

Chemistry 1B, Fall 2016  
Topics 21-22

**Chemistry 1B**

**Fall 2016**

Topics 21-22  
Chemical Kinetics

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*STRUCTURE and DYNAMICS*

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Chemistry 1B so far: **STRUCTURE**  
of atoms and molecules



Chemistry 1B now: **DYNAMICS**  
chemical kinetics



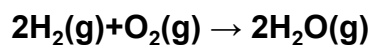
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# Chemistry 1B, Fall 2016

## Topics 21-22

thermodynamics (chem 1C, 163B) and kinetics (chem 1B, 163C)

Thermodynamics: Whether a reaction will occur  
?? spontaneously  
and "how far" it will proceed  
[*equilibrium conditions*]



$$\Delta H = -484 \text{ kJ} \quad \text{very exothermic}$$

equilibrium  
chem 1A-1C

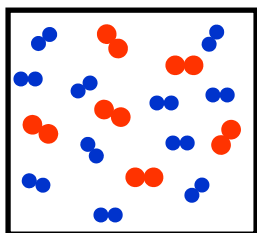
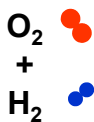
$$K_p = \frac{\left(\frac{P_{\text{H}_2\text{O}}}{1 \text{ atm}}\right)^2}{\left(\frac{P_{\text{H}_2}}{1 \text{ atm}}\right)^2 \left(\frac{P_{\text{O}_2}}{1 \text{ atm}}\right)} = 2 \times 10^{80}$$

'all' products at equilibrium

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thermodynamics (chem 1C, 163B) and kinetics (chem 1B, 163C)

HOWEVER:



nada (no reaction)  
almost forever

Kinetics: How **fast** a reaction proceeds, and  
the molecular steps involved in a  
reaction [*the mechanism of a reaction*].

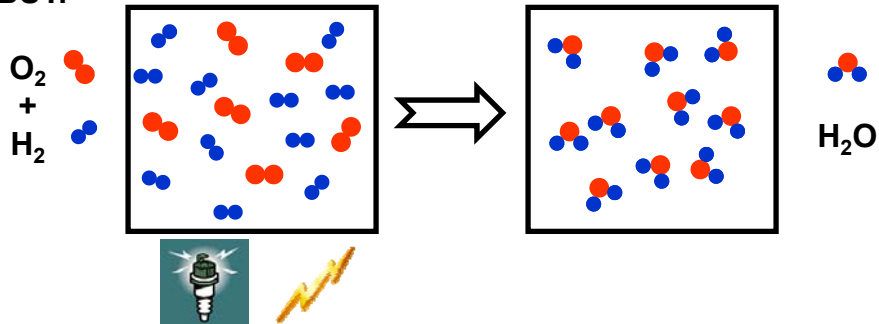
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# Chemistry 1B, Fall 2016

## Topics 21-22

*thermodynamics (chem 1C, 163B) and kinetics (chem 1B, 163C)*

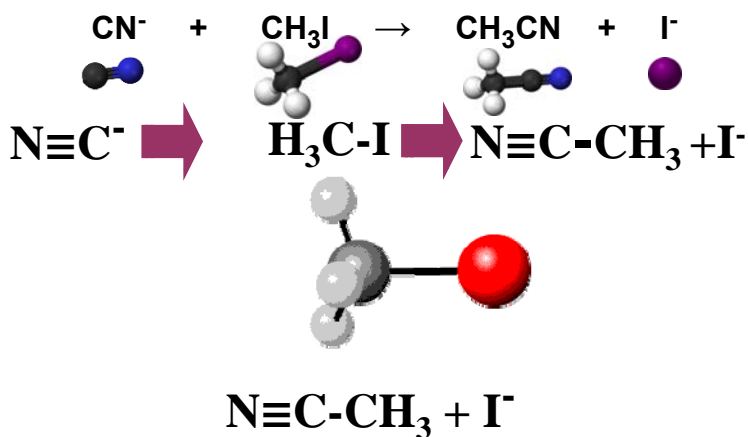
**BUT:**



Kinetics: How **fast** a reaction proceeds, and the molecular steps involved in a reaction [*the mechanism of a reaction*].

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*chemical kinetics (chapter 15)*



Kinetics: How **fast** a reaction proceeds, and the molecular steps involved in a reaction [*the mechanism of a reaction*].

[http://www.bluffton.edu/~bergerd/classes/CEM221/sn-e/SN2\\_alternate.html](http://www.bluffton.edu/~bergerd/classes/CEM221/sn-e/SN2_alternate.html)

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# Chemistry 1B, Fall 2016

## Topics 21-22

### *specific objectives for final exam material*

- Concepts and definitions
  - Lecture notes
  - HW10 Z15.55, Z15.52, Z15.68
- Numerical Problem Solving
  - Lecture notes
  - HW10 Z15.17, Z15.20, Z15.57, Z15.73, Z15.82
- Graphical interpretations
  - Lecture notes
  - HW10 Z15.36a, Z15.81

HW10 #67, S19-S20

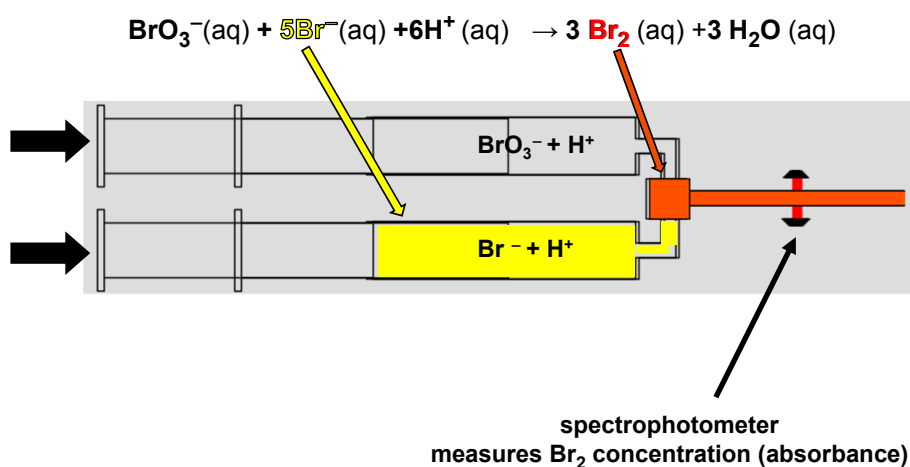
HW10 #64, #65, #68, #69, #71

HW10 #66, #70

**HW#10 DUE SUNDAY, 4<sup>th</sup> DECEMBER (last WebAssign)**

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### *measuring how fast a reaction goes*

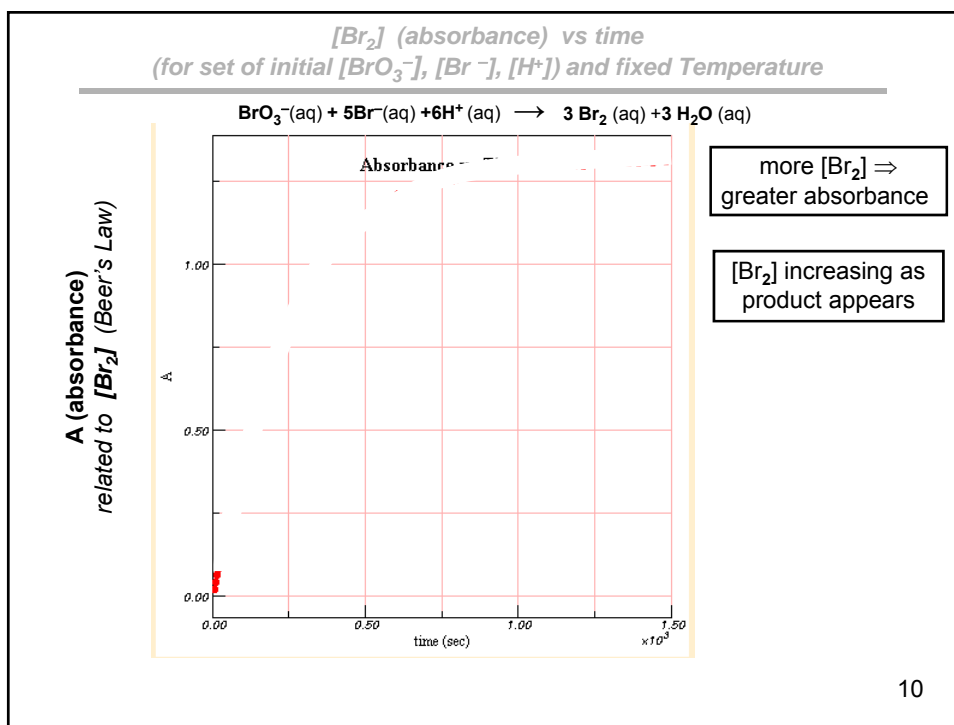
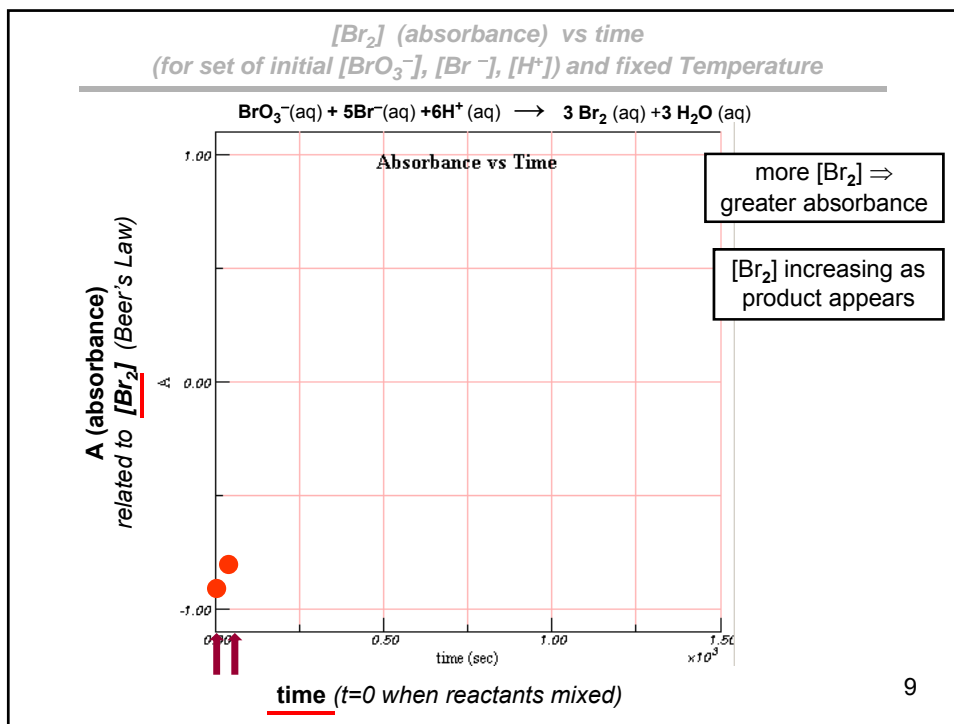


<http://www.chm.davidson.edu/vce/kinetics/BromateBromideReaction.html>

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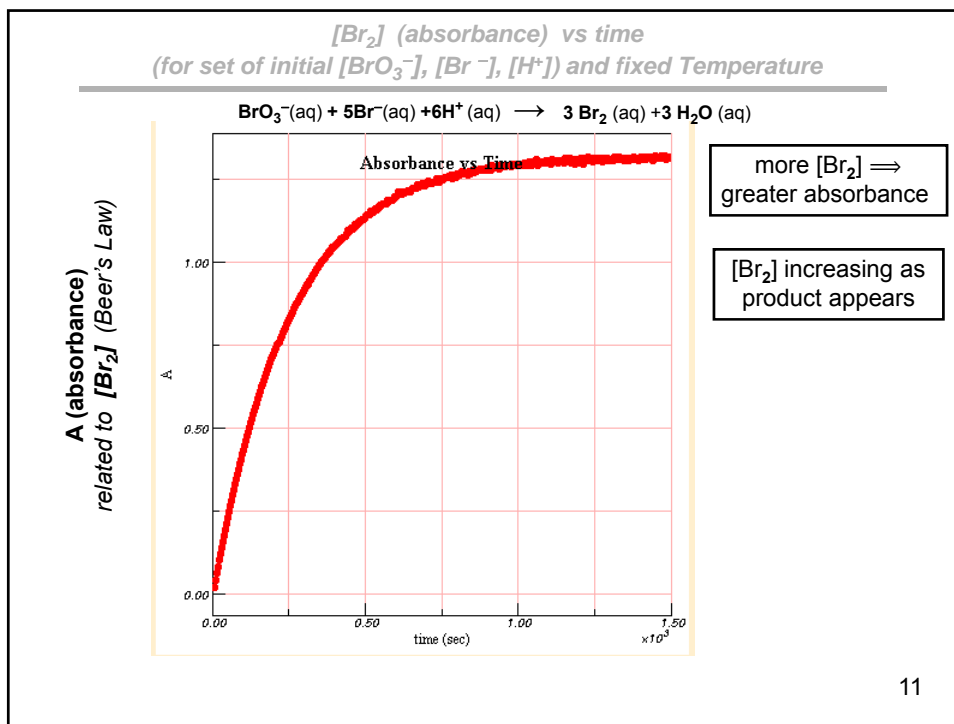
# Chemistry 1B, Fall 2016

## Topics 21-22



# Chemistry 1B, Fall 2016

## Topics 21-22



*Zumdahl Sec.15.1*

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**2NO<sub>2</sub>(g) → 2NO(g) + O<sub>2</sub>(g)**

**TABLE 15.1**  
Concentrations of Reactant and Products as a Function of Time for the Reaction 2NO<sub>2</sub>(g) → 2NO(g) + O<sub>2</sub>(g) (at 300°C)

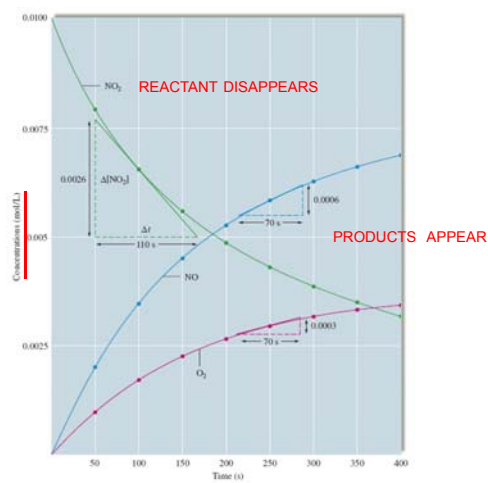
Time (±1 s)	Concentration (mol/L)		
	NO <sub>2</sub>	NO	O <sub>2</sub>
0	0.0100	<u>0</u>	<u>0</u>
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

t=0  
only reactant

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# Chemistry 1B, Fall 2016 Topics 21-22

Zumdahl section 15.1



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*DIFFERENTIAL rate of chemical reaction (appearance of product)*



reaction rate: [disappearance of  $\text{NO}_2(\text{g})$ ] =  $-\frac{\text{change of } [\text{NO}_2]}{\text{change of time}} = -\frac{\Delta[\text{NO}_2]}{\Delta t}$

DIFFERENTIAL reaction rate =  $\lim_{\Delta t \rightarrow 0} -\frac{\Delta[\text{NO}_2]}{\Delta t} = -\frac{d[\text{NO}_2]}{dt}$

**TABLE 15.1**  
Concentrations of Reactant and Products as a Function of Time for the Reaction  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  (at  $300^\circ\text{C}$ )

Time ( $\pm 1$ s)	Concentration (mol/L)		
	$\text{NO}_2$	$\text{NO}$	$\text{O}_2$
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“initial rate” at  $t=0$  ( $0 \rightarrow 50$  s)

$$\Delta t = t_2 - t_1 = (50 - 0)\text{s} = 50\text{s}$$

$$-\Delta[\text{NO}_2] = -(0.0079 - 0.0100)\text{ mol/L} = 0.0021\text{ mol/L}$$

$$\text{rate} \approx -\frac{\Delta[\text{NO}_2]}{\Delta t} = \frac{0.0021}{50}\text{ mol L}^{-1}\text{s}^{-1} = 4.2 \times 10^{-5}\text{ mol L}^{-1}\text{s}^{-1}$$

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# Chemistry 1B, Fall 2016

## Topics 21-22

*reaction rate changes as reaction proceeds (Z fig.15.1, Table 15.2)*

$$\text{reaction rate} = -\frac{d[\text{NO}_2]}{dt} = -(\text{slope of } [\text{NO}_2] \text{ vs } t)$$

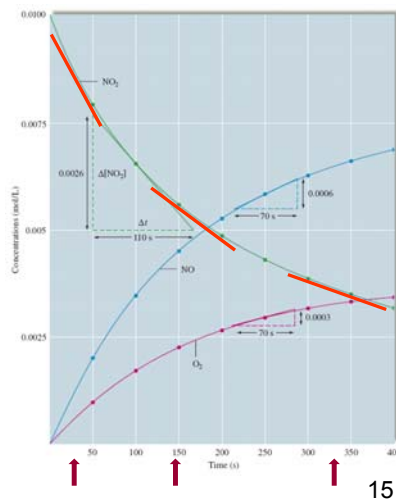
slope=tangent to curve

**TABLE 15.2**

Average Rate (in mol L<sup>-1</sup> s<sup>-1</sup>) of Decomposition of Nitrogen Dioxide as a Function of Time

$-\frac{\Delta[\text{NO}_2]}{\Delta t}$	Time Period (s)
$4.2 \times 10^{-5}$	0 → 50
$2.8 \times 10^{-5}$	50 → 100
$2.0 \times 10^{-5}$	100 → 150
$1.4 \times 10^{-5}$	150 → 200
$1.0 \times 10^{-5}$	200 → 250

Note: The rate decreases with time.



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*relations among rates of chemical reaction based on different components*



**TABLE 15.1**

Concentrations of Reactant and Products as a Function of Time for the Reaction  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  (at 300°C)

Time (±1 s)	Concentration (mol/L)		
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400	0.0031	0.0069	0.0035

in each  $\Delta t=50\text{s}$  interval

$$-\Delta[\text{NO}_2] = \Delta[\text{NO}] = 2\Delta[\text{O}_2]$$

disappearance NO <sub>2</sub>	appearance NO	appearance O <sub>2</sub>
----------------------------------	------------------	------------------------------

-0.021	0.021	0.011
mol L <sup>-1</sup> at t=0		

$$-\frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{NO}]}{dt} = + \text{?} \frac{d[\text{O}_2]}{dt}$$



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# Chemistry 1B, Fall 2016

## Topics 21-22

*relations among rates of chemical reaction based on different components*



**TABLE 15.1**

Concentrations of Reactant and Products as a Function of Time for the Reaction  $2\text{NO}_2(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{O}_2(\text{g})$  (at 300°C)

Time ( $\pm 1$ s)	Concentration (mol/L)		
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in each  $\Delta t = 50\text{s}$  interval

$$-\Delta[\text{NO}_2] = \Delta[\text{NO}] = 2\Delta[\text{O}_2]$$

disappearance  
 $\text{NO}_2$

appearance  
 $\text{NO}$        $\text{O}_2$

-0.021	0.021	0.011
$\text{mol L}^{-1}$ at $t=0$		

$$-\frac{d[\text{NO}_2]}{dt} = +\frac{d[\text{NO}]}{dt} = +\mathbf{2} \frac{d[\text{O}_2]}{dt}$$

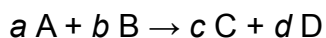
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*rate will (may) generally depend on concentrations*

higher concentrations  $\Rightarrow$  more collisions

more collisions  $\Rightarrow$  more reactions occurs

rate depends on concentrations



$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^m[\text{B}]^n$$

rate constant for a given Temperature

concentrations of reactants  
each raised to a power  
(usually integers)

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# Chemistry 1B, Fall 2016

## Topics 21-22

### generalized (differential) rate expression



general differential rate expression (can get more complicated):

$$-\frac{d[A]}{dt} = k_f [A]^m [B]^n - k_r [C]^k [D]^l$$

forward rate (loss of [A])  
k<sub>f</sub> rate constant of forward reaction

reverse rate (increase of [A])  
k<sub>r</sub> rate constant of reverse reaction

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### initial (differential) rate expression



$$-\frac{d[A]}{dt} = k_f [A]^m [B]^n - k_r [C]^k [D]^l$$

**INITIAL RATE** (initially only reactants present):

$$\begin{array}{l} [A]_0, [B]_0 \neq 0 \\ [C]_0, [D]_0 = 0 \end{array} \quad -\frac{d[A]_0}{dt} = k [A]_0^m [B]_0^n$$

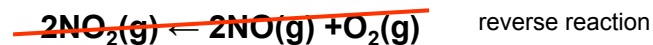
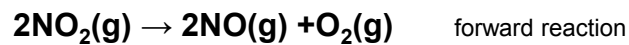
- k is rate constant (for eqn written as disappearance of A)
  - **DEFINITION OF RATE ORDER** rate is:
    - m<sup>th</sup> order in reactant [A]
    - n<sup>th</sup> order in reactant [B]
- Note: Only in certain instances (discuss soon) will the order of a reactant or product (m,n) be the same as its stoichiometric coefficient (a,b)*
- overall rate order is [m + n]<sup>th</sup> order (i.e. total order of reaction rate) 20

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*rate laws: initial rate*

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initial rate:

- only reactants present
- $[\text{NO}]_0 = [\text{O}_2]_0 = 0$
- no reverse reaction

$$-\frac{d[\text{NO}_2]_0}{dt} = k[\text{NO}_2]_0^n$$

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*skills for HW and final (HW10 #64-#65)*

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### **DIFFERENTIAL RATE EXPRESSIONS**

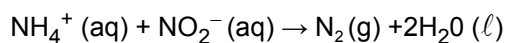
- Write rate expression in terms of reactant concentrations
- Determine order for each reactant from initial rate data
- Determine overall rate order
- Determine rate constant

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## Topics 21-22

*determining rate order from initial rate (table 15.4 p 723 Z)*



$$-\frac{d[\text{NH}_4^+]}{dt} = k [\text{NH}_4^+]_0^m [\text{NO}_2^-]_0^n \quad \text{differential initial rate}$$

**TABLE 15.4**

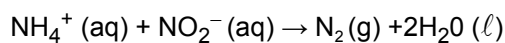
Initial Rates from Three Experiments for the Reaction  $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$

Experiment	Initial Concentration of $\text{NH}_4^+$	Initial Concentration of $\text{NO}_2^-$	Initial Rate ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	0.100 M	0.0050 M	$1.35 \times 10^{-7}$
2	0.100 M	0.010 M	$2.70 \times 10^{-7}$
3	0.200 M	0.010 M	$5.40 \times 10^{-7}$

to determine the order in a reactant (e.g. m or n):  
**identify two initial conditions (experiments) where the concentration of only one reactant has changed**

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*determining rate order from initial rate (table 15.4 p 723 Z)*



$$-\frac{d[\text{NH}_4^+]}{dt} = k [\text{NH}_4^+]_0^{m=1} [\text{NO}_2^-]_0^{n=1}$$

**TABLE 15.4**

Initial Rates from Three Experiments for the Reaction  $\text{NH}_4^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$

Experiment	Initial Concentration of $\text{NH}_4^+$	Initial Concentration of $\text{NO}_2^-$	Initial Rate ( $\text{mol L}^{-1} \text{s}^{-1}$ )
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3	0.200 M	0.010 M	$5.40 \times 10^{-7}$

$$(x \text{ rate}) = [x \text{ conc}]^n$$

$$(2) = (2)^1$$

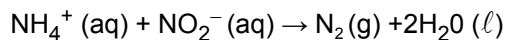
for  $[\text{NO}_2^-]^n$     1 vs 2:  $[\text{NH}_4^+]$  const, double  $[\text{NO}_2^-]$     rate doubles  $\Rightarrow n=1$   
 for  $[\text{NH}_4^+]^m$     2 vs 3:  $[\text{NO}_2^-]$  const, double  $[\text{NH}_4^+]$     rate doubles  $\Rightarrow m=1$

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# Chemistry 1B, Fall 2016

## Topics 21-22

### order of reaction



$$\text{initial rate of disappearance } [\text{NH}_4^+] = -\frac{d[\text{NH}_4^+]_0}{dt} = k[\text{NH}_4^+]_0^1[\text{NO}_2^-]_0^1$$

first order in  $[\text{NH}_4^+]$

first order in  $[\text{NO}_2^-]$

second order overall

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### given rate law: determine $k$ (rate constant) HW10 #64-65

Experiment	Initial Concentration of $\text{NH}_4^+$	Initial Concentration of $\text{NO}_2^-$	Initial Rate ( $\text{mol L}^{-1} \text{s}^{-1}$ )
1	0.100 M	0.0050 M	$1.35 \times 10^{-7}$
2	0.100 M	0.010 M	$2.70 \times 10^{-7}$
3	0.200 M	0.010 M	$5.40 \times 10^{-7}$

now that we know the order of the reaction  
to get  $k$  use any 'experiment' (or average of all)

$$\{\text{initial rate of disappearance of } \text{NH}_4^+\} = -\frac{d[\text{NH}_4^+]_0}{dt} = k[\text{NH}_4^+]_0^1[\text{NO}_2^-]_0^1$$

$$\text{from exp 1} \quad 1.35 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.100 \text{ mol L}^{-1})^1(0.0050 \text{ mol L}^{-1})^1$$

$$k = 2.70 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$$

$$\text{from exp 3} \quad 5.40 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1} = k(0.200 \text{ mol L}^{-1})^1(0.010 \text{ mol L}^{-1})^1$$

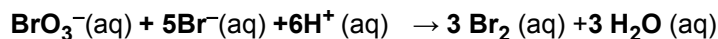
$$k = 2.70 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$$

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## Topics 21-22

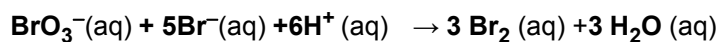
*more complicated*



*remember same reaction in stop-flow apparatus, earlier slide*

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*more complicated (see Table 15.5)*



**TABLE 15.5**  
The Results from Four Experiments to Study the Reaction  
 $\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\text{Br}_2(\text{l}) + 3\text{H}_2\text{O}(\text{l})$

Experiment	Initial Concentration of $\text{BrO}_3^-$ (mol/L)	Initial Concentration of $\text{Br}^-$ (mol/L)	Initial Concentration of $\text{H}^+$ (mol/L)	Measured Initial Rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.10	0.10	0.10	$8.0 \times 10^{-4}$
2	0.20	0.10	0.10	$1.6 \times 10^{-3}$
3	0.20	0.20	0.10	$3.2 \times 10^{-3}$
4	0.10	0.10	0.20	$3.2 \times 10^{-3}$

*from initial rate data determine n, m, and p*

$$\text{rate} = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-]^n[\text{Br}^-]^m[\text{H}^+]^p$$

$[\text{BrO}_3^-]^n$ : exp 1-2  $[\text{BrO}_3^-]$  doubles, rate x2  $\Rightarrow n=1$   
 $[\text{Br}^-]^m$ : exp 2-3  $[\text{Br}^-]$  doubles, rate x2  $\Rightarrow m=1$   
 $[\text{H}^+]^p$ : exp 1-4  $[\text{H}^+]$  doubles, rate x4  $\Rightarrow p=2$

$$2=[2]^1$$

$$(x \text{ rate})=[x \text{ conc}]^n$$

$$4=[2]^2$$



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# Chemistry 1B, Fall 2016

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### *order of the reaction*

---

$$\text{rate} = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2$$

first order in  $[\text{BrO}_3^-]$

first order in  $[\text{Br}^-]$

second order in  $[\text{H}^+]$

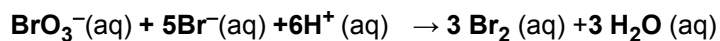
fourth order overall



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### *after determining order, evaluate rate constant*

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$$\text{rate} = -\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2$$

Experiment	Initial Concentration of $\text{BrO}_3^-$ (mol/L)	Initial Concentration of $\text{Br}^-$ (mol/L)	Initial Concentration of $\text{H}^+$ (mol/L)	Measured Initial Rate (mol $\text{L}^{-1}$ $\text{s}^{-1}$ )
1	0.10	0.10	0.10	$8.0 \times 10^{-4}$



$$\text{rate} = k \times (0.10 \text{ mol L}^{-1})^1 \times (0.10 \text{ mol L}^{-1})^1 \times (0.10 \text{ mol L}^{-1})^2 = 8.0 \times 10^{-4} \text{ L}^{-1} \text{ s}^{-1}$$

$$k = 8.00 \text{ L}^3 \text{ mol}^{-3} \text{ s}^{-1}$$

will be identical (within experimental) using any of the 'experiments'

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# Chemistry 1B, Fall 2016

## Topics 21-22

### *skills for HW and final*

---

#### differential rate expressions

- ✓ • Write rate expression in terms of reactant concentrations
- ✓ • Determine order for each reactant from initial rate data
- ✓ • Determine overall rate order
- ✓ • Determine rate constant

---

#### integral rate expression

- Determine order of reaction from plot of 'concentration' vs time
- Half-life of a reaction

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### *integrated rate expression*

---

differential rate gives **change** of reactant or product concentrations with time

$$\frac{d[\text{reactant}]}{dt} = \dots$$

integrated rate gives **value** of reactant or product concentrations with time

$$[\text{reactant}] = f(t)$$

from calculus  $x = \int dx$  and  $t = \int dt$   
                  ↑          ↓          ↑          ↓  
                  value  change  value  change

**INTEGRATE !!!**

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math 11 or 19

$$\int dt = ?$$

$$\int \frac{dx}{x} = ?$$

$$\int \frac{dx}{x^2} = ?$$

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integrated rate expression for **first-order reaction**

differential rate law:  $-\frac{d[A]}{dt} = k[A]$  **first order** disappearance of reactants

$$\frac{d[A]}{[A]} = -k dt$$

$$\int \frac{d[A]}{[A]} = -\int k dt$$

$$\ln[A] = \underbrace{-k t}_{\text{slope}} + \underbrace{C}_{\text{intercept}}$$

integrated rate law:  $\ln[A] = -k t + \ln[A]_0$  when  $t = 0$   $[A] = [A]_0$

**first order:** a plot of  $\ln[A]$  vs  $t$  would be a straight line with slope  $-k$  and intercept  $\ln [A]_0$

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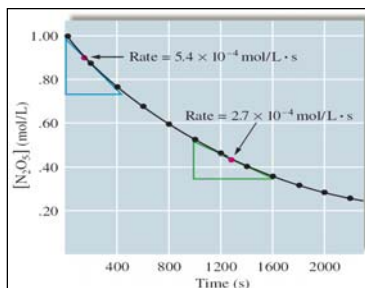
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## Topics 21-22

### *integrated first order reaction*



$$\text{rate} = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]^n$$



[N<sub>2</sub>O<sub>5</sub>] vs t

How could we tell  
if  $n=1$  (first order in  $\text{N}_2\text{O}_5$ )?  
[not using multiple experiments with various  
initial concentrations]

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### *integrated rate law (first-order)*

$$\ln[\text{N}_2\text{O}_5] = -kt + \ln[\text{N}_2\text{O}_5]_0 \quad (\text{if reaction is first order})$$

plot  $\ln[\text{N}_2\text{O}_5]$  vs t

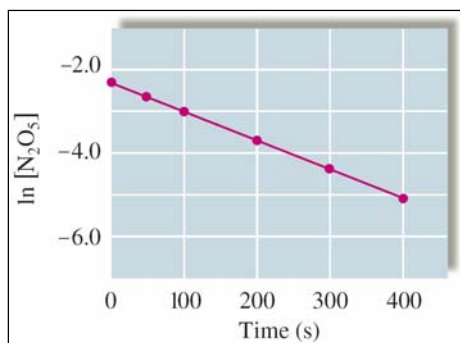
do we get straight line ??

(yes  $n=1$ , no  $n \neq 1$ )

**YES !!**

**$n=1$**

**it is first-order**



slope =  $-k$   
 $t=0$  intercept is  $\ln[\text{N}_2\text{O}_5]_0$

$$\text{rate} = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]^1$$

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## Topics 21-22

### other integrated rate laws

$$-\frac{d[A]}{dt} = k \quad \text{zero-th order reaction; differential rate law}$$

$$\int d[A] = -k \int dt \quad [A] = -kt + [A]_0 \quad \text{zeroth order reaction; integrated rate law}$$

plot  $[A]$  vs  $t$  gives straight line



$$-\frac{d[A]}{dt} = k[A]^2 \quad \text{second order reaction; differential rate law}$$

$$\int \frac{d[A]}{[A]^2} = -k \int dt \quad \frac{1}{[A]} = +kt + \frac{1}{[A]_0} \quad \text{second order reaction; integrated rate law}$$

plot  $[A]^{-1}$  vs  $t$  gives straight line

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### more complicated integrated rate laws (don't fret)

$$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-]^1[\text{Br}^-]^1[\text{H}^+]^2$$

more complicated to get integrated rate-laws for

rate expressions which depend on several reactant concentrations :

use  $[\text{Br}^-]_0$  and  $[\text{H}^+]_0 \gg [\text{BrO}_3^-]_0$  ; plot  $\ln [\text{BrO}_3^-]$  vs  $t$

$[\text{Br}^-]$  and  $[\text{H}^+]$  change relatively little (**constant**)

reaction 'pseudo' first-order; i.e.  $\text{rate} \approx (k [\text{Br}^-] [\text{H}^+]^2) [\text{BrO}_3^-]^1$

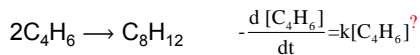
$$\approx \underbrace{\text{constant}}_{= (k [\text{Br}^-]_0 [\text{H}^+]_0^2)}$$

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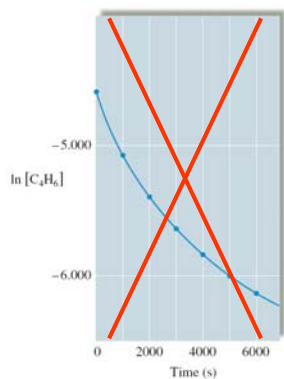
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## Topics 21-22

*first order or second order ??? Example 15.5 and (HW10 #66)*



same rate data plotted two ways



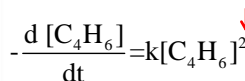
(a)  $\ln [\text{C}_4\text{H}_6]$  vs  $t$

straight line  $\Rightarrow$  first order



(b) or  $\frac{1}{[\text{C}_4\text{H}_6]}$  vs  $t$

straight line  $\Rightarrow$  second order



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$t_{1/2}$  half-life vs rate constant

time for concentration of reactant to drop by factor of 2

$$[A]_{t+t_{1/2}} = \frac{1}{2}[A]_t \quad \text{e.g. when half the original reactant left } [A]_{t_{1/2}} = \frac{1}{2}[A]_0$$

first-order reaction (e.g. radioactive decay)

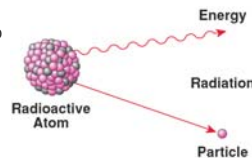
$$\ln[A]_t = -kt + \ln[A]_0 \quad \text{and} \quad \ln[A]_{t+t_{1/2}} = -k(t+t_{1/2}) + \ln[A]_0$$

$$\ln[A]_t - \ln[A]_{t+t_{1/2}} = \ln\left(\frac{[A]_t}{[A]_{t+t_{1/2}}}\right) = kt_{1/2}$$

$$\boxed{\frac{[A]_t}{[A]_{t+t_{1/2}}} = 2 \quad \text{def of } t_{1/2}}$$

$$\ln(2) = kt_{1/2}$$

$$\boxed{t_{1/2} = \frac{\ln(2)}{k} = \frac{0.693}{k} \quad \text{eqn 15.3}}$$



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## Topics 21-22

### $t_{1/2}$ half-life vs rate constant zero<sup>th</sup> and 2<sup>nd</sup> order

still the definition of half-life

time for concentration of reactant to drop by factor of 2

$$[A]_{t+t_{1/2}} = \frac{1}{2}[A]_t \quad \text{e.g. when half the original reactant left } [A]_{t_{1/2}} = \frac{1}{2}[A]_0$$

but:

order	0 <sup>th</sup>	1 <sup>st</sup>	2 <sup>nd</sup>
$t_{1/2}$	$\frac{[A]_{at\ t}}{2k}$	$\frac{0.693}{k}$	$\frac{1}{k[A]_{at\ t}}$

larger  $k \Rightarrow$  shorter  $t_{1/2}$

only for 1<sup>st</sup> order is the half the same throughout the reaction (*independent of the 'current' concentration of [A]*)

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### summary (also understand section 15.5; 1-5, 6\*)

**TABLE 15.6**

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 the straight line	Slope = $-k$	Slope = $-k$	Slope = $k$
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

know how to use; all needed formulas given on exam

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## Topics 21-22

Chemistry 1B  
SAMPLE FINAL EXAMINATION QUESTIONS

$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$   
 $c = 3.000 \times 10^8 \text{ m/s}$   
 $m_e = 9.109 \times 10^{-31} \text{ kg}$   
 $m_p = 1.672 \times 10^{-27} \text{ kg}$

$R = 8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   
 $R = 0.08206 \text{ L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

$\bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$   
 $\frac{1}{\lambda} = Z^2 (1.097 \times 10^7 \text{ m}^{-1}) \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad n_2 > n_1$

$(m\Delta u) \Delta x \geq \frac{h}{4\pi}$   
 $E_n = -\left(2.18 \times 10^{-18} \text{ J}\right) \frac{Z^2}{n^2}$   
 $r_n = \left(5.29 \times 10^{-12} \text{ m}\right) \frac{n^2}{Z}$

**wavelength range of visible light:**  
 $\lambda \approx 3.8 \times 10^{-7} \text{ m to } 7.0 \times 10^{-7} \text{ m}$

**Integrated Rate Laws:**

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

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

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

$k = Ae^{-E_a/RT}$   
 $\ln k = \ln A - \frac{E_a}{RT}$   
 $t_{1/2} = \frac{0.693}{k}$  For first-order reaction

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end of topics 21-22

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# Chemistry 1B, Fall 2016

## Topics 21-22

### initial rate (2 vs 3)

$$\text{initial rate of disappearance } [NH_4^+] = -\frac{d[NH_4^+]}{dt}\bigg|_0 = k[NH_4^+]_0^m [NO_2^-]_0^n$$

Experiment	Initial Concentration of $NH_4^+$	Initial Concentration of $NO_2^-$	Initial Rate (mol L <sup>-1</sup> s <sup>-1</sup> )
1	0.100 M	0.0050 M	$1.35 \times 10^{-7}$
2	0.100 M	0.010 M	$2.70 \times 10^{-7}$
3	0.200 M	0.010 M	$5.40 \times 10^{-7}$

$$\text{rate} = k [NH_4^+]^m [NO_2^-]^n$$

$$3: \quad 5.40 \times 10^{-7} = k [0.200M]^m [0.010M]^n$$

$$2: \quad 2.70 \times 10^{-7} = k [0.100M]^m [0.010M]^n$$

$$\text{divide 3/2} \quad \frac{3}{2}: \quad \frac{5.40 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{k [0.200M]^m [0.010M]^n}{k [0.100M]^m [0.010M]^n}$$

$$\frac{3}{2}: \quad 2.00 = [2]^m \Rightarrow m = 1$$

$$(x \text{ rate}) = [x \text{ conc}]^n$$

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### initial rate (x rate) = [x conc]<sup>n</sup>

$$\text{initial rate} = \dots [A]_0^n \quad n^{\text{th}} \text{ order in A}$$

**double initial concentration of A i.e. [2x]**

and initial rate changes by  $\Rightarrow$  implies order n  $\frac{\text{rate 2}}{\text{rate 1}} = \left(\frac{\text{conc 2}}{\text{conc 1}}\right)^n$

if the initial concentration of one **reactant doubles [2x]** and the reaction rate

doubles (x2)  $\Rightarrow$  n=1  $2=[2]^1$

quadruples (x4)  $\Rightarrow$  n=2  $4=[2]^2$

octuples (x8)  $\Rightarrow$  n=3  $8=[2]^3$

$(x \text{ rate}) = [x \text{ conc}]^n$  also holds for other concentration multiples e.g. [3x] triple initial concentration, n=2, rate 9 times faster

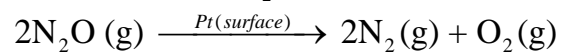
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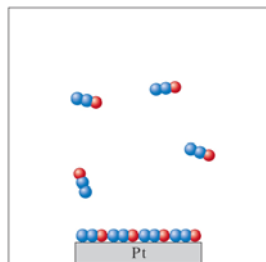
## Topics 21-22

*zero<sup>th</sup> order reaction: fully occupied surface catalyst*

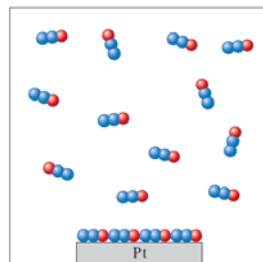
*decomposition of N<sub>2</sub>O on platinum surface*



$$-\frac{d[\text{N}_2\text{O}]}{dt} = k = k[\text{N}_2\text{O}]^0 \quad \text{zero}^{\text{th}} \text{ order}$$



(a)



(b)



after surface covered, higher [N<sub>2</sub>O] leads to no greater rate of decomposition

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