Chemistry 1B

Fall 2016

Topics 21-22
Chemical Kinetics

Chemistry 1B so far: STRUCTURE
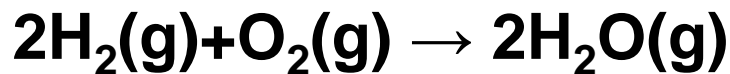
of atoms and molecules

Chemistry 1B now: DYNAMICS

chemical kinetics

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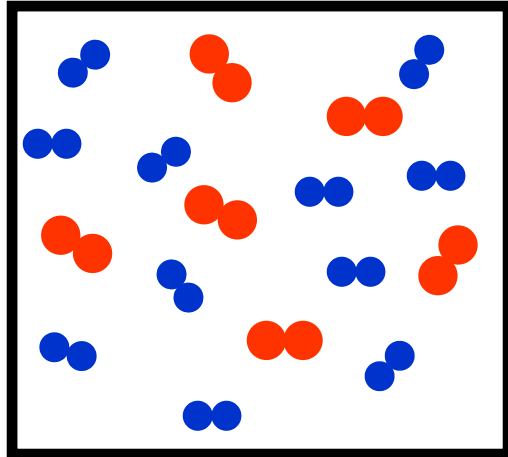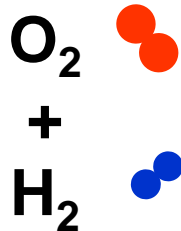and "how far" it will proceed
[*equilibrium conditions*]

$$2H_2(g)+O_2(g) \rightarrow 2H_2O(g)$$

$$\Delta H = -484 \, kJ$$ **very exothermic**

**equilibrium
chem 1A-1C**

$$K_p = \frac{\left(\dfrac{P_{H_2O}}{1 \text{ atm}}\right)^2}{\left(\dfrac{P_{H_2}}{1 \text{ atm}}\right)^2 \left(\dfrac{P_{O_2}}{1 \text{ atm}}\right)} = 2 \times 10^{80}$$ **'all' products at equilibrium**
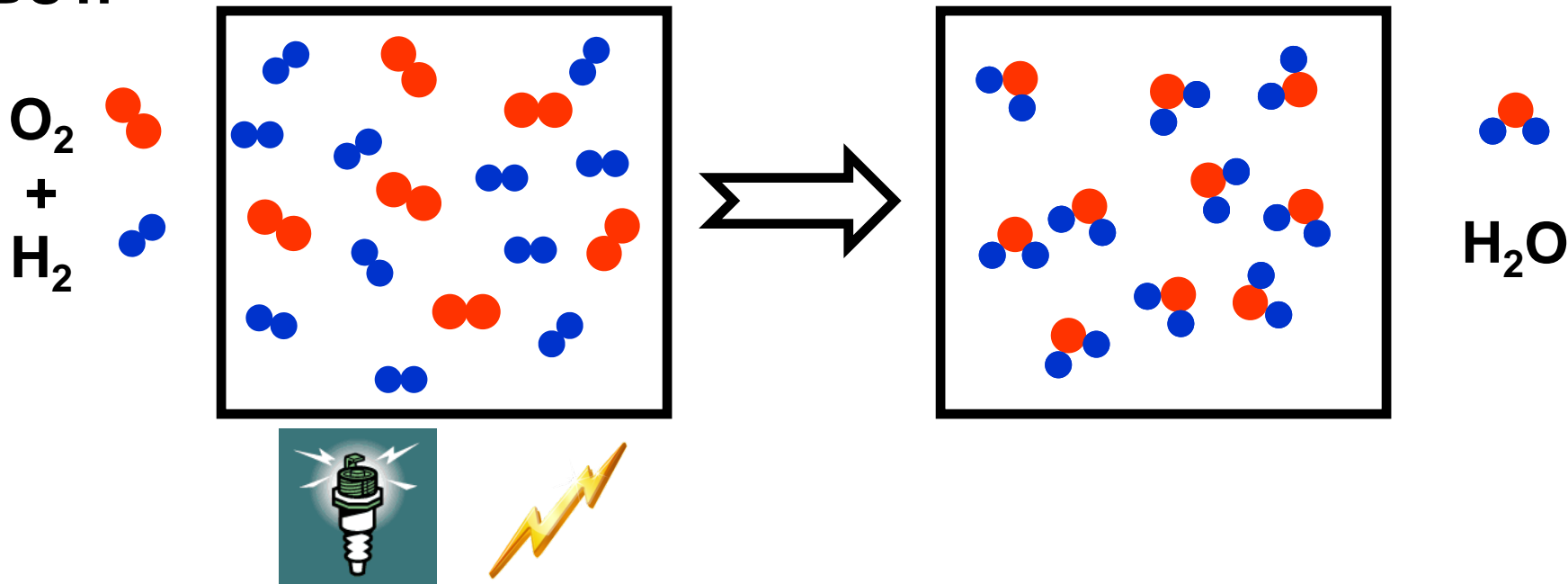
3

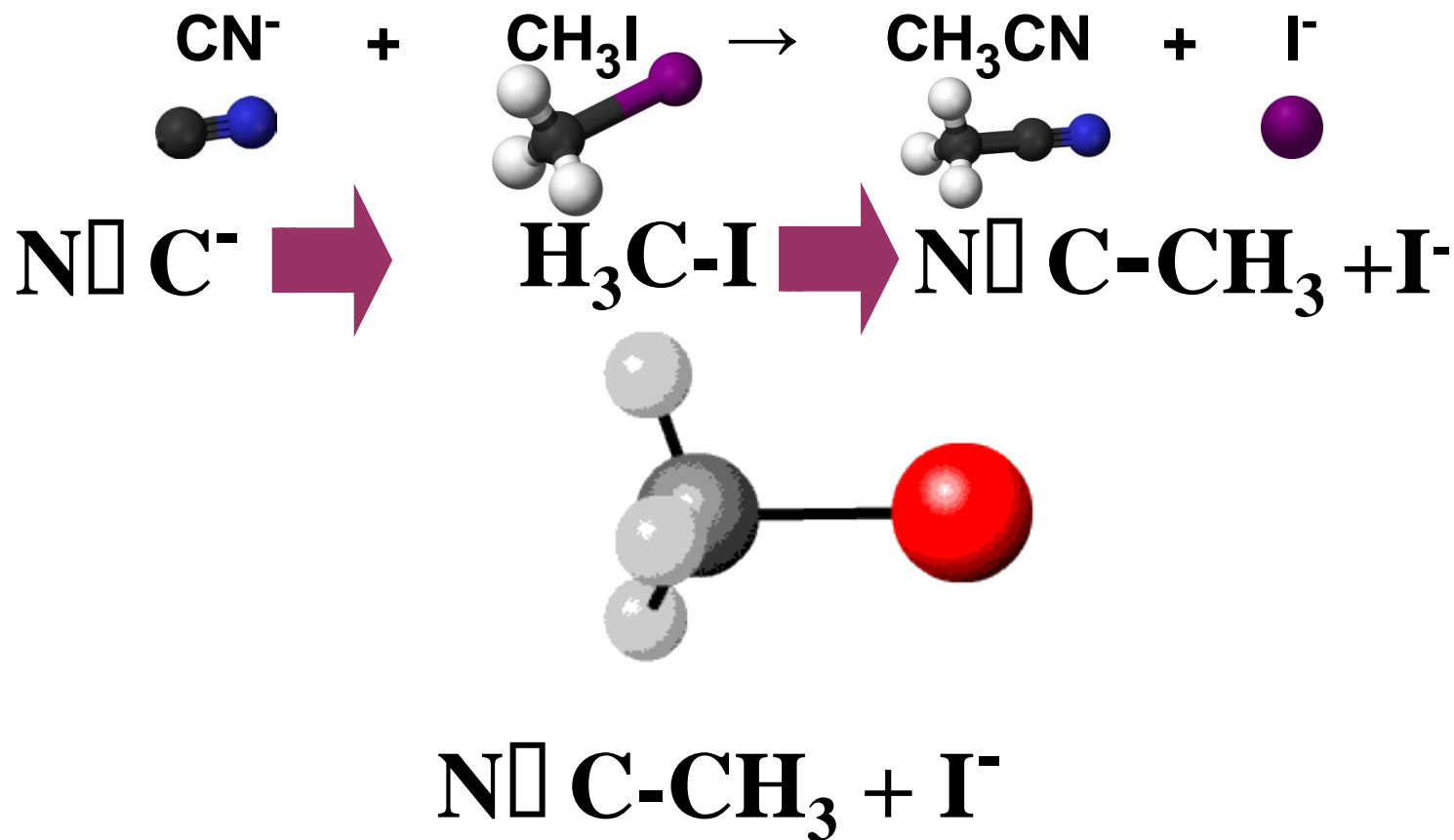**HOWEVER:**

O$_2$
+
H$_2$

nada (no reaction)
almost forever

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

BUT:

O_2

$+$

H_2

H_2O

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

$$CN^- \ + \ CH_3I \ \rightarrow \ CH_3CN \ + \ I^-$$

$$N{\equiv}C^- \ \Rightarrow \ H_3C\text{-}I \ \Rightarrow \ N{\equiv}C\text{-}CH_3 + I^-$$

$$N{\equiv}C\text{-}CH_3 + I^-$$

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

- Concepts and definitions
    - Lecture notes
    - HW10 Z15.55, Z15.52, Z15.68   } HW10 #67, S19-S20
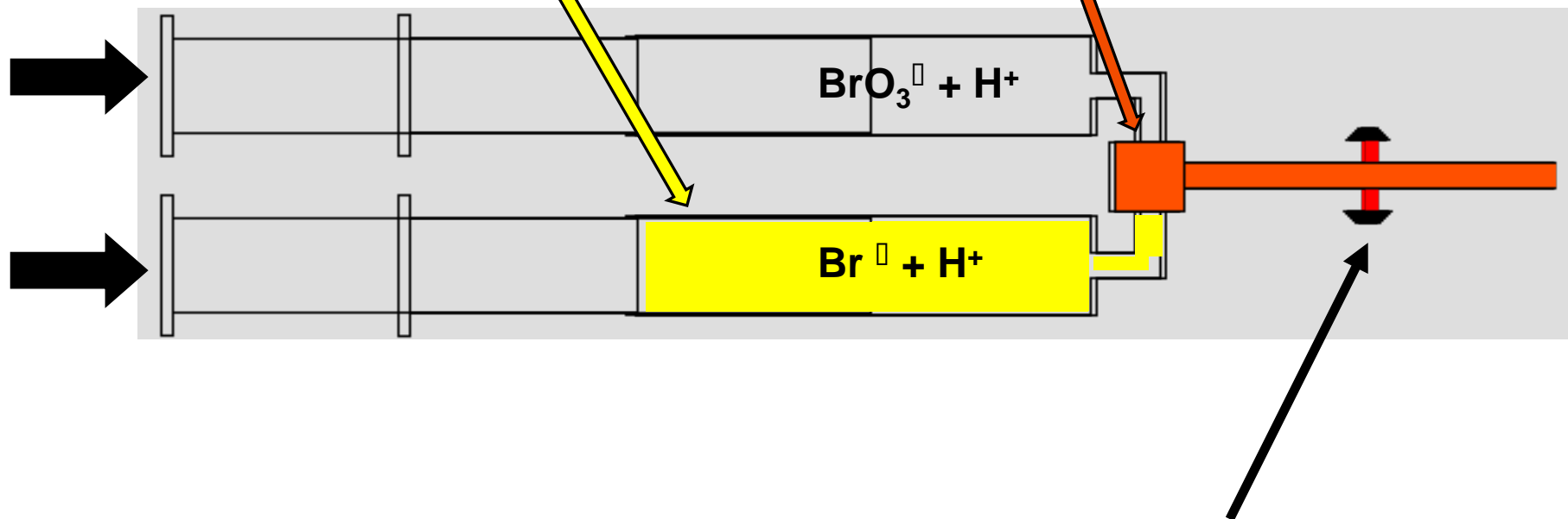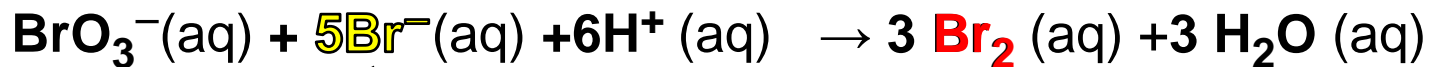
- Numerical Problem Solving
    - Lecture notes
    - HW10 Z15.17, Z15.20, Z15.57,   } HW10 #64,#65,#68,
        Z15.73, Z15.82   #69,#71

- Graphical interpretations
    - Lecture notes
    - HW10 Z15.36a, Z15.81   } HW10 #66,#70

HW#10 DUE SUNDAY, 4th DECEMBER (last WebAssign)
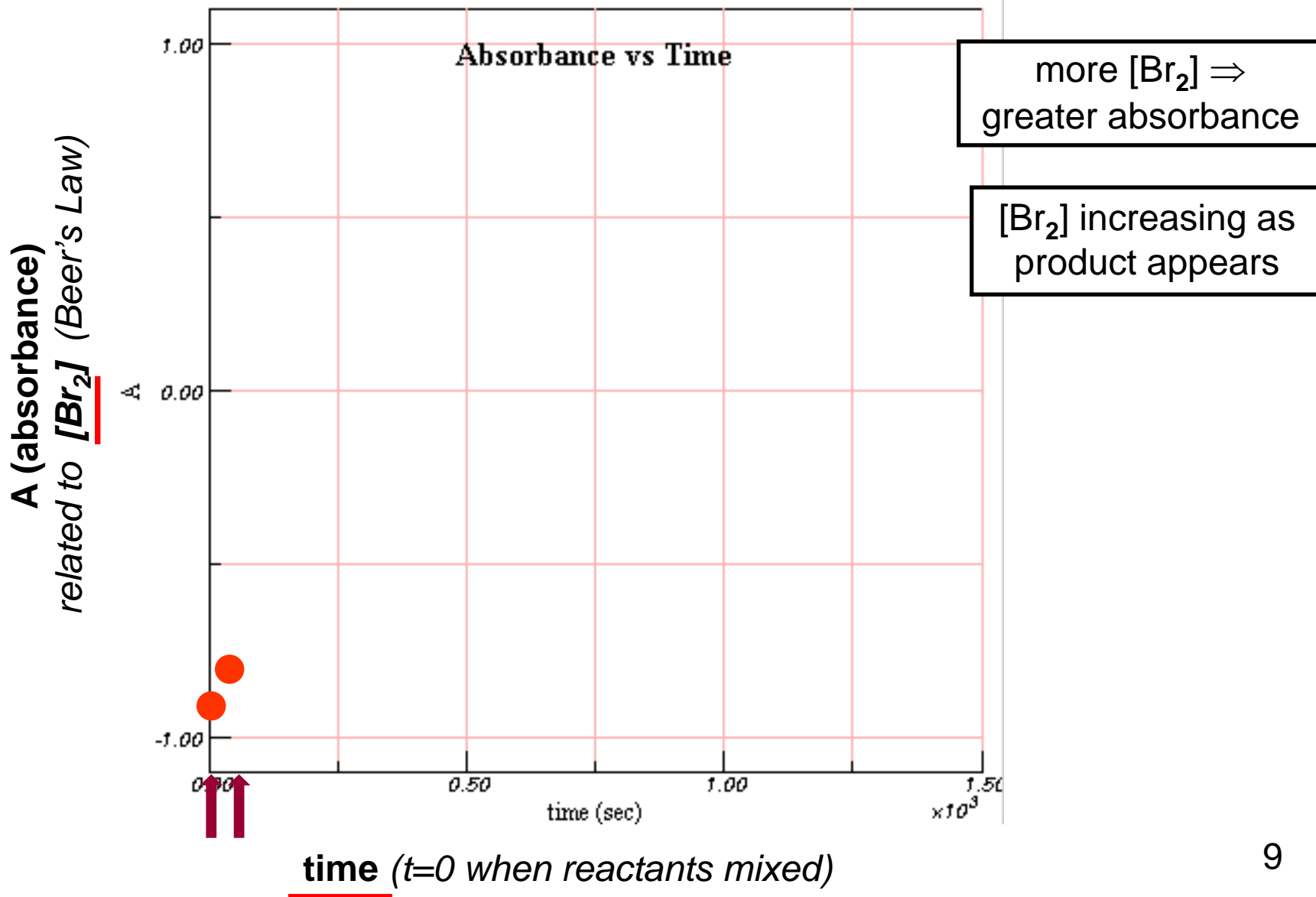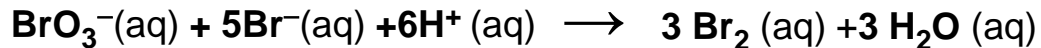
$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ (aq) \rightarrow 3\ Br_2\ (aq) + 3\ H_2O\ (aq)$$

spectrophotometer
measures Br_2 concentration (absorbance)

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

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BrO_3^-(aq) **+ 5Br⁻**(aq) **+6H⁺** (aq) $\longrightarrow$ **3 Br₂** (aq) **+3 H₂O** (aq)

A (absorbance)
related to [Br₂] (Beer's Law)

Absorbance vs Time

A

1.00

0.00

-1.00

0.00   0.50   1.00   1.50
                                          ×10³
time (sec)

time *(t=0 when reactants mixed)*

more [Br₂] $\Rightarrow$ greater absorbance

[Br₂] increasing as product appears

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$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3\ Br_2(aq) + 3\ H_2O(aq)$$

A (absorbance)
related to [Br₂] (Beer's Law)

more [Br₂] ⇒
greater absorbance

[Br₂] increasing as
product appears

BrO$_3^-$(aq) + 5Br$^-$(aq) +6H$^+$ (aq) $\longrightarrow$ 3 Br$_2$ (aq) +3 H$_2$O (aq)

A (absorbance)
related to [Br$_2$] (Beer's Law)

more [Br$_2$]
greater absorbance

[Br$_2$] increasing as
product appears

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

TABLE 15.1

Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ (at 300°C)

Time (±1 s)	Concentration (mol/L)		
	NO_2	NO	O_2
0	0.0100	0	0
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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2NO$_2$(g) → 2NO(g) +O$_2$(g)

REACTANT DISAPPEARS

PRODUCTS APPEAR

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

reaction rate: $[\text{disappearance of } NO_2(g)] = -\dfrac{change\ of\ [NO_2]}{change\ of\ time} = -\dfrac{\Delta[NO_2]}{\Delta t}$

$$\text{DIFFERENTIAL reaction rate} = \lim_{\Delta t \to 0} -\frac{\Delta[NO_2]}{\Delta t} = -\frac{d[NO_2]}{dt}$$

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"initial rate" at t=0 *(0→ 50 s)*

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

$$-\Delta[NO_2] = -(0.0079 - 0.0100) \text{ mol/L} = 0.0021 \text{ mol/L}$$

$$rate \approx -\frac{\Delta[NO_2]}{\Delta t} = \frac{0.0021}{50} \text{ mol L}^{-1}\text{s}^{-1} = 4.2 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

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$$\text{reaction rate} = -\frac{d[NO_2]}{dt} = -(\text{slope of } [NO_2] \text{ vs t})$$

slope=tangent to curve

TABLE 15.2

Average Rate (in mol L^{-1} s^{-1}) of Decomposition of Nitrogen Dioxide as a Function of Time

$-\dfrac{\Delta[NO_2]}{\Delta t}$	Time Period (s)
4.2×10^{-5}	$0 \rightarrow 50$
2.8×10^{-5}	$50 \rightarrow 100$
2.0×10^{-5}	$100 \rightarrow 150$
1.4×10^{-5}	$150 \rightarrow 200$
1.0×10^{-5}	$200 \rightarrow 250$

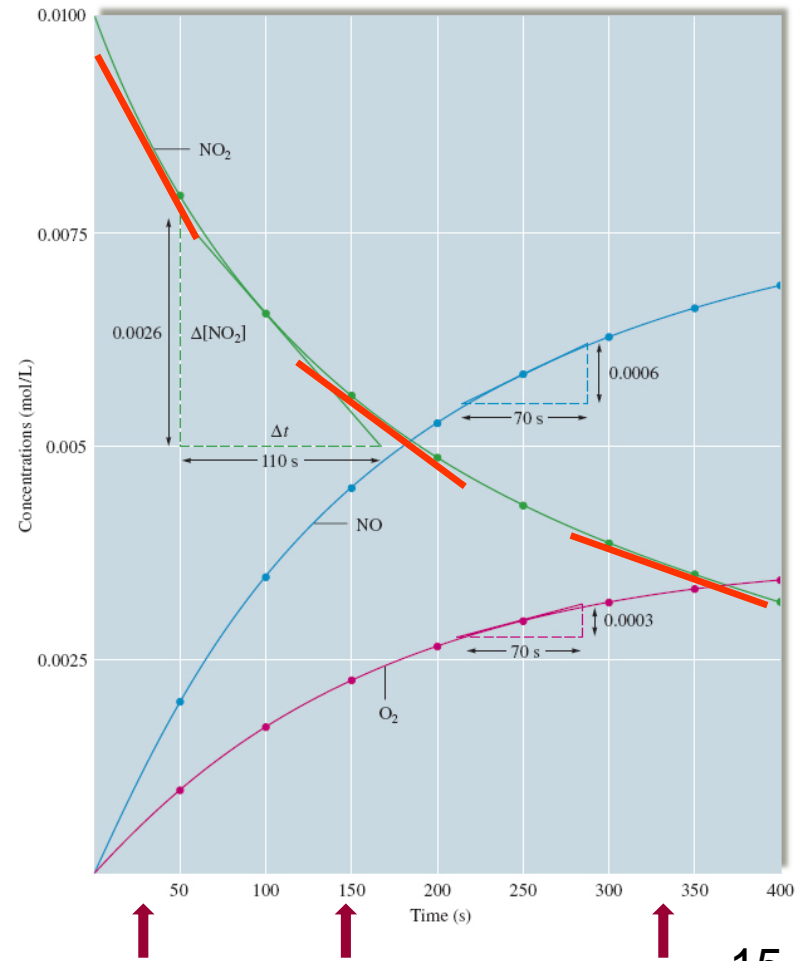Note: The *rate* decreases with time.

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

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in each $\Delta t = 50s$ interval

$- \Delta[NO_2] = \Delta[NO] = 2\Delta[O_2]$

disappearance NO_2	appearance NO O_2

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

$$-\frac{d[NO_2]}{dt} = +\frac{d[NO]}{dt} = + \textbf{\textcolor{red}{?}} \; \frac{d[O_2]}{dt}$$

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2NO$_2$(g) → 2NO(g) +O$_2$(g)

TABLE 15.1

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

Time (±1 s)	Concentration (mol/L)		
	NO$_2$	NO	O$_2$
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50	0.0079	0.0021	0.0011
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in each Δt=50s interval

- Δ[NO$_2$] = Δ[NO] = 2Δ[O$_2$]

disappearance NO$_2$	appearance NO O$_2$

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

$$-\frac{d[NO_2]}{dt} = +\frac{d[NO]}{dt} = +\, \mathbf{2}\, \frac{d[O_2]}{dt}$$

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higher concentrations $\Rightarrow$ more collisions

more collisions $\Rightarrow$ more reactions occurs

rate depends on concentrations

a A + b B $\rightarrow$ c C + d D
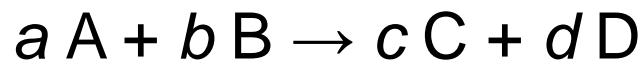
$$-\frac{d[A]}{dt} = k[A]^m[B]^n$$

rate constant for a given Temperature

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

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generalized *(differential)* rate expression

$$aA + bB \xrightarrow{k_f} cC + dD \qquad \text{forward reaction}$$

$$aA + bB \xleftarrow{k_r} cC + dD \qquad \begin{array}{l}\text{reverse reaction}\\ \text{(products recombine)}\end{array}$$

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_f *rate constant of forward reaction*

reverse rate (increase of [A])
k_r *rate constant of reverse reaction*

$$aA + bB \xrightarrow{k_f} cC + dD \qquad \text{forward reaction}$$

$$aA + bB \xleftarrow{k_r} cC + dD \qquad \text{reverse reaction}$$

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

INITIAL RATE (initially only reactants present):

$$[A]_o, [B]_o \neq 0 \qquad -\frac{d[A]_0}{dt} = k[A]_0^m[B]_0^n$$
$$[C]_o, [D]_o = 0$$

- *k* is rate constant (for eqn written as disappearance of A)
- **DEFINITION OF RATE ORDER** rate is:
  - m^{th} order in reactant [A]
  - n^{th} 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]th* order (i.e. total order of reaction rate)

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2NO$_2$(g) $\rightarrow$ 2NO(g) +O$_2$(g)   forward reaction

~~**2NO$_2$(g) $\leftarrow$ 2NO(g) +O$_2$(g)**~~   reverse reaction

initial rate:
- only reactants present
- [NO]$_o$=[O$_2$]$_o$=0
- no reverse reaction

$$-\frac{d[NO_2]_0}{dt} = k[NO_2]_0^n$$

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

$$NH_4^+ \text{ (aq)} + NO_2^- \text{ (aq)} \rightarrow N_2 \text{ (g)} + 2H_2O \text{ } (\ell)$$
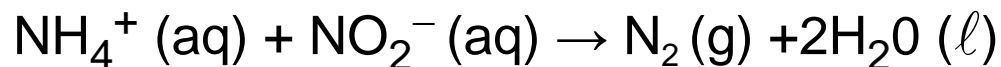
$$-\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^m \left[NO_2^-\right]_0^n$$

differential initial rate

TABLE 15.4

Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-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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$$NH_4^+ \text{ (aq)} + NO_2^- \text{ (aq)} \rightarrow N_2 \text{ (g)} + 2H_2O \text{ (ℓ)}$$

$$-\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^{m=1}\left[NO_2^-\right]_0^{n=1}$$

TABLE 15.4

Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

(x rate)= [x conc]^n
(2)=(2)^1

for $[NO_2^-]^n$ 1 vs 2: $[NH_4^+]$ const, double $[NO_2^-]$ rate doubles   ⇨ n=1

for $[NH_4^-]^m$ 2 vs 3: $[NO_2^-]$ const, double $[NH_4^+]$ rate doubles   ⇨ m=1

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NH_4^+ (aq) + NO_2^- (aq) $\rightarrow$ N_2 (g) +2$H_2$0 (ℓ)
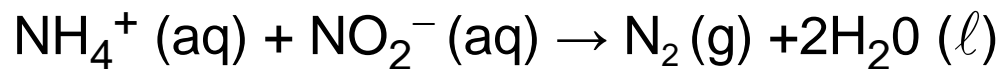
initial rate of disappearance $\left[NH_4^+ \right] = -\dfrac{d\left[NH_4^+ \right]_0}{dt} = k\left[NH_4^+ \right]_0^{1}\left[NO_2^- \right]_0^{1}$

first order in [NH_4^+]

first order in [NO_2^-]

second order overall

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

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

$$\{\text{initial rate of disappearance of } NH_4^+\} = -\frac{d\left[NH_4^+\right]_0}{dt} = k\left[NH_4^+\right]_0^1\left[NO_2^-\right]_0^1$$

from exp 1

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

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

from exp 3

$$5.40 \times 10^{-7} \, mol \, L^{-1} s^{-1} = k(0.200 \, mol \, L^{-1})^1(0.010 \, mol \, L^{-1})^1$$

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

$$\text{BrO}_3^-(\text{aq}) + 5\text{Br}^-(\text{aq}) + 6\text{H}^+(\text{aq}) \rightarrow 3\,\text{Br}_2(\text{aq}) + 3\,\text{H}_2\text{O}(\text{aq})$$

remember same reaction in stop-flow apparatus, earlier slide

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3\,Br_2(aq) + 3\,H_2O(aq)$$

TABLE 15.5

The Results from Four Experiments to Study the Reaction
$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(l) + 3H_2O(l)$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol L^{-1} s^{-1})
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

from initial rate data determine n, m, and p

$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^{n}_{1}\left[Br^-\right]^{m}_{1}\left[H^+\right]^{p}_{2}$$

$[BrO_3^-]^{n}$: exp 1-2 $[BrO_3^-]$ doubles, rate x2 $\Rightarrow$ n= 1 $2=[2]^1$

$[Br^-]^{m}$: exp 2-3 $[Br^-]$ doubles,   rate x2 $\Rightarrow$ m= 1   *(x rate)=[x conc]^n*

$[H^+]^{p}$: exp 1-4 $[H^+]$ doubles,   rate x4 $\Rightarrow$ p= 2 $4=[2]^2$

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$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

first order in $[BrO_3^-]$

first order in $[Br^-]$

second order in $[H^+]$

fourth order overall

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+ (aq) \rightarrow 3\ Br_2\ (aq) + 3\ H_2O\ (aq)$$

$$rate = -\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

Experiment	Initial Concentration of BrO_3^- (mol/L)	Initial Concentration of Br^- (mol/L)	Initial Concentration of H^+ (mol/L)	Measured Initial Rate (mol L^{-1} s^{-1})
1	0.10	0.10	0.10	8.0×10^{-4}

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

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

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

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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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integral rate expression

• Determine order of reaction from plot of 'concentration' vs time

• Half-life of a reaction

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

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

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

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

$$\text{from calculus } x = \int dx \quad \text{and} \quad t = \int dt$$

value   *change*   *value*   *change*

INTEGRATE !!!

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$$\int dt = ?$$

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

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

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

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

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

$\ln[A] = -k\,t + C$

slope   intercept

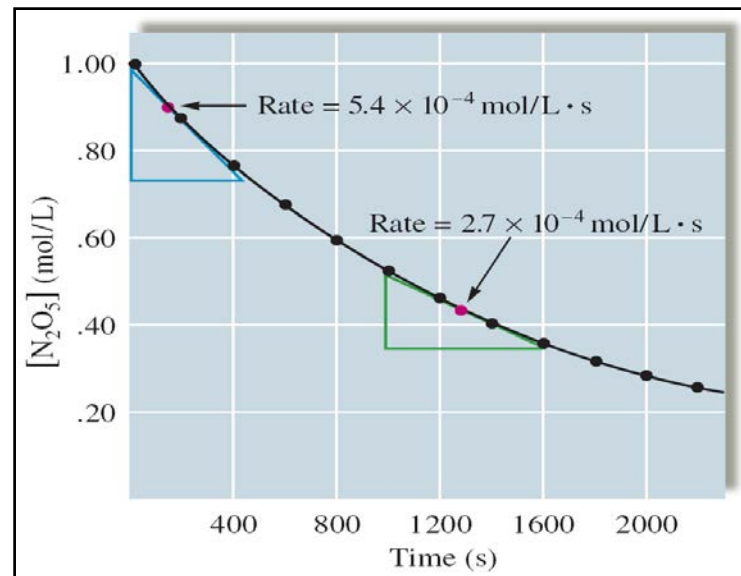integrated rate law: $\ln[A] = -k\,t + \ln[A]_0$ *when* $t = 0$ $[A] = [A]_0$

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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2N$_2$O$_5$ (soln) → 4NO$_2$(soln) + O$_2$(g)

$$\text{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]^n$$

[N$_2$O$_5$]   vs t

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

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$$\ln\left[N_2O_5\right] = -\underline{kt} + \underline{\ln\left[N_2O_5\right]_0} \quad \textit{(if reaction is first order)}$$

plot **ln [N$_2$O$_5$]** vs **t**

do we get straight line ??

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

YES !!
n=1
it is first-order
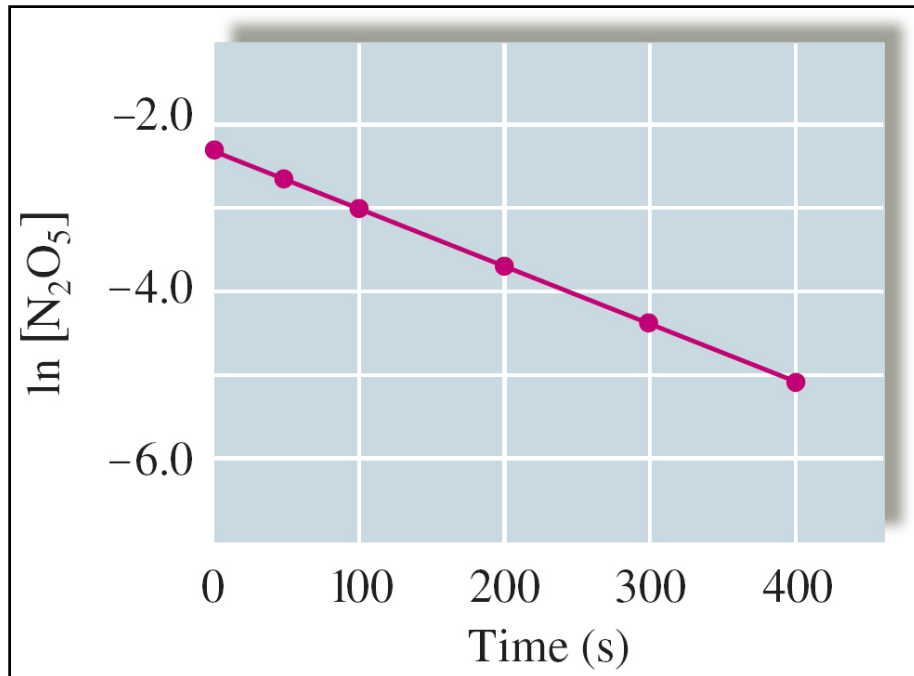
slope = **-k**
t=0 intercept is **ln [N$_2$O$_5$]$_o$**

$$\textbf{rate} = -\frac{d[N_2O_5]}{dt} = k[N_2O_5]^{1}$$

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other integrated rate laws

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

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

plot [A] vs t gives straight line

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

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

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

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$$-\frac{d\left[BrO_3^-\right]}{dt} = k\left[BrO_3^-\right]^1\left[Br^-\right]^1\left[H^+\right]^2$$

more complicated to get integrated rate-laws for

rate expressions which depend on several reactant concentrations :

use $[Br^-]_o$ and $[H^+]_o$ >> $[BrO_3^-]_o$; plot ln $[BrO_3^-]$ vs t

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

reaction 'pseudo' first-order; i.e   rate$\approx$ *(k [Br⁻] [H⁺]²)* $[BrO_3^-]^{\mathbf{1}}$

$\approx\approx$ constant = (k [Br⁻]$_o$ [H⁺]$_o^2$)

$$2C_4H_6 \longrightarrow C_8H_{12} \qquad -\frac{d\,[C_4H_6]}{dt}=k[C_4H_6]^?$$

same rate data plotted two ways

(a) $\ln[C_4H_6]$ vs t $\qquad$ or $\qquad$ $\dfrac{1}{[C_4H_6]}$ vs t

$$-\frac{d\,[C_4H_6]}{dt}=k[C_4H_6]^2$$
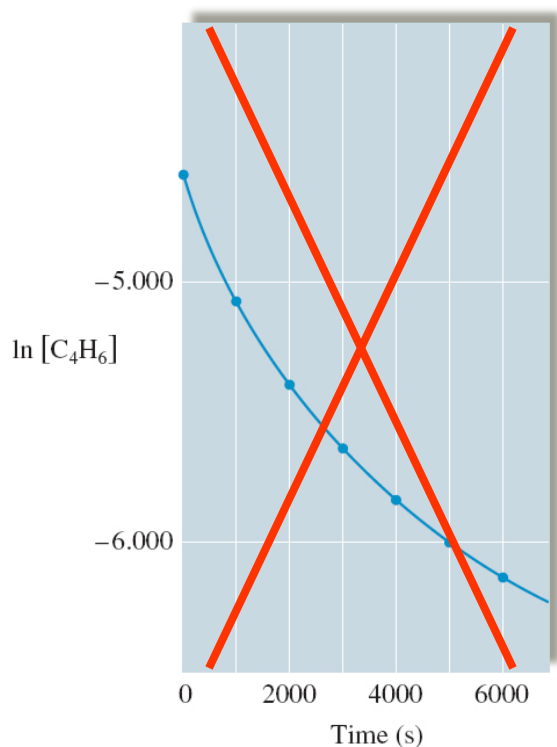
straight line $\Rightarrow$ first order $\qquad\qquad$ straight line $\Rightarrow$ second order
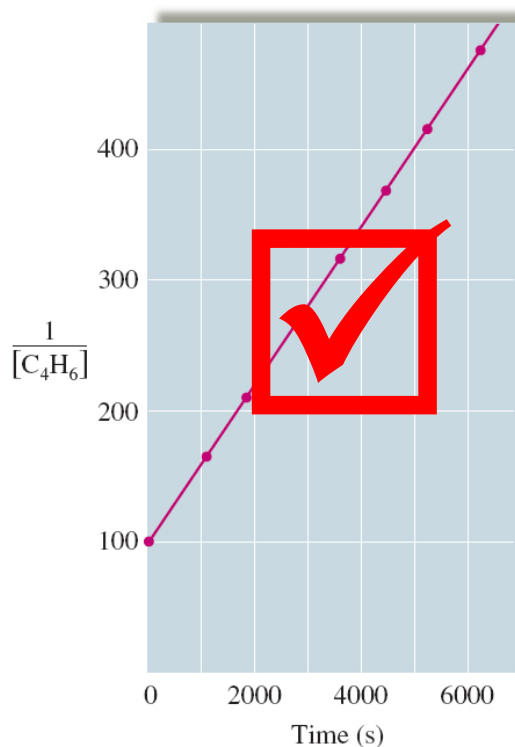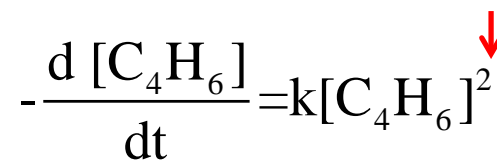
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time for concentration of reactant to drop by factor of 2

$$[A]_{t+t_{1/2}} = \frac{1}{2}[A]_t \qquad \text{e.g. when half the original reactant left } [A]_{t_{1/2}} = \frac{1}{2}[A]_o$$
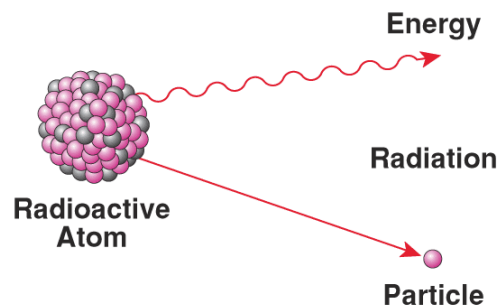
first-order reaction (e.g. radioactive decay)

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

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

Energy

Radiation

Radioactive
Atom

Particle

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

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

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

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still the definition of half-life

time for concentration of reactant to drop by factor of 2

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

but:

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

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

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

TABLE 15.6

Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ 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	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\dfrac{1}{[A]} = kt + \dfrac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\dfrac{1}{[A]}$ versus t
Relationship of rate constant to the slope of the straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \dfrac{[A]_0}{2k}$	$t_{1/2} = \dfrac{0.693}{k}$	$t_{1/2} = \dfrac{1}{k[A]_0}$

know how to use; **all needed formulas given on exam**

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Chemistry 1B
SAMPLE FINAL EXAMINATION QUESTIONS

$h = 6.626 \times 10^{-34}$ J s

$c = 3.000 \times 10^{8}$ m/s

$m_e = 9.109 \times 10^{-31}$ kg

$m_p = 1.672 \times 10^{-27}$ kg

$R = 8.3145$ JK^{-1}mol^{-1}

$R = 0.08206$ L atm K^{-1}mol^{-1}

$$\tilde{v} = \frac{1}{\lambda} = \frac{v}{c}$$

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

$$(m\Delta u)\, \Delta x \geq \frac{h}{4\pi}$$

$$E \approx = -(2.18 \times 10^{-18} \text{ J}) \frac{Z_{\text{eff}}^2}{n^2}$$

$$r \approx (5.29 \times 10^{-12} \text{ m}) \frac{n^2}{Z_{\text{eff}}}$$

wavelength range of visible light :

$\lambda \approx 3.5 \times 10^{-7}$ m to 7.0×10^{-7} m

Integrated Rate Laws:

$$[A] = -kt + [A]_0 \qquad \text{zeroth-order}$$

$$\ln[A] = -kt + \ln[A]_0 \quad \text{first-order}$$

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

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

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

$$t_{1/2} = \frac{0.693}{k} \quad \text{for first-order reaction}$$

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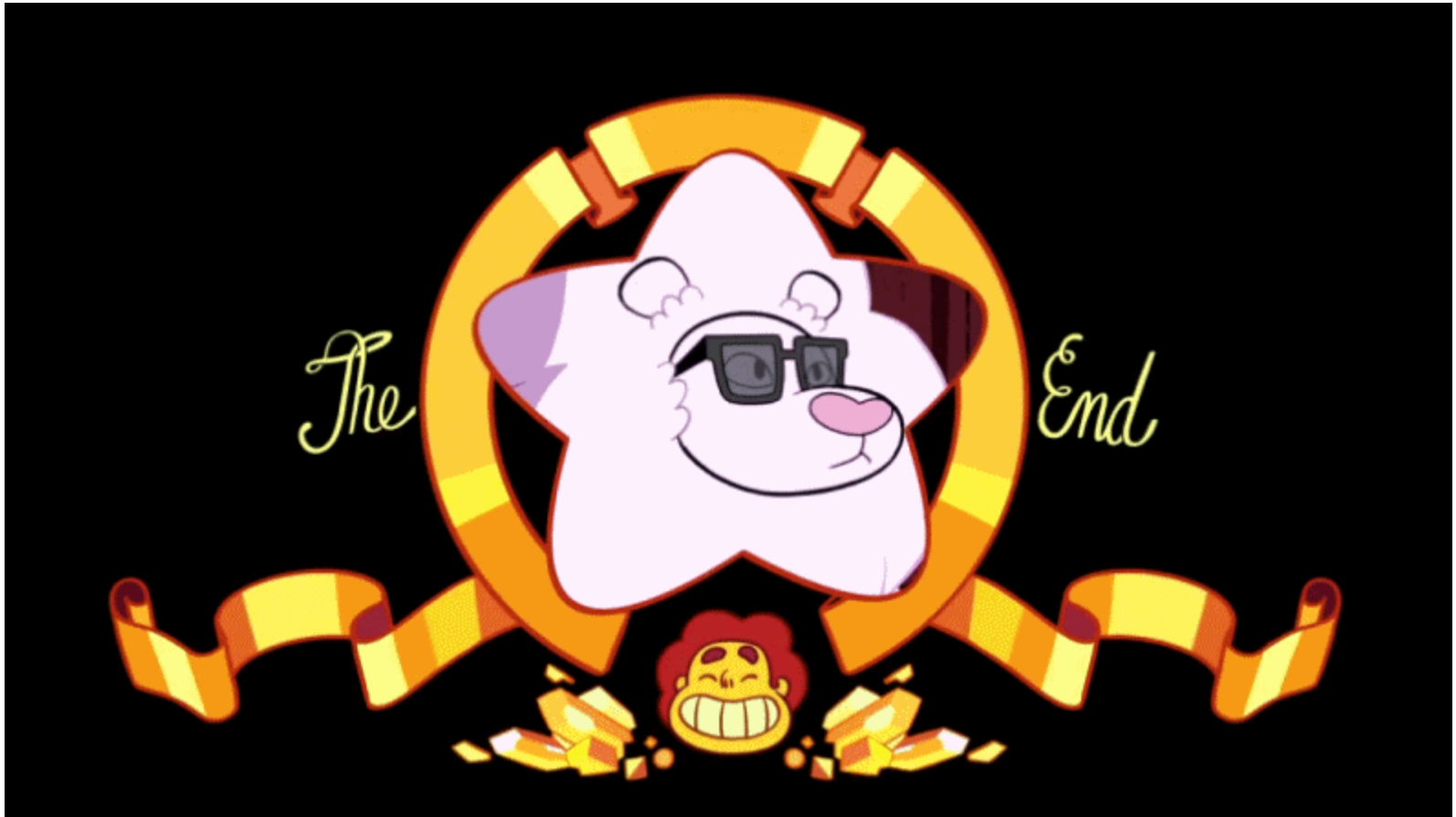
end of topics 21-22

initial rate of disappearance $\left[NH_4^+ \right] = -\dfrac{d\left[NH_4^+ \right]_0}{dt} = k\left[NH_4^+ \right]_0^m \left[NO_2^- \right]_0^n$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate (mol L^{-1} s^{-1})
1	0.100 M	0.0050 M	1.35×10^{-7}
2	0.100 M	0.010 M	2.70×10^{-7}
3	0.200 M	0.010 M	5.40×10^{-7}

rate $= k \quad [NH_4^+]^m \quad [NO_2^-]^n$

$3: \quad 5.40 \times 10^{-7} = k\left[0.200M \right]^m \left[.010M \right]^n$

$2: \quad 2.70 \times 10^{-7} = k\left[0.100M \right]^m \left[.010M \right]^n$

divide 3/2 $\quad \dfrac{3}{2}: \quad \dfrac{5.40 \times 10^{-7}}{2.70 \times 10^{-7}} = \dfrac{k\left[0.200M \right]^m \left[.010M \right]^n}{k\left[0.100M \right]^m \left[.010M \right]^n}$

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

(x rate)= [x conc]^n

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initial rate = ….. $[A]_0^n$ n^{th} order in A

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

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

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

doubles (x2) ➡ n=1 $2=[2]^1$
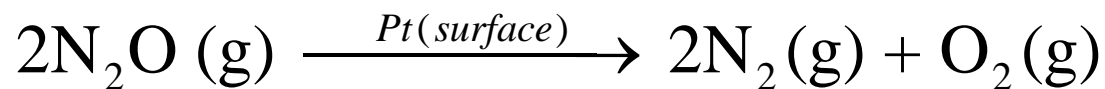
quadruples (x4) ➡ n=2 $4=[2]^2$

octuples (x8) ➡ n=3 $8=[2]^3$

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

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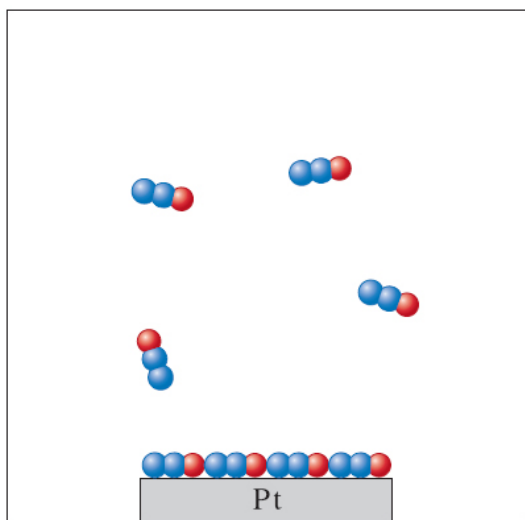*decomposition of N$_2$O on platinum surface*

$$2N_2O\ (g) \xrightarrow{\quad Pt(surface) \quad} 2N_2\ (g) + O_2\ (g)$$

$$-\frac{d[N_2O]}{dt} = k = k[N_2O]^0 \qquad \text{zero}^{\text{th}}\ \text{order}$$

(a)

(b)

N_2O
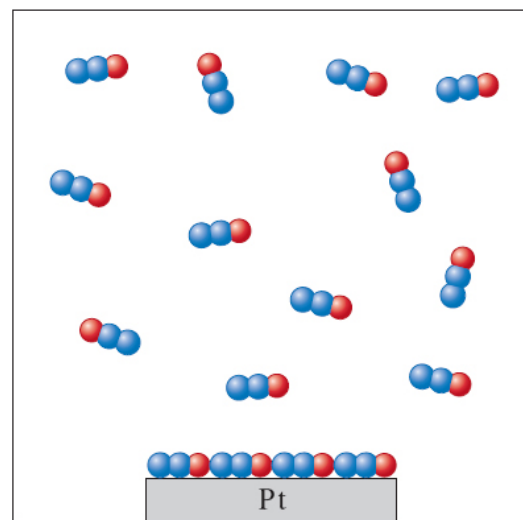
after surface covered, higher [N$_2$O] leads to no greater rate of decomposition