rate_2}{Rate_1}$$

For a certain reaction, the rate constant doubles when the temperature increases from 15 to 25°C, Calculate

(a) The activation energy, E_a

$$\ln \frac{k_2}{k_1} = \ln \frac{2}{1} = \frac{E_a}{8.31} \left(\frac{298 - 288}{298 \times 288} \right)$$

$$E_a = 4.94 \times 10^4 \text{ J} = 49.4 \text{ kJ}$$

(b) The rate constant, k , at 100°C , taking k at 25°C to be $1.2 \times 10^{-2} \text{ L/mol}\cdot\text{s}$

$$\ln \frac{k_2}{k_1} = \frac{49,000 \text{ J/mol}}{8.31 \text{ J/mol}\cdot\text{K}} \left(\frac{373 \text{ K} - 298 \text{ K}}{373 \times 298} \right) = 3.98$$

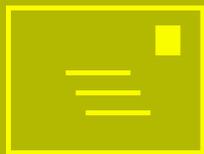
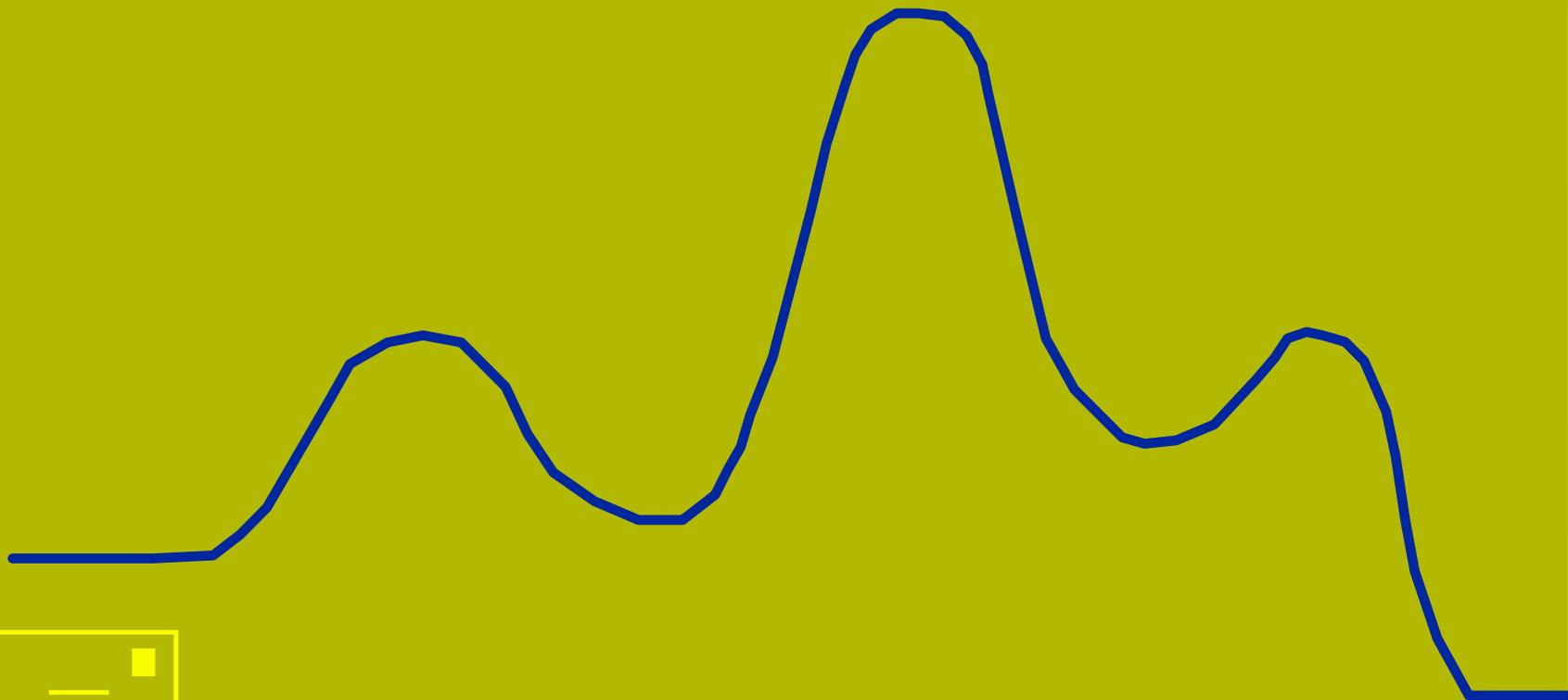
$$\frac{k_2}{k_1} = e^{3.98} = 53$$

$$\therefore k_2 = 53 (1.2 \times 10^{-2} \text{ L/mol}\cdot\text{s}) = 0.64 \text{ L/mol}\cdot\text{s}$$

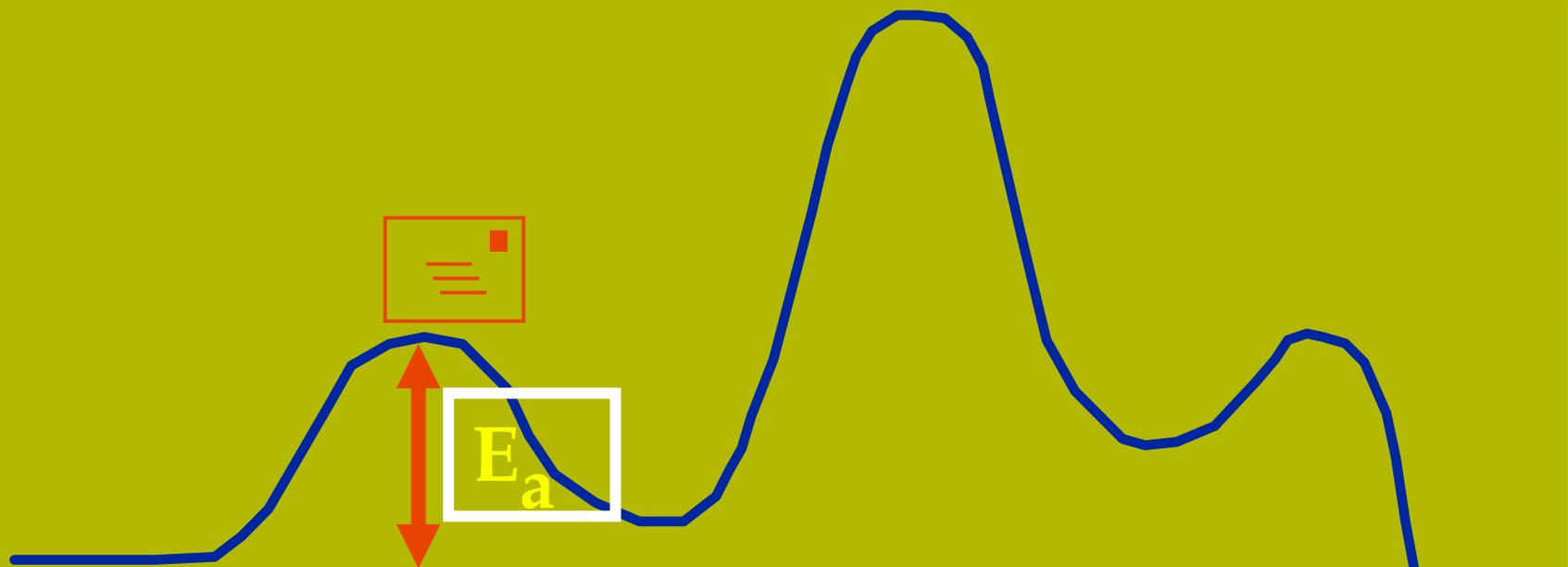
increase

Mechanisms and rates

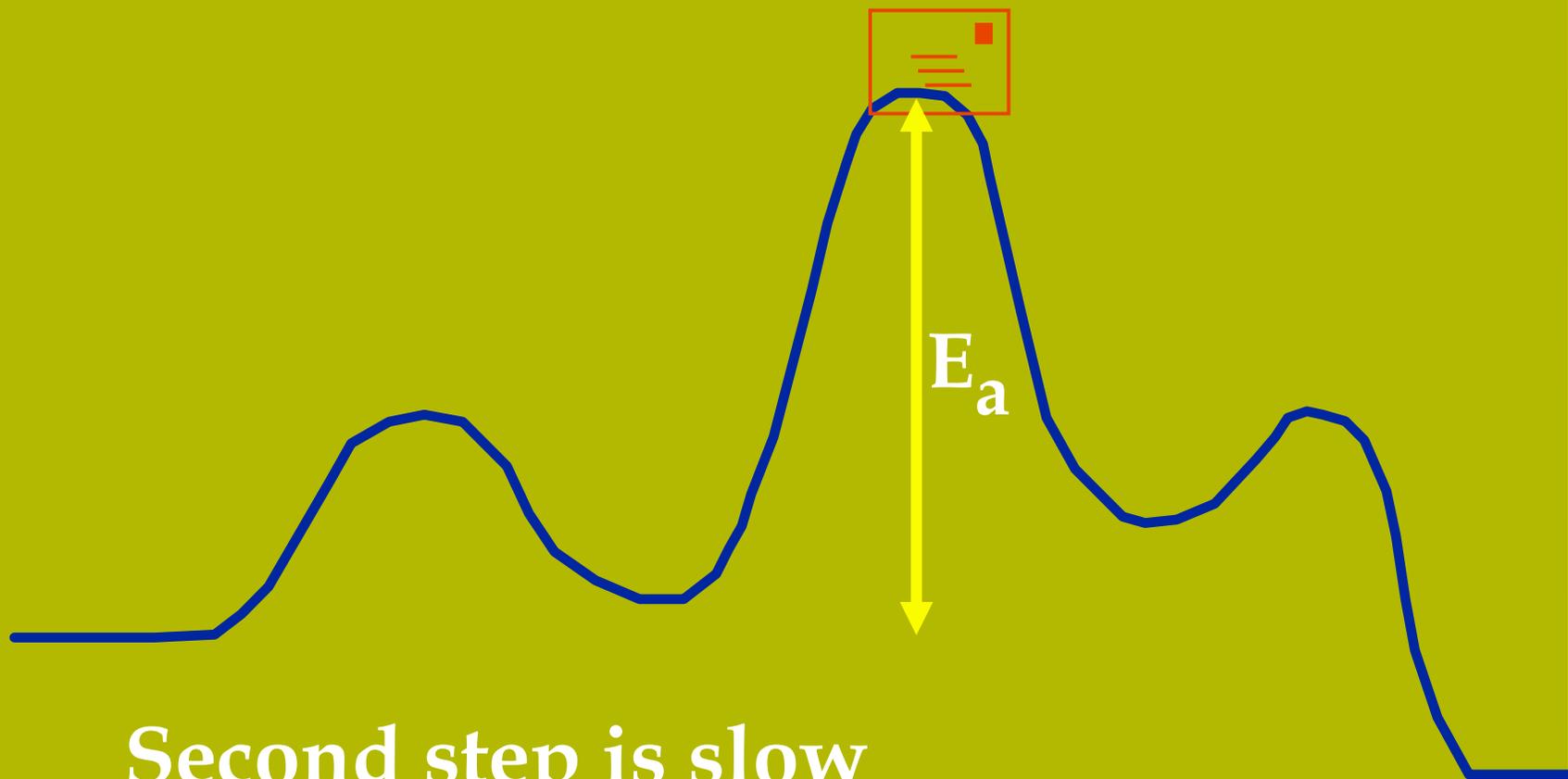
- There is an activation energy for each elementary step.
- Activation energy determines k .
- $k = Ae^{- (E_a/RT)}$
- k determines rate
- Slowest step (rate determining) must have the highest activation energy.



This reaction takes place in three steps



First step is fast
Low activation energy

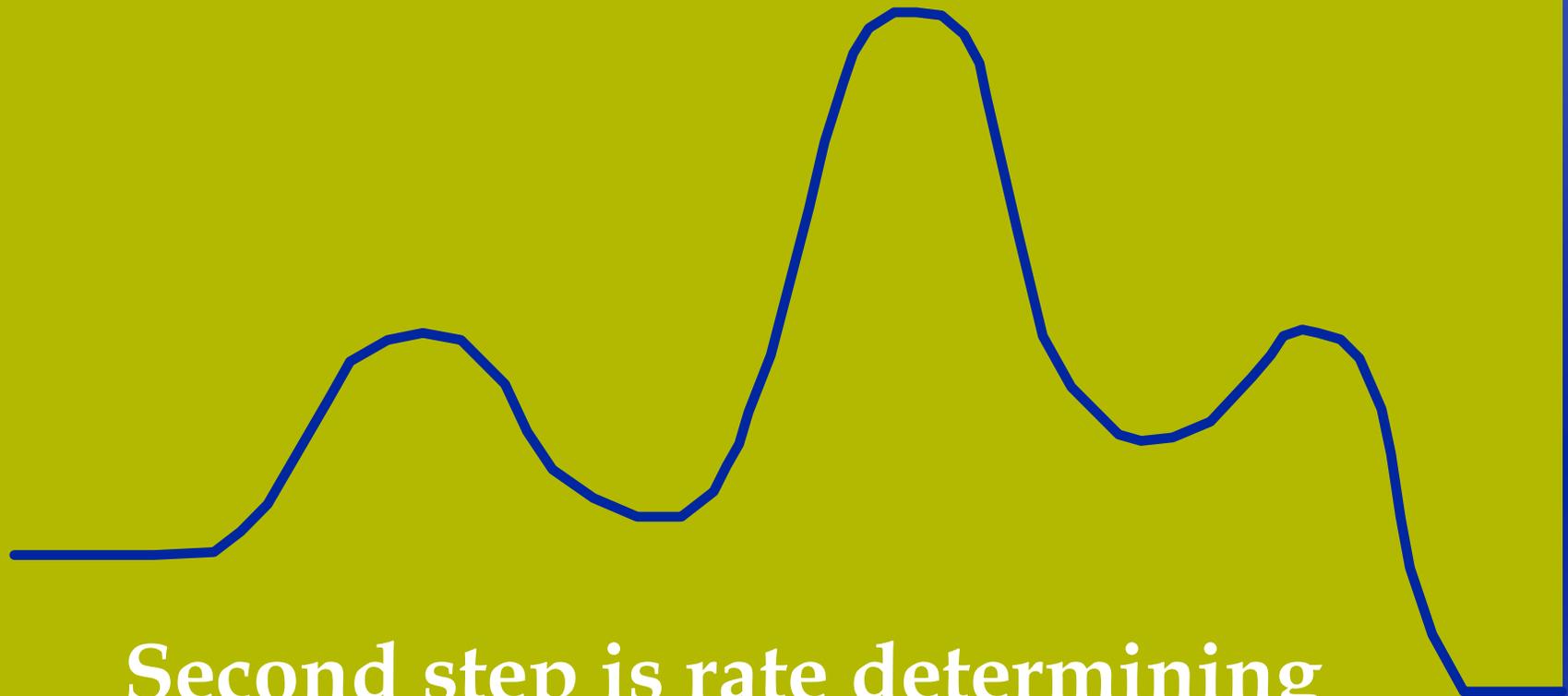


**Second step is slow
(High activation energy)**

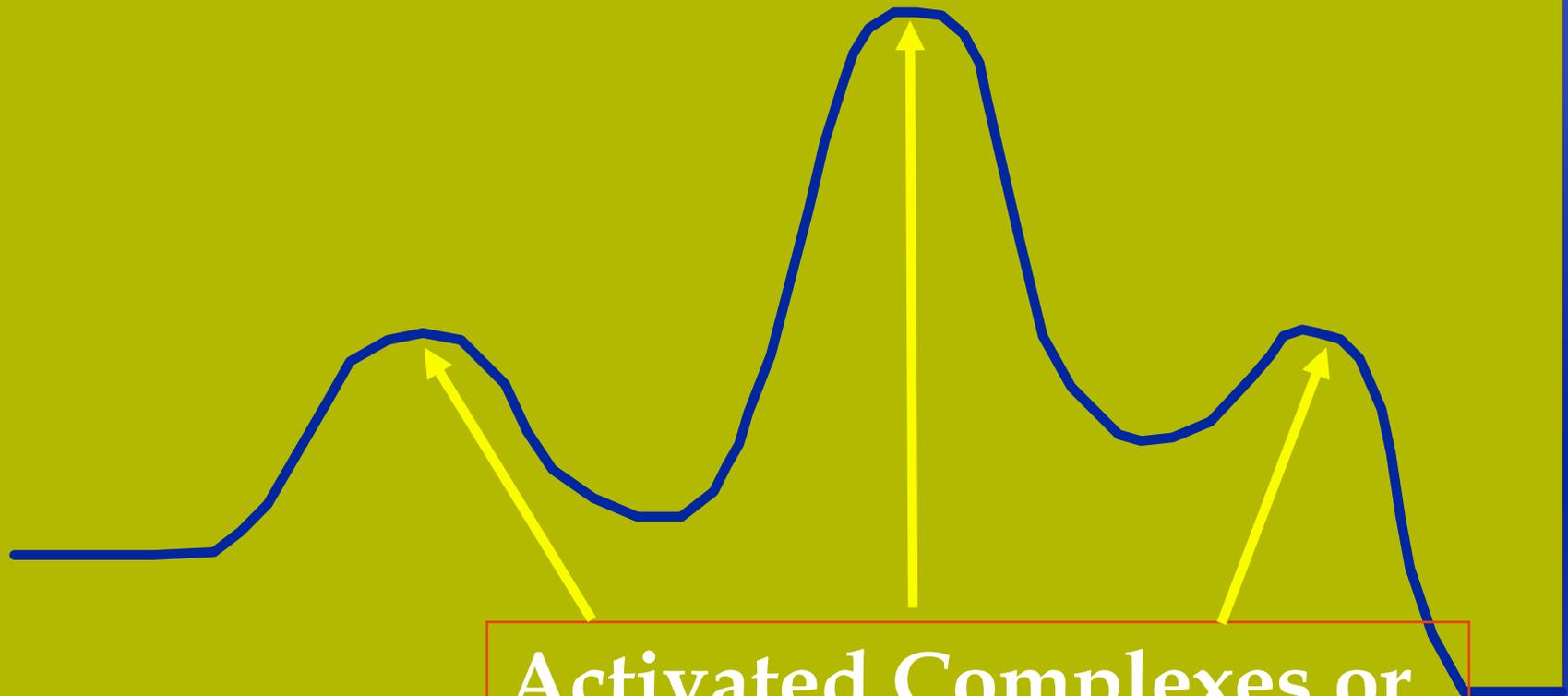


Third step is fast

Low activation energy



Second step is rate determining



**Activated Complexes or
Transition States**

12.8 Catalysis

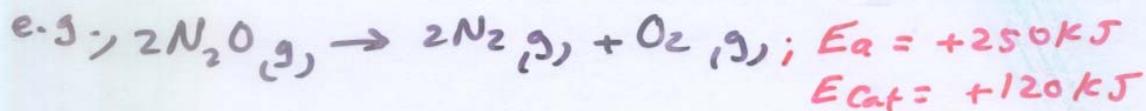
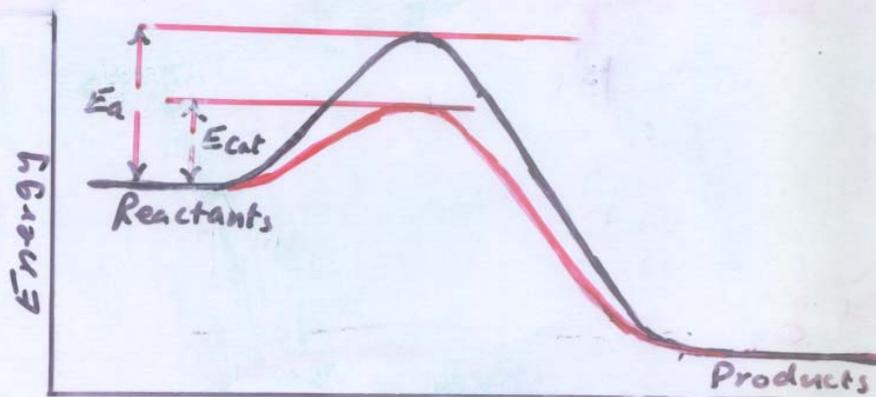
- A catalyst is a substance that speeds up a reaction without being used up in the reaction.
- Enzymes are biological catalysts.
- **Homogenous Catalysts** are in the same phase as the reactants.
- **Heterogeneous Catalysts** are in a different phase as the reactants.

How Catalysts Work

- Catalysts allow reactions to proceed by a different mechanism - a new pathway.
- New pathway has a lower activation energy.
- More molecules will have this activation energy.
- Do not change ΔE between reactants and products

How does the Catalyst function?

It lowers E_a ,
 $E_{cat.} < E_a$



* The catalyst provides an alternative pathway of lower energy for the reaction.

* Catalyst does not affect

(1) $E_{reactant}$ or $E_{product}$

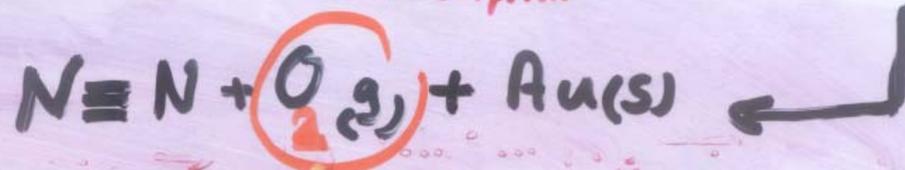
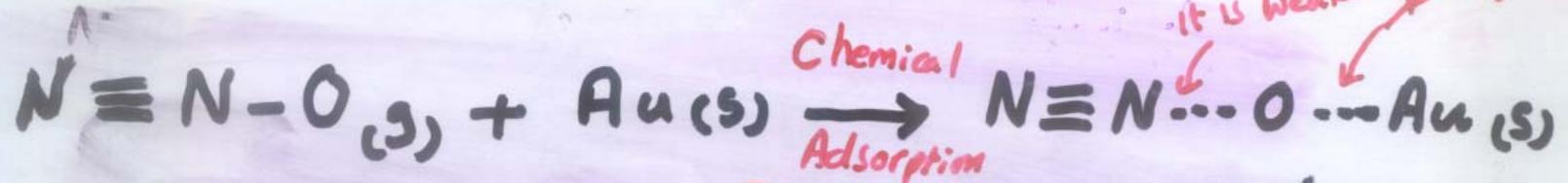
(2) The value of K_c or the position of equilibrium

(3) The yield of product

} It allows (only) reaching equilib. more rapidly

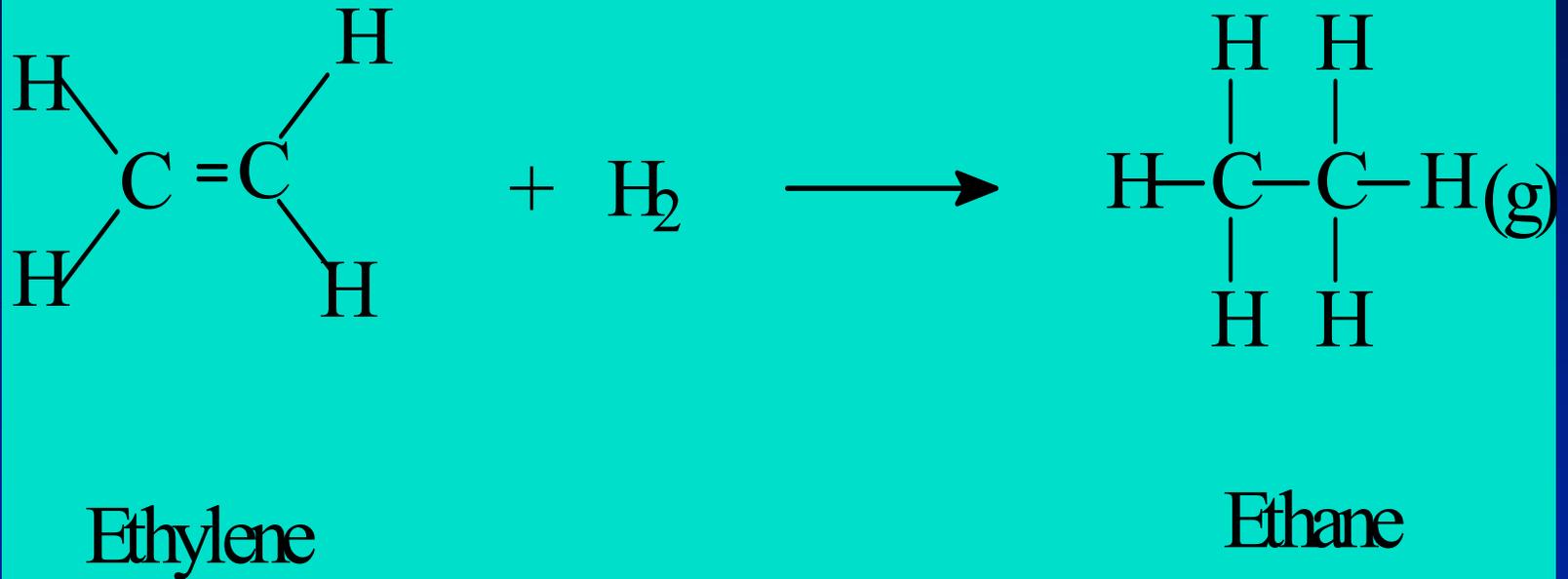
Heterogeneous catalyst

Mechanism of catalytic decomposition of N_2O on Au



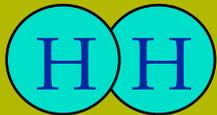
Heterogeneous catalysis

Hydrogenation of ethylene



Heterogenous Catalysts

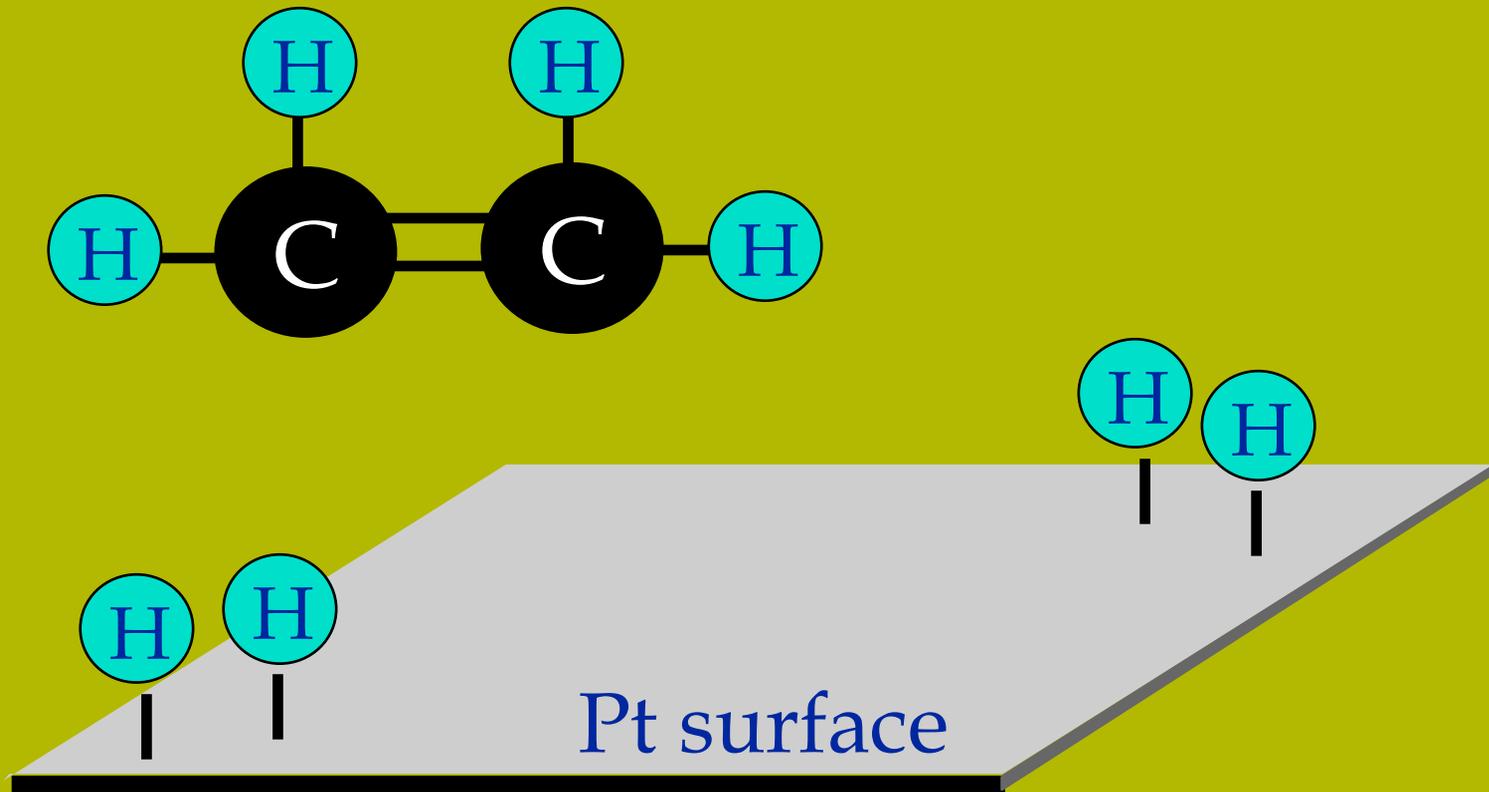
Hydrogenation of ethylene



- Hydrogen bonds to surface of metal.
- Break H-H bonds

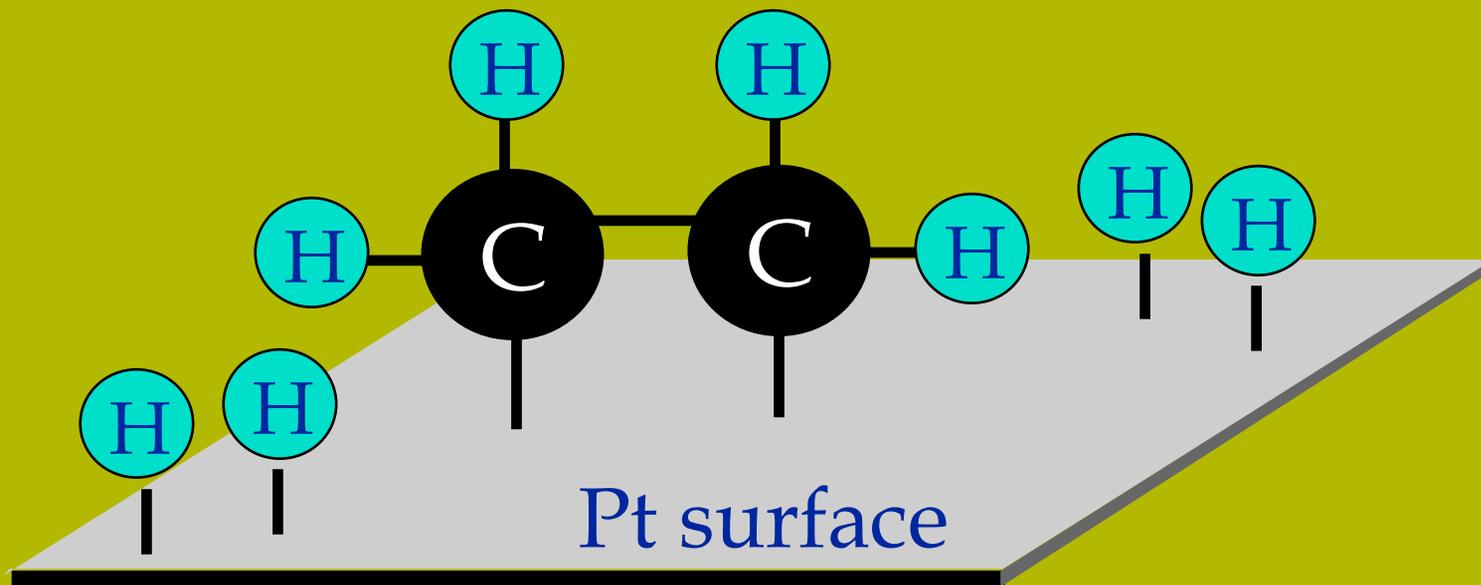


Heterogeneous Catalysts



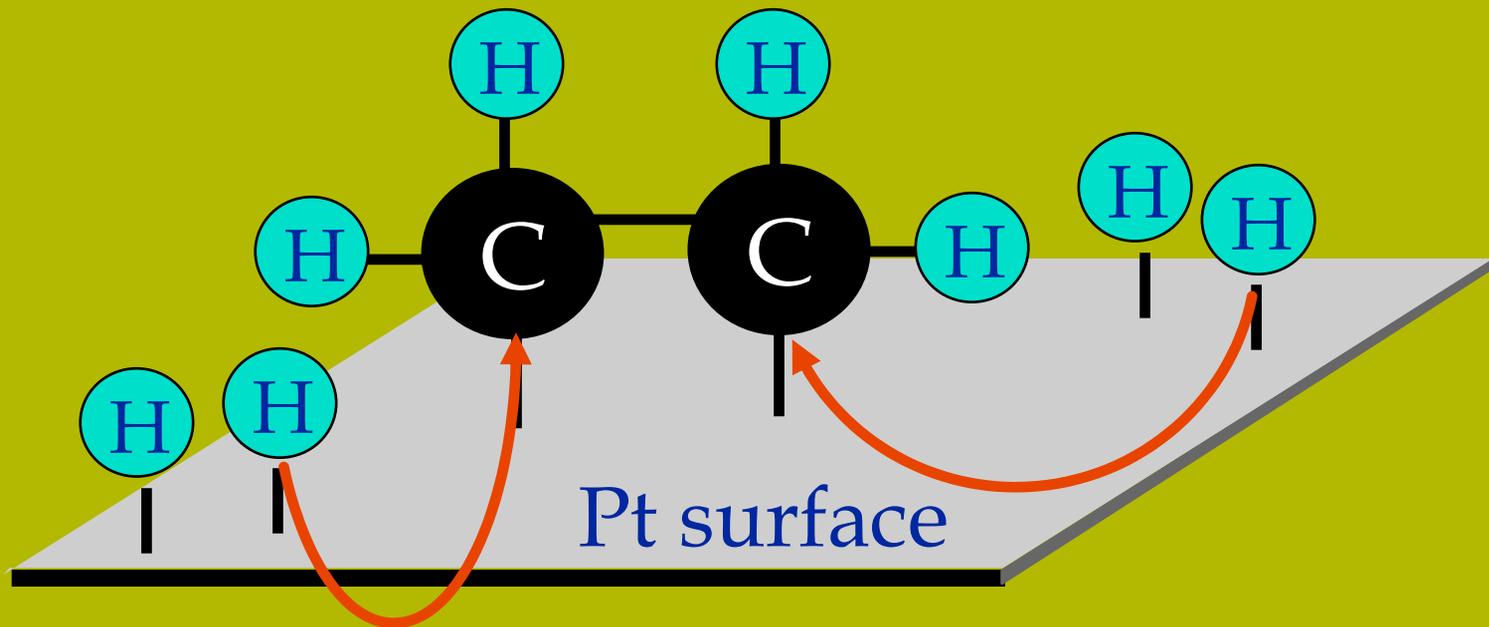
Heterogeneous Catalysts

- The double bond breaks and bonds to the catalyst.

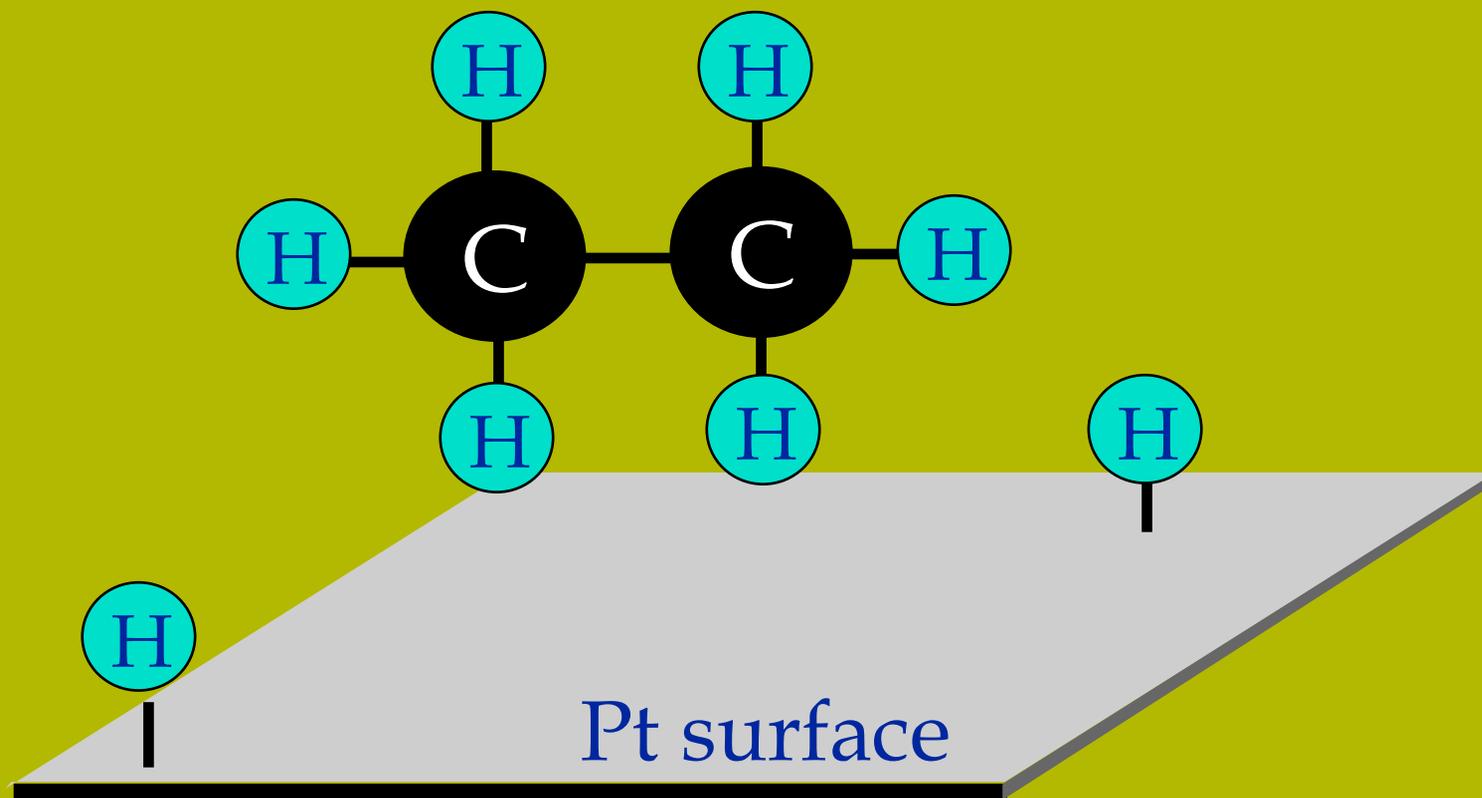


Heterogeneous Catalysts

- The hydrogen atoms bond with the carbon



Heterogeneous Catalysts



Catalysts and rate

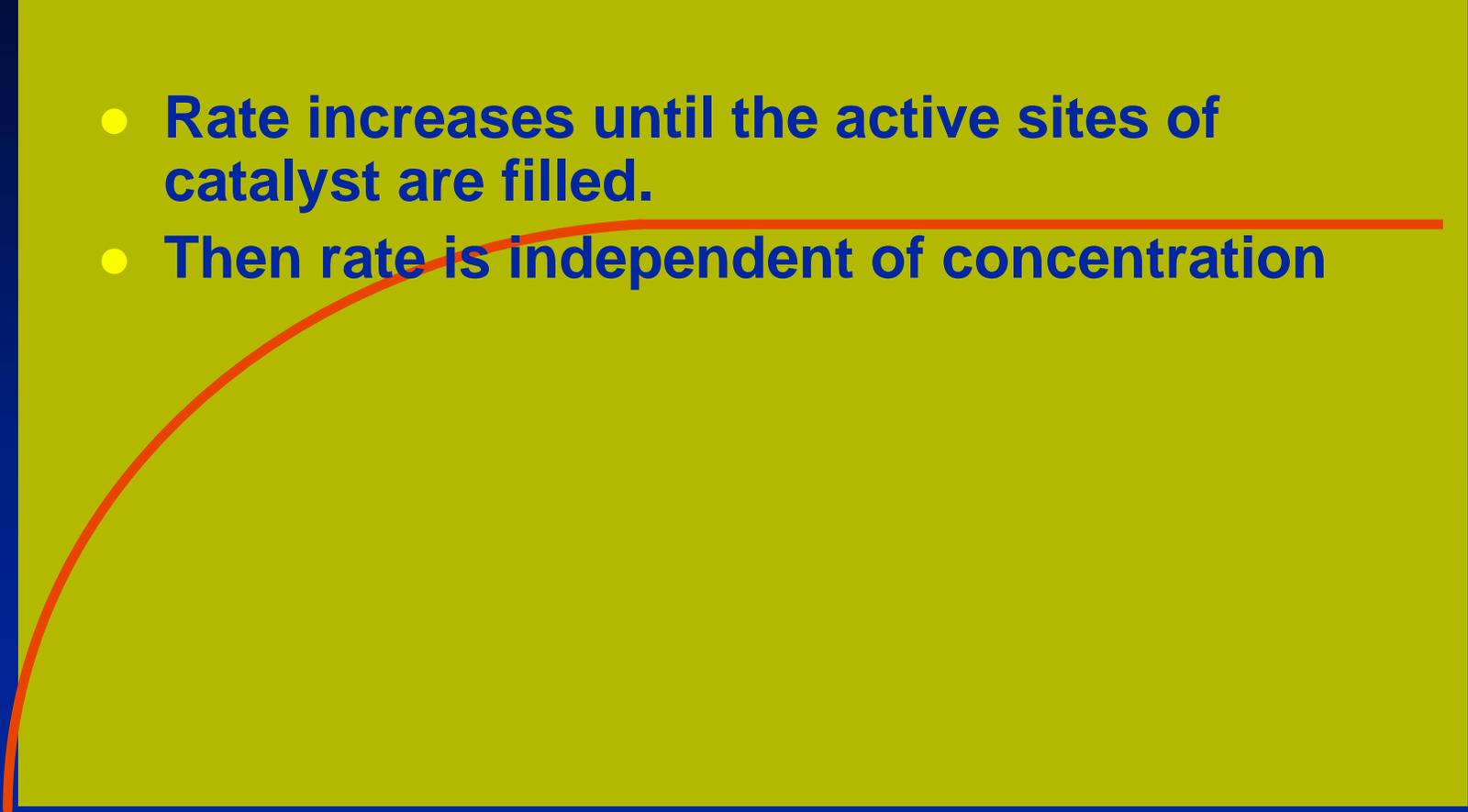
- Catalysts will speed up a reaction but only to a certain point.
- Past a certain point adding more reactants won't change the rate.
- Zero Order

Catalysts and rate.

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- Rate increases until the active sites of catalyst are filled.
- Then rate is independent of concentration

Concentration of reactants



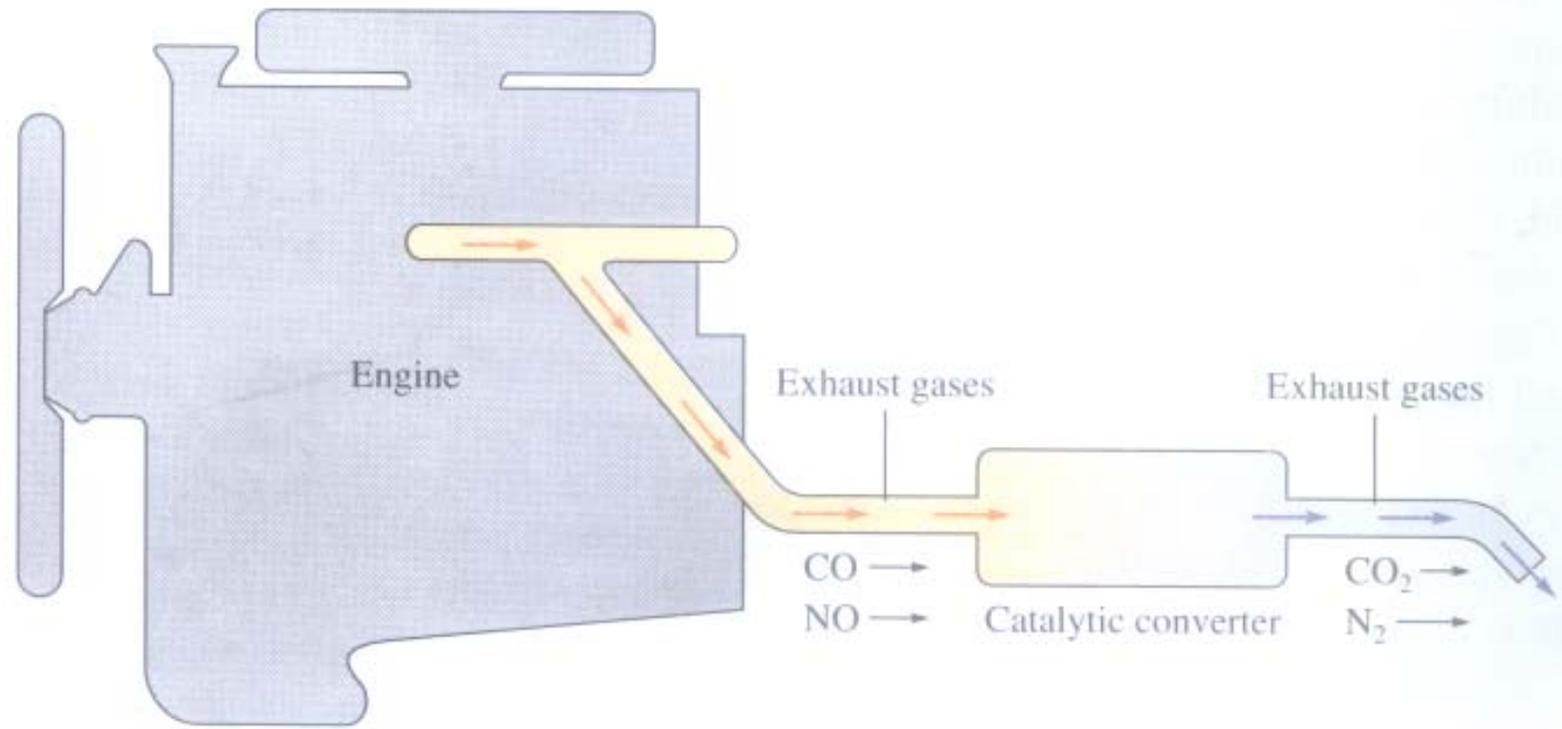
Negative effect of chemical catalysis



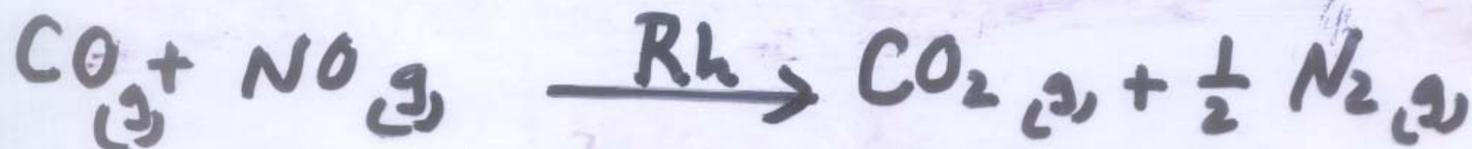
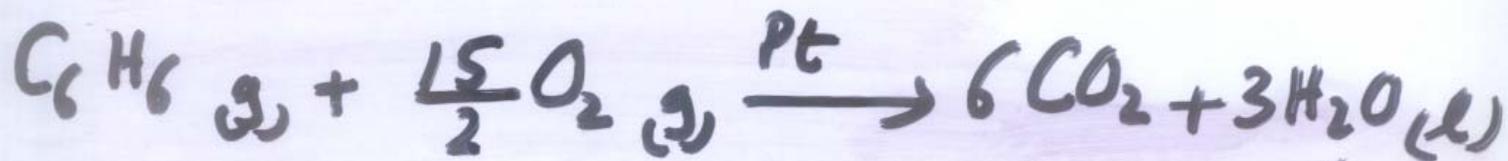
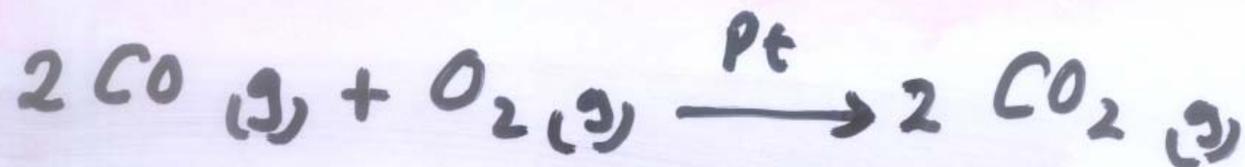
Catalytic converter in automobiles

- Nitrogen reacts with oxygen in a high temperature combustion process as follows:
- $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}(\text{g})$
- Nitric oxide, **NO** catalyzes ozone **production** in the troposphere (atmosphere closest to earth).
- **NO** catalyzes the **decomposition** of ozone in the upper atmosphere
- Both effects are unfortunate environmentally
- How do we prevent **NO** emission from vehicles?

Catalytic converter in automobiles



The mechanism is :



Problem: Solid Catalyst is easily "poisoned"

- Lead in the gasoline poisons the Pt-Rh catalyst.
- Thus Unleaded gasoline should be used.

Homogenous Catalysts in gases

- Homogeneous catalysts exist in the gaseous and liquid phases
- Nitrogen reacts with oxygen in a high temperature combustion process as follows:
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- Chlorofluorocarbons catalyze the decomposition of ozone.
- Enzymes regulating the body processes. (Protein catalysts)

Homogeneous catalysis in gases

Effect of ozone in the lower atmosphere

- Bonds in $\text{N}\equiv\text{N}$, $\text{O}=\text{O}$ are very strong at normal temperatures
- At significantly high temperatures (internal combustion engine of automobiles) NO is formed. Most of it is converted back to N_2 but some escapes; where does it go? Atmosphere
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$
 $\text{NO}_2(\text{g}) \xrightarrow{\text{Light}} \text{NO}(\text{g}) + \text{O}(\text{g})$
- $\text{O}_2(\text{g}) + \text{O}(\text{g}) \longrightarrow \text{O}_3(\text{g})$
- NO acts as a catalyst; it assists production of ozone without being consumed (Book p. 594)

Effect of NO in the upper atmosphere



Effect of Freons on ozone layer

- Freons were used as refrigerants and propellants in aerosol
- Most common is CCl_2F_2 . They migrate eventually to upper atmosphere and decompose there by the high energy of light

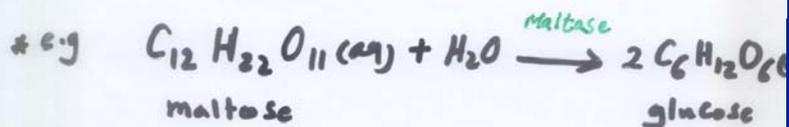


Enzymes

Reactions in living organisms are catalyzed by enzymes.

* Enzymes: protein molecules of high molar mass.

* e.g., decomposition of H_2O_2



* Without enzyme, more than 50 years may be required to digest a meal.