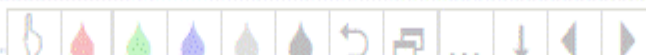# Announcements – Lecture VII – Tuesday, Feb 13th

1. Exam 1:   **Saturday, February 24th, ISB 155/160 (General Chemistry Labs)**
                Session I: 1:00-2:55, Last Name, A-J
                Session II: 3:00-4:55, Last Name, K-Z
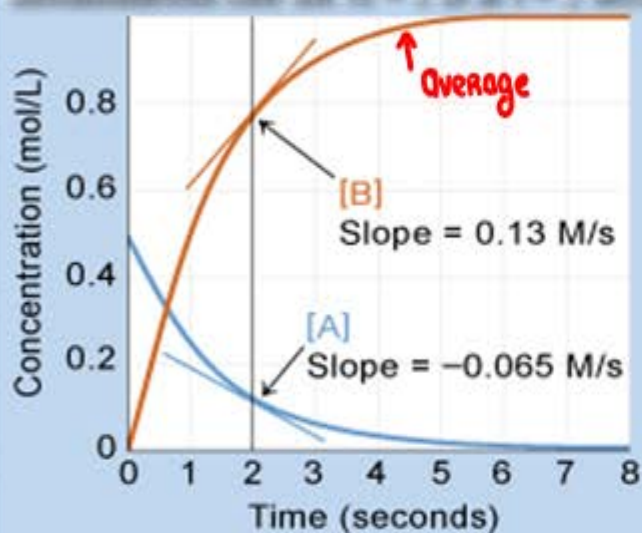
2. Quiz 2:   **Place in basket.**

3. iClicker: **Pick any letter a-e**
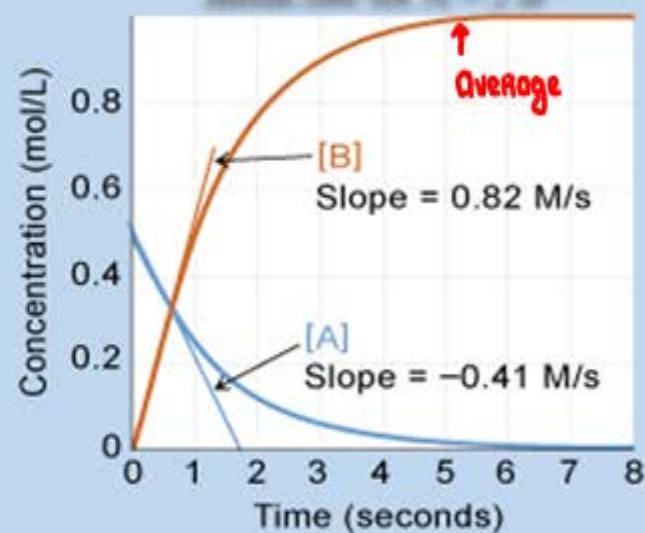
14.2   Expressing the Rate of a Reaction
Instantaneous and Initial Rates

Instantaneous rate for A = 2 B at t = 2 seconds

Average

[B]
Slope = 0.13 M/s

[A]
Slope = −0.065 M/s

Concentration (mol/L)
0.8
0.6
0.4
0.2
0

Time (seconds)
0 1 2 3 4 5 6 7 8

Initial rate for A = 2 B

Average

[B]
Slope = 0.82 M/s

[A]
Slope = −0.41 M/s

Concentration (mol/L)
0.8
0.6
0.4
0.2
0

Time (seconds)
0 1 2 3 4 5 6 7 8

Initial Rates are where the Rate of Formation
and the Rate of Dissopearance is line.

Thus this is our Region of choice.

14.3   Rate Laws

Concentration and Reaction Rate

It should come as no surprise that the rate of formation or Dissapearance is directly proportional to the concentration.

$$a A + b B = c C + d D$$

Initial Reaction Rate $= k [A]^x [B]^y$

   x : is referred to as the order with respect to A.
   y : is referred to as the order with respect to B.
   x+y : is the overall order of the reaction.
   k : is the rate constant.

NOTE : x and y are not necessarily equal to a and b.
        x and y can only be determined experimentally.
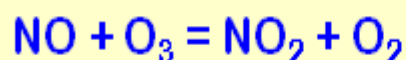
NOTE : Our discussion will initially be confined to orders: 0, 1 and 2.

For A :   Zero order :   Rate $= k [A]^0$
          First order :   Rate $= k [A]^1$
          Second order : Rate $= k [A]^2$

Determining Rate Law Using the Method of Initial Rates

$NO + O_3 = NO_2 + O_2$

a) What is the rate law?

b) What is the rate constant?

Exp	$[NO]_o$, M	$[O_3]_o$, M	Initial Rate, Ms^{-1}
1	0.139	0.0436	0.527
2	0.139	0.0872	1.05
3	0.278	0.0436	1.05
4	0.278	0.0872	2.11

Exp 1 $Rate_1 = k[NO]_1^x[O_3]_1^y$

$0.527 = k(0.139)^x(0.0436)^y$

Exp 2. $Rate_2 = k[NO]_2^x[O_3]_2^y$

$1.05 = k(0.139)^x(0.0872)^y$

$\dfrac{Rate_2}{Rate_1} : \dfrac{1.05}{0.527} = \dfrac{k(0.139)^x(0.0872)^y}{k(0.139)^x(0.0436)^y}$

$1.99 = 2^y$

$y = 1$

Exp 1. $0.527 = k(0.139)^x(0.0436)^y$

Exp 3 $Rate_3 = k[NO]_3^x[O_3]_3^y$

$1.05 = k(0.278)^x(0.0436)^y$

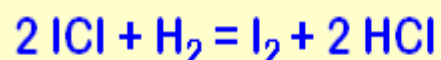$\dfrac{Rate_3}{Rate_1} : \dfrac{1.05}{0.527} = \dfrac{k(0.278)^x(0.0436)^y}{k(0.139)^x(0.0436)^y}$

$1.99 = 2^x : x = 1$

$Rate = k[NO][O_3]$

Exp 1 : $0.527 = k(0.139)(0.0436)$

$k = 86.9 \ M^{-1}s^{-1}$

Determining Rate Law Using the Method of Initial Rates

$2 ICl + H_2 = I_2 + 2 HCl$

Exp	$[ICl]_o$, M	$[H_2]_o$, M	Initial Rate, Ms^{-1}
1	0.309	0.114	7.07e-3
2	0.618	0.114	1.41e-2
3	0.309	0.228	2.83e-2
4	0.618	0.228	5.65e-2

a) What is the overall order of the reaction **3.**

Previously we did this the long way   this time we will do it the short way [1]

$$Rate = k [ICl]^x [H_2]^y$$

Exp 1 & 3 : $[ICl]$ is held constant while $[H_2]$ increases by a factor of 2.

Exp 1 & 2 . $[H_2]$ is held constant while $[ICl]$ increases by a factor of 2.

$$\frac{2.83 \times 10^{-2}}{7.07 \times 10^{-3}} = 4.00$$

$$\frac{1.41 \times 10^{-2}}{7.07 \times 10^{-3}} = 1.99$$

$$2^y = 4$$
$$y = 2$$

$$2^x = 2$$
$$x = 1$$

Overall order : $2 + 1 = 3$

Integrated Rate Laws

Integrated Rate Laws for Reactions of Type A → Products

Reaction Order	Rate Law	Integrated Rate Law
Zero order	rate = $k[A]^0 = k$	$[A]_t = [A]_0 - kt$
First order ✱	rate = $k[A]$	$\ln\dfrac{[A]_t}{[A]_0} = -kt$
Second order	rate = $k[A]^2$	$\dfrac{1}{[A]_t} = \dfrac{1}{[A]_0} + kt$

t: time

$[A]_0$: Initial concentration of A @ time = 0

$[A]_t$: Concentration of A @ time = t

$A = Products$

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

$\dfrac{d[A]}{dt} = -k[A]$ ... if Δ is very small.

$(\frac{1}{[A]})d[A] = -kdt$

$\displaystyle\int_{t=0}^{t=t}(\frac{1}{[A]})d[A] = -k\int_{t=0}^{t=t}dt$

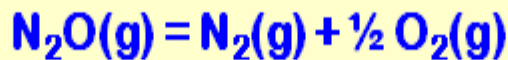$\ln[A]_t - \ln[A]_0 = -kt$

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

Integrated Rate Laws

The decomposition of nitrous oxide
$$N_2O(g) = N_2(g) + \tfrac{1}{2}O_2(g)$$
is **second order in N_2O** with a rate constant of **$1.20 \times 10^{-3}\,M^{-1}s^{-1}$**.
If the initial concentration of N_2O is **1.79 M**, the concentration of N_2O will be **0.187 M** after how many **seconds**.   **~?,000 s**

↳ 4

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

$[A]_0 = 1.79\,M$
$[A]_t = 0.187\,M$
$k = 1.20 \times 10^{-3}\,M.s^{-1}$
$t = ?$

$$\frac{1}{0.187} = \frac{1}{1.79} + 1.20\times10^{-3}t$$

$$5.348 = 0.5587 + 1.20\times10^{-3}t$$

$$1.20\times10^{-3}t = 5.348 - 0.5587$$

$$t = \frac{4.7893}{1.20\times10^{-3}} = 3,991\,s$$

Determining the Rate Equation: Graphical Method

Description

The rate law for reactions involving a single reactant can be determined using the graphical method. This method involves constructing a series of plots of concentration vs. time data and analyzing the plots to extract the reaction order and the rate constant.

The general reaction used for this tutor is:

$$A \longrightarrow C$$

The concentration vs. time data at right were collected by running the reaction at a constant temperature. These are data taken for a single trial of the reaction.

Rate = [_____] [A][_____]

Submit

time, min	[A], mol/L	time, min	[A], mol/L
0	0.7245	5	0.4046
1	0.6605	6	0.3406
2	0.5965	7	0.2766
3	0.5325	8	0.2126
4	0.4686		

See Class Web Site.

[A]

Time

- ● [A] vs. Time
- ○ ln[A] vs. Time
- ○ 1/[A] vs. Time
- ☐ Least Squares

Plot