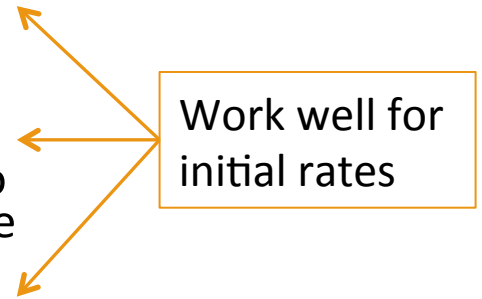
CH 302 – Unit 3 Review 2

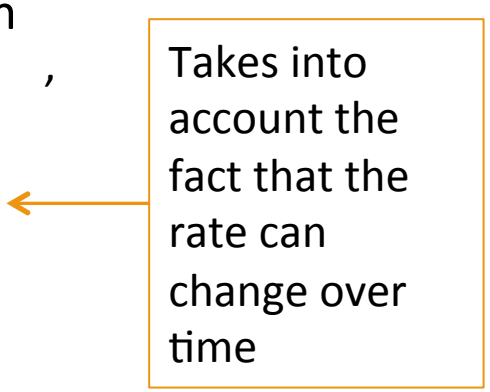
FUNDAMENTALS OF KINETICS

Introduction to Kinetics

There are four types of kinetics questions types that we have discussed in this class:

1. Overall rate of a reaction (think stoichiometry): If you can measure the rate of formation for a product, you can use stoichiometry to determine the rates for all other products and reactants
2. Rate Laws: The rate law is a fundamental equation used to calculate the rate of a reaction from the rate constant, *k*, and the concentrations of the reactants raised to the power of their "order". The overall reaction order is the sum of the orders of the reactants.
3. Empirical Rate Law: Because the order of reactants are not necessarily based on stoichiometry, you must run an experiment to measure this value based on the initial rate of reaction at different starting concentrations
4. Integrated Rate Law: Knowing the order of a reaction, you can determine the rate or concentrations of a reactant at any given point in time (calculus is necessary here because if the rate is dependent on concentration, the rate is changes as the reaction proceeds)





Overall Rate of a Reaction

The fundamental rate of a reaction can be described by the rate of change of any reactant or product of the reaction. A few important notes:

1. Coefficients play an important role: if *b* = 3, the rate of consumption for B is 3 times the overall reaction rate; if *d* = 4, the rate of formation for D is 4 times the overall reaction rate
2. The rate of change for different species can be interconverted: based on the information above, we can say that the rate of formation for D is 4/3 the rate of consumption of B
3. The rate of change for reactants and products are always opposite in sign

$$aA + bB \rightarrow cC + dD$$

$$rate = \frac{-\Delta[A]}{a\Delta t} = \frac{-\Delta[B]}{b\Delta t} = \frac{+\Delta[C]}{c\Delta t} = \frac{+\Delta[D]}{d\Delta t}$$

$$\frac{-d\Delta[B]}{b\Delta t} = \frac{\Delta[D]}{\Delta t}$$

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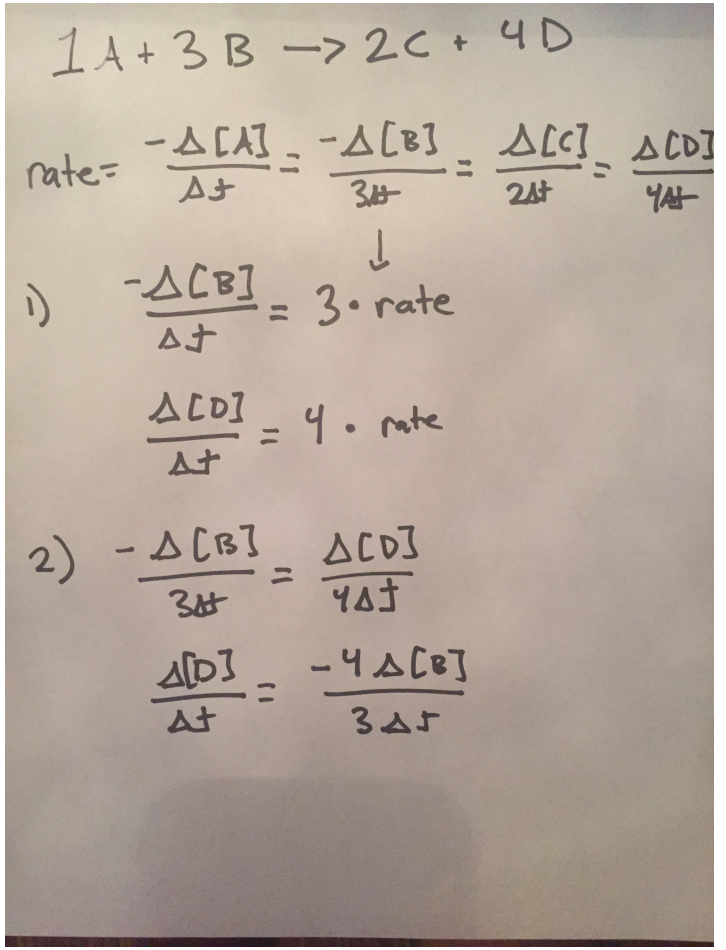

Rate of a Reaction - Example

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

1. Write an expression that represents the overall rate of the reaction in terms of each of the reactants and products
2. Write the rate of formation of ammonia (NH_3) in terms of hydrogen (H_2).
3. Suppose the initial rate of formation of ammonia is 0.6M/s. Write the overall initial rate of the reaction.

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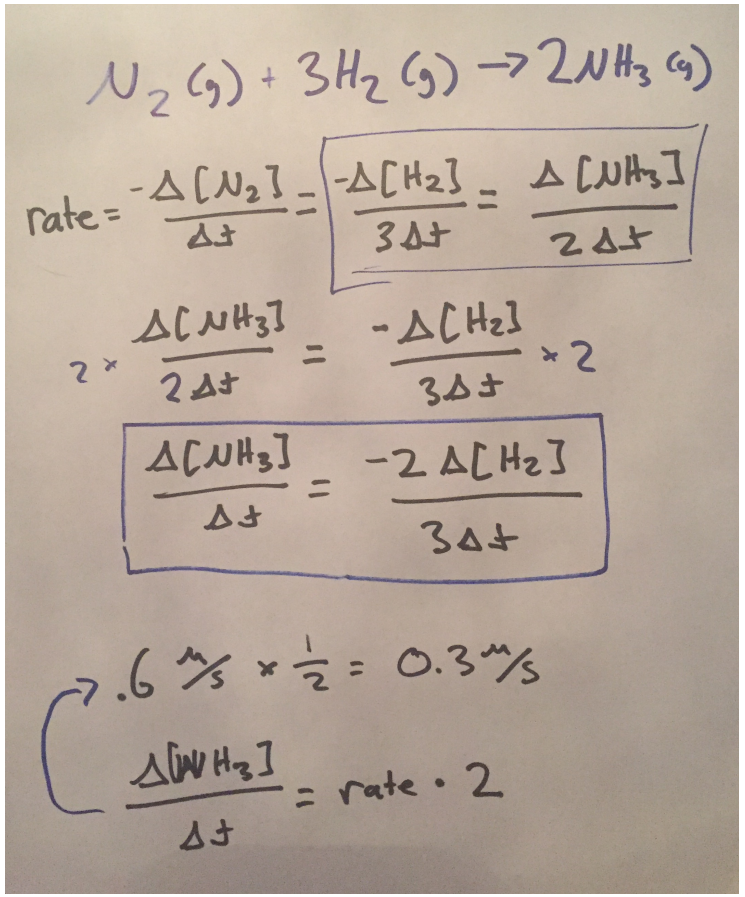


Introduction to Rate Laws

$$aA + bB \rightarrow cC + dD$$

$$rate = k[A]^x[B]^y$$

Rate of reaction in the units of M/s

Rate constant (measured value). Units depend on the order of reaction; must cancel units of $[A]^x$, $[B]^y$ to get rate = M/s

x = order of A
y = order of B
x + y = overall order of the reaction
Order is usually positive integers, but can be fractional or negative in rare cases

Introduction to Rate Laws

What is the order? You have to use experimental data to figure it out.

$$aA \rightarrow cC + dD$$

$$rate = k[A]^x$$

0th Order: rate is independent of [A]

$$rate = k \qquad k = M/s$$

First Order: rate is directly proportional to [A]

$$rate = k[A] \qquad k = 1/s$$

Second Order: rate is proportional to $[A]^2$

$$rate = k[A]^2 \qquad k = 1/Ms$$

Introduction to Rate Laws

Again, you must determine the rate law based on experimental data.

$$aA + bB \rightarrow cC + dD$$

$$rate = k[A]^x[B]^y$$

0th Order:

$$rate = k \qquad k = M/s$$

First Order:

$$rate = k[A] \text{ or } rate = k[B] \qquad k = 1/s$$

Second Order:

$$rate = k[A][B] \text{ or } rate = k[A]^2 \text{ or } rate = k[B]^2 \qquad k = 1/Ms$$

Overall Reaction Order

Order can be applied to the total reaction:

- In this case, the order of the reaction is the sum of the exponents in the rate law.
- Our units of *k* are dependent on the order of the total reaction:
  - 0^{th} order: $k = Ms^{-1}$
  - 1^{st} order: $k = s^{-1}$
  - 2^{nd} order: $k = M^{-1}s^{-1}$
  - 3^{rd} order: $k = M^{-2}\,s^{-1}$

These are all based on the fact that the rate must be in Ms^{-1}, and you are cancelling out the concentration terms on the rate law

Empirical Rate Laws

You can set up an experiment where you measure the initial rate of a reaction at different starting points. This provides you with all the information necessary to derive the rate law for a reaction.

Consider the bromination of pentene:

$2C_5H_{10} + Br_2 \rightarrow 2\ C_5H_{11}Br$

Start with the rate law:

$rate = k\ [C_5H_{10}]^x[Br_2]^y$

Then use the data to solve for x, y.

Trial #	$[C_5H_{10}]$	$[Br_2]$	Rate
1	2M	2M	10M/s
2	4M	2M	20M/s
3	4M	4M	40M/s

Empirical Rate Laws: solution

Trial #	$[C_5H_{10}]$	$[Br_2]$	Rate
1	2M	2M	10M/s
2	4M	2M	20M/s
3	4M	4M	40M/s

Between trials 1, 2: we doubled the concentration of pentene and the rate doubled. No change was made to bromine.

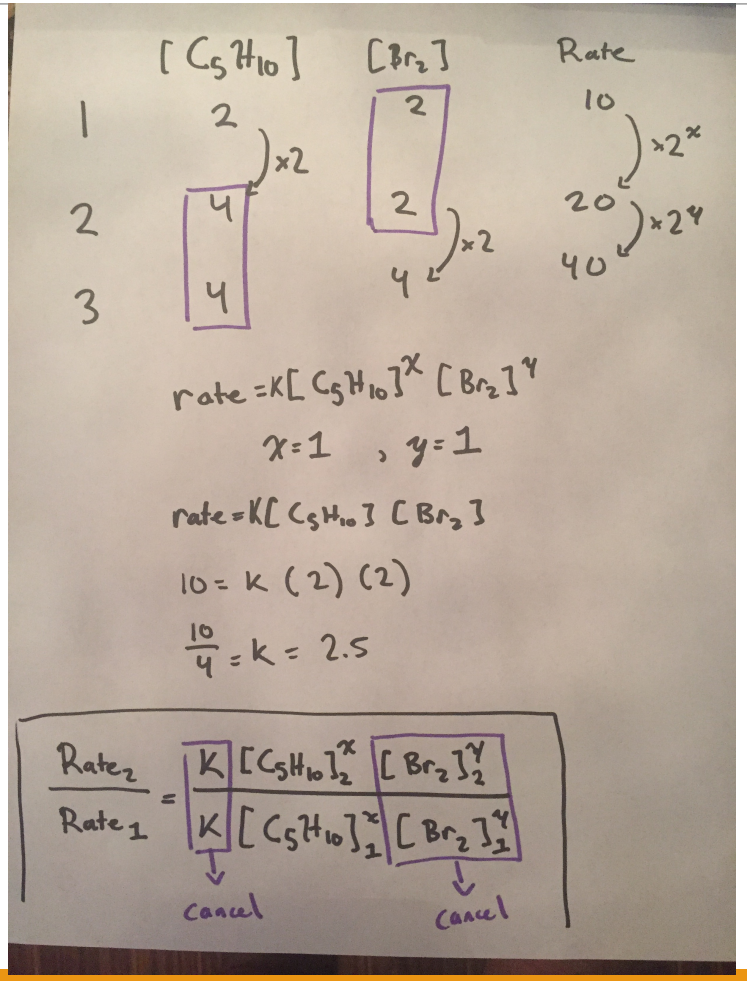
Between trials 2, 3: we doubled the concentration of bromine and the rate doubled. No change was made in pentene. This is indicative of a reaction that is first order in bromine.

Now that we know the order of the reaction, we can set up our equation: rate = $k[C_5H_{10}]^1[Br_2]^1$. The reaction is second order overall.

We can use any trial to solve for k. For example: 10M/s = k(2M)(2M), k = (10M/s)/ $(2M)^2$, **$k = 2.5M^{-1}S^{-1}$**

Important: trials 1, 3 don't make for a great comparison at the beginning because both reagents have different concentrations. It's difficult to determine which reagent is causing the rate to change

Empirical Rate Laws: solution



Exam Question (do on your own)

For the reaction:

$A + B_2 + 2C \rightarrow D$,

You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of k?

	Initial [A] M	Initial [B_2] M	Initial [C] M	Initial rate M/s
1	0.01	0.01	0.10	1.20×10^3
2	0.02	0.01	0.10	4.80×10^3
3	0.03	0.01	0.20	2.16×10^4
4	0.04	0.02	0.10	3.84×10^4

$$\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x[B_2]_2^y[C]_2^z}{k[A]_1^x[B_2]_1^y[C]_1^z}$$

Exam Question

For the reaction:

A + B_2 + 2C -> D,

You run an experiment to determine the initial rates of the reaction under 4 different starting conditions. Write the complete rate law for the reaction. What is the value of k?

Rate = 1.2 x $10^{10}[A]^2[B_2][C]$

(units of *k* omitted)

	Initial [A] M	Initial [B_2] M	Initial [C] M	Initial rate M/s
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$$\frac{Rate_2}{Rate_1} = \frac{k[A]_2^x[B_2]_2^y[C]_2^z}{k[A]_1^x[B_2]_1^y[C]_1^z}$$

Integrated Rate Laws

- **First Order: general formula, slope-intercept formula, half life**

$rate = k[A]$

$$\ln\frac{[A]_0}{[A]} = kt \qquad \ln[A] = \ln[A]_0 - kt \qquad \frac{\ln(2)}{k} = t_{1/2}$$

- **0th Order: general formula, slope-intercept formula, half life**

$rate = k$

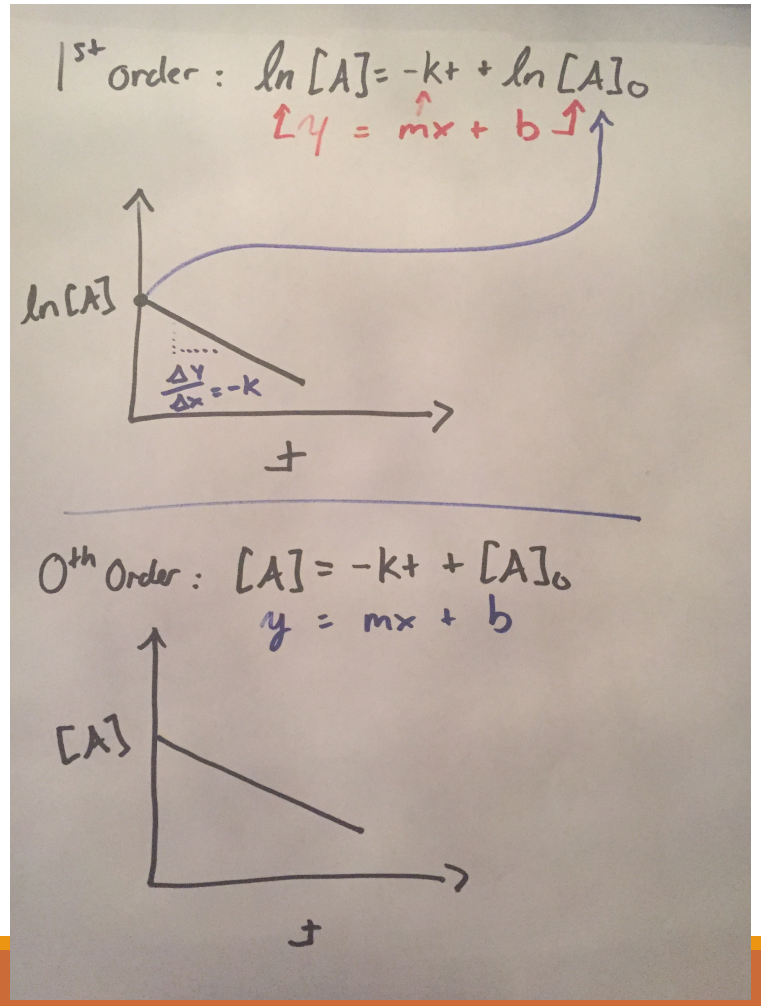
$$[A]_0 - [A] = kt \qquad [A] = [A]_0 - kt \qquad \frac{[A]_0}{2k} = t_{1/2}$$

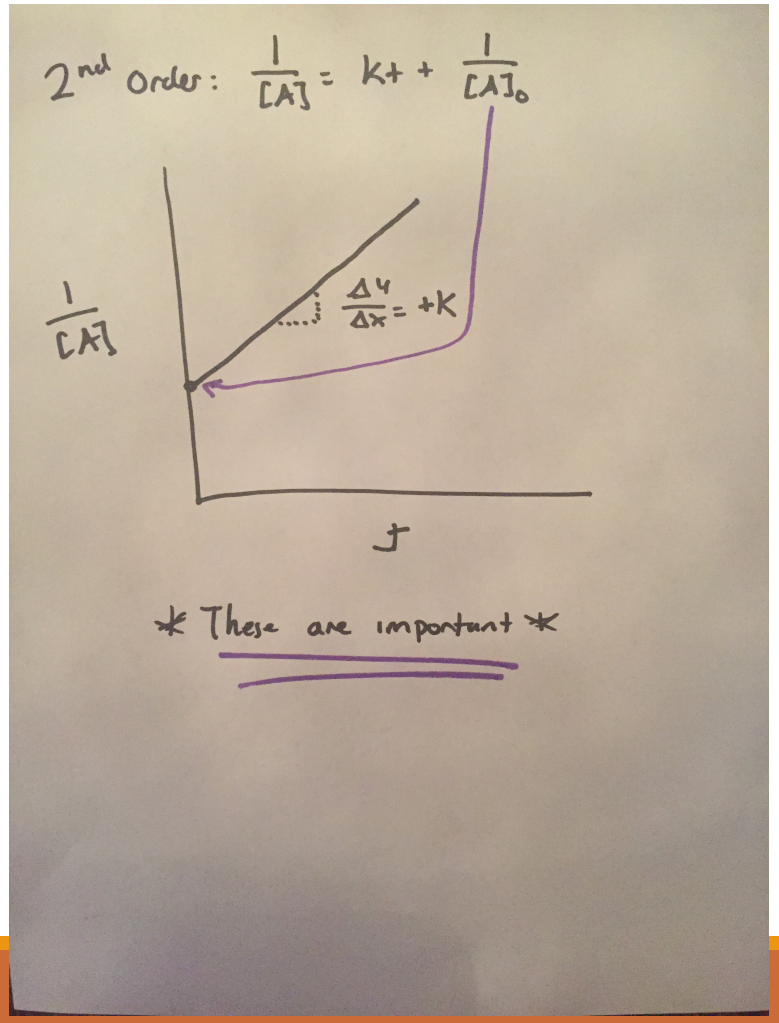
- **2nd Order: general formula, slope-intercept formula, half life**

$rate = k[A]^2$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt \qquad \frac{1}{[A]} = \frac{1}{[A]_0} + kt \qquad \frac{1}{k[A]_0} = t_{1/2}$$

Integrated Rate Laws





Conceptual Note: Integrated Rate Laws

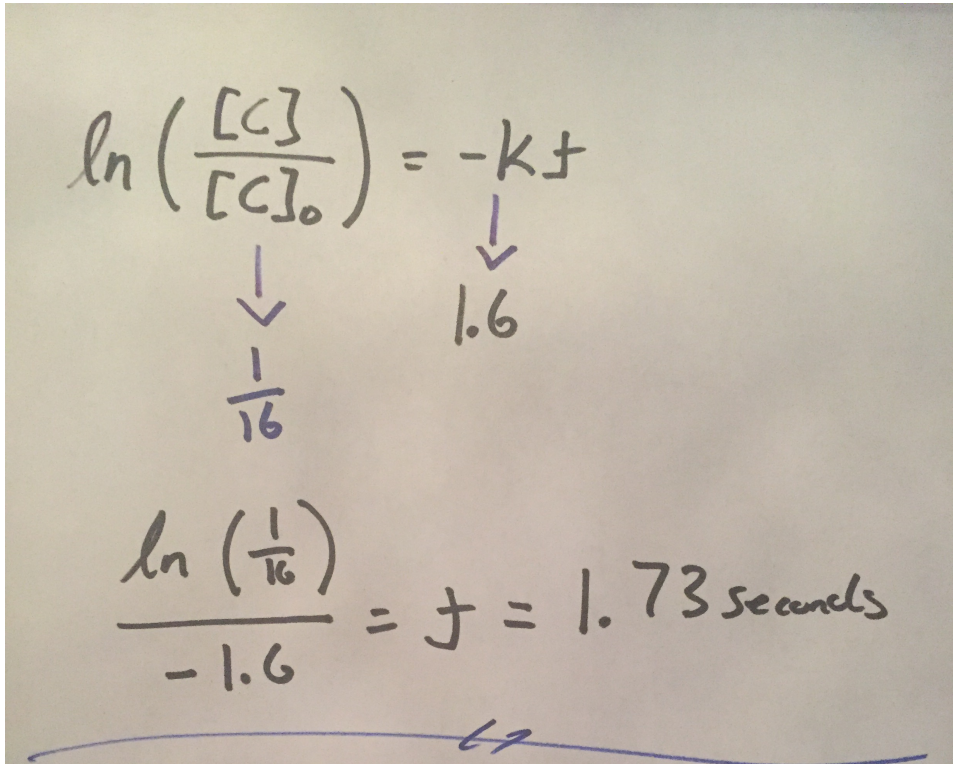
- **Integrated rate laws take into account a single reactant that has 0^{th} order, 1^{st} order, or 2^{nd} order kinetics.** These equations fail when:
  - The reaction has any significant backward rate
  - The reaction is at equilibrium (backwards rate equals the forward rate)
  - When the overall rate depends on the concentration of another reactant (we will discuss “psuedo-first order” on Thursday, which is a way of getting around this problem in an experimental setting)

Exam Question

For the reaction below:

cyclobutane(g) → 2 ethylene(g)

at 800K, a plot of ln[cyclobutane] vs t gives a straight line with a slope of -1.6 s^{-1}.
Calculate the time needed for the concentration of cyclobutane to fall to 1/16 of its initial value.

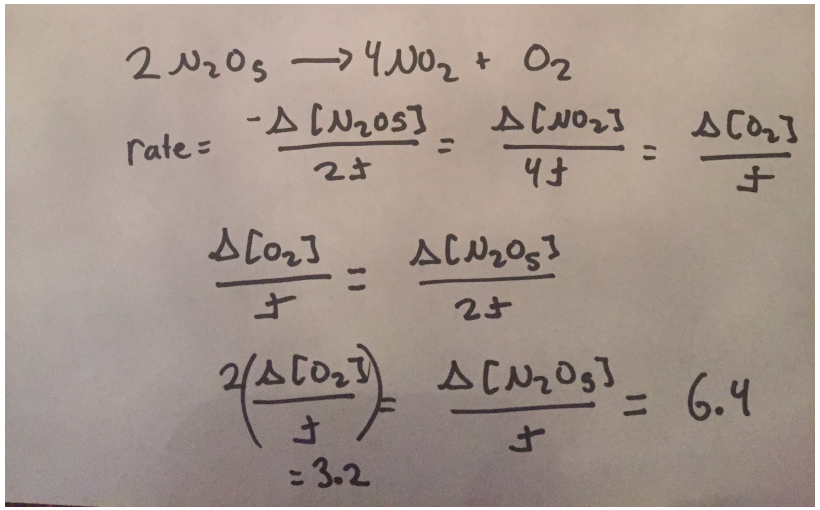


Exam Question

The initial rate of formation of O_2 in the following reaction is 3.2M/s.

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

What is the initial rate of consumption of N_2O_5?



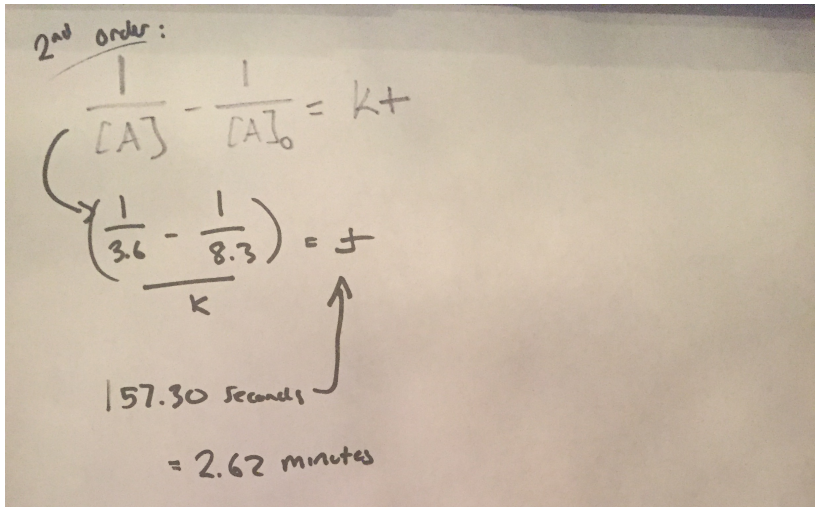
Exam Question

Consider the reaction:

$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$; rate = $k[NO_2]^2$

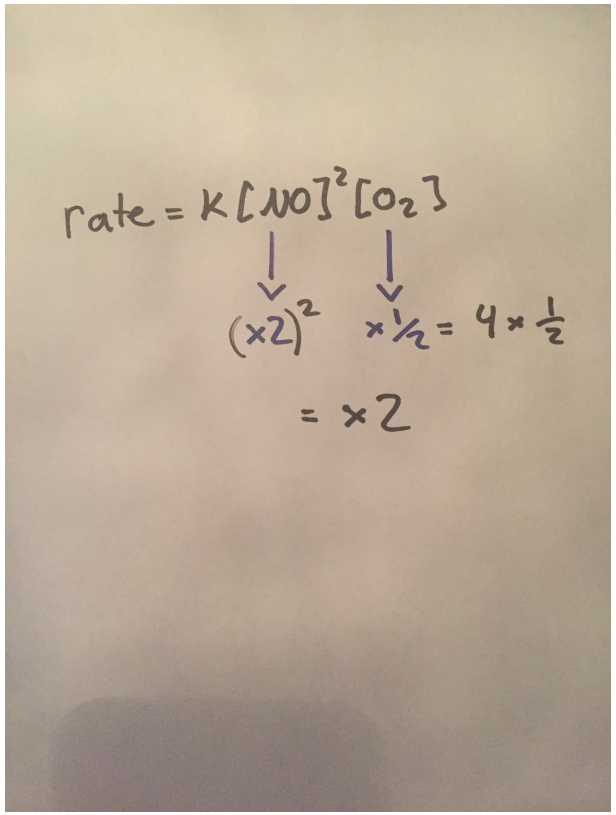
How long will it take for the concentration of NO_2 to decrease from 8.3M to 3.6M? Answer in minutes.

$k = 1 \times 10^{-3}\ M^{-1}S^{-1}$



Homework Question

For the given reaction:

$2NO + O_2 \rightarrow 2NO_2$ rate = $k[NO]^2 [O_2]$,

We carry out two experiments at the same temperature, but in the second experiment the initial concentration of NO is doubled while the initial concentration of O_2 is halved. The initial rate in the second experiment will be how many times that of the first?