

# KINETICS Practice Problems and Solutions

Name: \_\_\_\_\_  
Period: \_\_\_\_\_ Date: \_\_\_\_\_

AP Chemistry  
Dr. Mandes

The following questions represent potential types of quiz questions. Please answer each question completely and thoroughly. The solutions will be posted on-line on Monday.

5. Please do #18 in chapter 12 of your text.
- This increases the  $[H_2]$ , which will increase the rate, but has no effect on  $k$
  - Due to Arrhenius equation, changing temperature changes the value of  $k$ .
  - Catalyst function by lowering the activation energy, so due to Arrhenius equation, changing the activation energy changes the value of  $k$ .

6. Consider the reaction:  $P_4 + 6 H_2 \rightarrow 4 PH_3$ . A rate study of this reaction was conducted at 298 K. The data that were obtained are shown in the table.

$[P_4]$ , mol/L	$[H_2]$ , mol/L	Initial Rate, mol/(L · s)
0.0110	0.0075	$3.20 \times 10^{-4}$
0.0110	0.0150	$6.40 \times 10^{-4}$
0.0220	0.0150	$6.39 \times 10^{-4}$

- What is the order with respect to:  $P_4$  0.  
 $H_2$  1.
  - Write the rate law for this reaction.  $rate = k[H_2]$
  - Determine the value and units of the rate constant,  $k$ . **plug and chug using the rate law & data from exp't 1 and solving for  $k$ , we get  $k = 0.0427 s^{-1}$**
7. Consider the reaction:  $SO_2 + O_3 \rightarrow SO_3 + O_2$ . A rate study of this reaction was conducted at 298 K. The data that were obtained are shown in the table.

$[SO_2]$ , mol/L	$[O_3]$ , mol/L	Initial Rate, mol/(L · s)
0.25	0.40	0.118
0.25	0.20	0.118
0.75	0.20	1.062

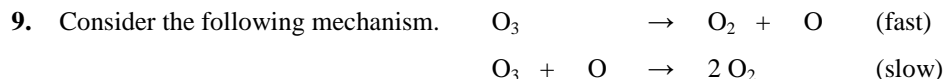
- What is the order with respect to:  $SO_2$  2.  
 $O_3$  0.
- Write the rate law for this reaction.  $rate = k[SO_2]^2[O_3]^0$
- Determine the value and units of the rate constant,  $k$ . **plug and chug using the rate law & data from exp't 1 and solving for  $k$ , we get  $k = 2.36 mol^{-1} L s^{-1}$**

8. Consider the following mechanism.  $A_2 + B_2 \rightarrow R + C$  (slow)  
 $A_2 + R \rightarrow C$  (fast)

- Write the overall balanced chemical equation.  $2 A_2 + B_2 \rightarrow 2 C$
- Identify any intermediates within the mechanism. **R**
- What is the order with respect to each reactant?  $A_2$  **1<sup>st</sup>**;  $B_2$  **1<sup>st</sup>**

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d. Write the rate law for the overall reaction.  $\text{rate} = k [\text{A}_2][\text{B}_2]$



- Write the overall balanced chemical equation.  $2 \text{O}_3 \rightarrow 3 \text{O}_2$
- Identify any intermediates within the mechanism.  $\text{O}$
- What is the order with respect to each reactant?  $\text{O}_3$  2<sup>nd</sup> (once in rds, then once when sub for intermediate)
- Write the rate law for the overall reaction.  $\text{rate} = k [\text{O}_3]^2$

10. Consider the reaction:  $2\text{B} \rightarrow \text{C} + 3\text{D}$ . In one experiment it was found that at 300 K the rate constant is 0.134 L/(mol·s). A second experiment showed that at 450 K, the rate constant was 0.569 L/(mol·s). Determine the activation energy for the reaction.

at 300 K:  $k_{300} = Ae^{\frac{-E_a}{RT}}$

at 450 K:  $k_{450} = Ae^{\frac{-E_a}{RT}}$

$$\ln \frac{k_{450}}{A} = \frac{-E_a}{RT}$$

$$\ln(k_{450}) - \ln(A) = \frac{-E_a}{RT} \quad \text{where } \ln(A) = \ln(k_{300}) - \frac{-E_a}{RT}$$

so that

$$\ln(k_{450}) - [\ln(k_{300}) - \frac{-E_a}{RT}] = \frac{-E_a}{RT}$$

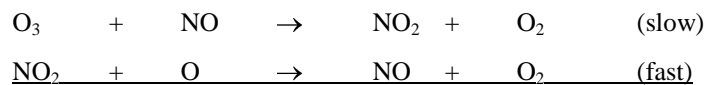
$$\ln\left(\frac{k_{450}}{k_{300}}\right) = \frac{E_a}{R} \left(\frac{1}{T_{300}} - \frac{1}{T_{450}}\right)$$

plug and solve for  $E_a$ ,  $E_a = 10.8 \text{ kJ}$

### **MORE PROBLEMS>>>>**

**Determining rate law from mechanisms** (use the rate-determining step to get the orders).

1. One method for the destruction of ozone in the upper atmosphere is:



overall rxn  $\text{O}_3 + \text{O} \rightarrow 2\text{O}_2$

- Which species is an intermediate? \_\_\_\_\_
- Which species is a catalyst? \_\_\_\_\_
- Which is the rate-determining step (rds)? \_\_\_\_\_
- Number of times each reactant is used in the rds? \_\_\_\_\_
- Write the rate law for the reaction. \_\_\_\_\_

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**Determining rate law from Initial Rates.** (Use the ratio of initial rates to get the orders).

2. Consider the table of initial rates for the reaction:  $2\text{ClO}_2 + 2\text{OH}^- \rightarrow \text{ClO}_3^- + \text{ClO}_2^- + \text{H}_2\text{O}$ .

Experiment	$[\text{ClO}_2]_0$ , mol/L	$[\text{OH}^-]_0$ , mol/L	Initial Rate, mol/(L · s)
1	0.050	0.100	$5.75 \times 10^{-2}$
2	0.100	0.100	$2.30 \times 10^{-1}$
3	0.100	0.050	$1.15 \times 10^{-1}$

- a. Order with respect to  $\text{ClO}_2$ : \_\_\_\_\_
- b. Order with respect to  $\text{OH}^-$ : \_\_\_\_\_
- c. Rate law for this reaction: \_\_\_\_\_
- d. Value and units for the rate constant: \_\_\_\_\_
3. Consider the table of initial rate for the reaction between hemoglobin (Hb) and carbon monoxide.

Experiment	$[\text{HB}]_0$ , $\mu\text{mol/L}$	$[\text{CO}]_0$ , $\mu\text{mol/L}$	Initial Rate, $\mu\text{mol}/(\text{L} \cdot \text{s})$
1	2.21	1.00	0.619
2	4.42	1.00	1.24
3	3.36	2.40	2.26

- a. Order with respect to HB: \_\_\_\_\_
- b. Order with respect to CO: \_\_\_\_\_
- c. Rate law for this reaction: \_\_\_\_\_
- d. Value and units for the rate constant: \_\_\_\_\_

**Part II Select Response** Select the best answer to each question.

1. If the reaction:  $2\text{HI} \rightarrow 2\text{H}_2 + \text{I}_2$  HI is first order, which of the following will yield a linear plot?
- a.  $\log [\text{HI}]$  vs time      b.  $1/[\text{HI}]$  vs time      e.  $[\text{HI}]^2$  vs time  
 c.  $[\text{HI}]$  vs time      d.  $\ln[\text{HI}]$  vs time
2. Consider the reaction:  $\text{X} \rightarrow \text{Y} + \text{Z}$ . Which of the following is a possible rate law for the reaction?
- a. rate =  $k[\text{X}]$       b. rate =  $k[\text{Y}][\text{Z}]$       e. rate =  $k[\text{Z}]$   
 c. rate =  $k[\text{Y}]$       d. rate =  $k[\text{X}][\text{Y}]$
3. Consider the rate law: rate =  $k[\text{Y}]^m[\text{Z}]^n$ . How are the exponents  $m$  and  $n$  determined?
- a. by using the balanced chemical equation  
 b. by using the subscripts of the chemical formulas  
 c. by using the coefficients of the chemical formulas  
 d. by educated guess  
 e. by experiment
4. The following data were obtained for the reaction of NO with  $\text{O}_2$ .
- | $[\text{NO}]_0$    | $[\text{O}_2]_0$   | Initial Rate         |
|--------------------|--------------------|----------------------|
| $1 \times 10^{18}$ | $1 \times 10^{18}$ | $2.0 \times 10^{18}$ |
| $2 \times 10^{18}$ | $1 \times 10^{18}$ | $8.0 \times 10^{18}$ |

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$3 \times 10^{18}$

$1 \times 10^{18}$

$18.0 \times 10^{18}$

$1 \times 10^{18}$

$2 \times 10^{18}$

$4.0 \times 10^{18}$

$1 \times 10^{18}$

$3 \times 10^{18}$

$6.0 \times 10^{18}$

Which of the following is the correct rate law?

a.  $\text{rate} = k[\text{NO}][\text{O}_2]$

b.  $\text{rate} = k[\text{NO}][\text{O}_2]^2$

e.  $\text{rate} = k[\text{NO}]^2[\text{O}_2]^2$

c.  $\text{rate} = k[\text{NO}]^2[\text{O}_2]$

d.  $\text{rate} = k[\text{NO}]^2$

5. If the reaction  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  is second order, which of the following will yield a linear plot?

a.  $\log [\text{HI}]$  vs time

b.  $1/[\text{HI}]$  vs time

e.  $[\text{HI}]^2$  vs time

c.  $[\text{HI}]$  vs time

d.  $\ln[\text{HI}]$  vs time

6. Which of the following statements is typically true for a catalyst?

a. The concentration of the catalyst will go down as the reaction proceeds.

b. The catalyst provides a new pathway in the reaction mechanism.

c. The catalyst speeds up the reaction.

d. Two of the above.

e. None of the above.

7. The catalyzed reaction has a \_\_\_\_\_ activation energy and thus causes a \_\_\_\_\_ reaction rate.

a. higher, lower

b. higher, higher

e. higher, steady

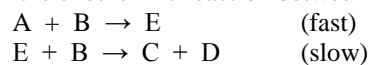
c. lower, higher

d. lower, steady

# ***KINETICS Practice Problems and Solutions***

**Part II Constructed Response** Thoroughly and completely answer each question on **a separate piece** of paper.

8. Consider the exothermic reaction between reactants A and B?



- What is the order with respect to reactants A and B? 1, 2
- What is the rate law for the reaction?
- Sketch a potential energy diagram for this reaction. Identify the activation energy for the overall forward reaction. Identify the location of reactants, intermediate(s), activated complex(es), and products.

9. A first-order reaction is 38.5% complete in 480 s.

- Calculate the value of the rate constant.
- What is the value of the half-life.
- How long will it take for the reaction to reach 95% completion.

10. The rate of the reaction  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$  depends only on the concentration of nitrogen dioxide. The following data were collected.

<u>time, (s)</u>	<u><math>[\text{NO}_2]_0, (\text{M})</math></u>
0	0.500
$1.20 \times 10^3$	0.444
$3.00 \times 10^3$	0.381
$4.50 \times 10^3$	0.340
$9.00 \times 10^3$	0.250
$1.80 \times 10^4$	0.174

- Determine the rate law.
- Write the integrated rate law.
- Determine the value of the rate constant for the reaction.
- Calculate the  $[\text{NO}_2]$  at  $2.40 \times 10^4$  s after the start of the reaction.

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Determining rate law from time and concentration data. (Use the integrated rate laws and graphing to get orders).

4. The rate of this rxn depends only on  $\text{NO}_2$ :  $\text{NO}_2 + \text{CO} \rightarrow \text{NO} + \text{CO}_2$ .

The following data were collected.

Time (s)	$[\text{NO}_2]$ (mol/L)
0	0.500
1200.	0.444
3000.	0.381
4500.	0.340
9000.	0.250
18000.	0.174

- a. Order with respect to  $\text{NO}_2$ : \_\_\_\_\_
- b. Rate law for this reaction: \_\_\_\_\_
- c.  $[\text{NO}_2]$  at  $2.7 \times 10^4$  s after the start of the rxn. \_\_\_\_\_
5. The following data were obtained for the decomposition of  $\text{N}_2\text{O}_5$  in  $\text{CCl}_4$ .

The following data were collected.

Time (s)	$[\text{N}_2\text{O}_5]$ (mol/L)
0	1.46
423	1.09
753	0.89
1116	0.72
1582	0.54
1986	0.43
2343	0.35

- a. Order with respect to  $\text{N}_2\text{O}_5$ : \_\_\_\_\_
- b. Rate law for this reaction: \_\_\_\_\_
- c.  $[\text{N}_2\text{O}_5]$  at  $3.5 \times 10^3$  s after the start of the rxn. \_\_\_\_\_

## SOLUTIONS!!!!!! TO "MORE PROBLEMS">>>>>

1. a. Which species is an intermediate?  $\text{NO}_2$
- b. Which species is a catalyst?  $\text{NO}$
- c. Which is the rate-determining step (rds)? slow step
- d. Number of times each reactant is used in the rds?  
 $\text{O}_3$  is used once so order is 1  
 $\text{O}$  is used zero times, so order is 0
- e. Write the rate law for the reaction.  
rate =  $k[\text{O}_3]^1$
-

## **KINETICS Practice Problems and Solutions**

Note that for a free-response question you must show the work (ratio of rate laws), but not for multiple choice

$$2. \quad \frac{rate_2}{rate_1} = \frac{k[ClO_2]_2^m [OH^-]_2^n}{k[ClO_2]_1^m [OH^-]_1^n}$$

$$\frac{0.230}{0.0575} = \frac{0.100^m}{0.0500^m}$$

$$4 = 2^m$$

$$2 = m, \text{ so order is } 2$$

$$\frac{rate_2}{rate_3} = \frac{k[ClO_2]_2^m [OH^-]_2^n}{k[ClO_2]_3^m [OH^-]_3^n}$$

$$\frac{0.230}{0.115} = \frac{0.100^m}{0.0500^m}$$

$$2 = 2^n$$

$$1 = n, \text{ so order is } 1$$

a. Order with respect to  $ClO_2$ :

2

b. Order with respect to  $OH^{1-}$ :

1

c. Rate law for this reaction:

$$\text{so, rate} = k[ClO_2]^2 [OH^{1-}]^1$$

d. Value and units for the rate constant:

$$k = 230 \frac{L^2}{mol^2 \cdot s}$$

get the value by subbing the data for exp't 1 into the rate law and solving for k

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$$3. \quad \frac{rate_2}{rate_1} = \frac{k[HB]_2^m [CO]_2^n}{k[HB]_1^m [CO]_1^n}$$

$$\frac{1.24}{0.619} = \frac{4.42^m}{2.21^m} s$$

$$2 = 2^m$$

$$1 = m, \text{ so the order is } 1$$

$$\frac{rate_3}{rate_1} = \frac{k[HB]_3^m [CO]_3^n}{k[HB]_1^m [CO]_1^n}$$

$$\frac{2.26}{0.619} = \frac{3.36^1}{2.21^1} \frac{2.41^n}{1.00^n}$$

$$2.4 = 2.4^n$$

$$1 = n, \text{ so the order is } 1$$

a. Order with respect to HB:

1

b. Order with respect to CO:

1

c. Rate law for this reaction:

$$\text{so, rate} = k[HB]^1 [CO]^1$$

d. Value and units for the rate constant:

$$k = 0.28 \frac{L}{mol \cdot s}$$

get the value by subbing the data for exp't 1 into the rate law and solving for k

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## **KINETICS Practice Problems and Solutions**

4.

- Graph for zeroth order:  $[\text{NO}_2]$  vs. time [y vs. x;  $y = ax + b$ ]

$$\text{slope} = -1.72 \times 10^{-5} \qquad \text{y-intercept} = 0.451 \qquad r^2 = 0.901$$

$$\text{General integrated rate law: } [A] = -kt + [A]_0$$

$$\text{This reaction's integrated rate law: } [\text{H}_2\text{O}_2] = (-1.72 \times 10^{-5})t + 0.451 \qquad r^2 = 0.901$$

- Graph for first order:  $\ln[\text{NO}_2]$  vs. time [y vs. x;  $y = ax + b$ ]

$$\text{slope} = -5.78 \times 10^{-5} \qquad \text{y-intercept} = -0.770 \qquad r^2 = 0.971$$

$$\text{General integrated rate law: } \ln[A] = -kt + \ln[A]_0$$

$$\text{This reaction's integrated rate law: } \ln[\text{NO}_2] = (-5.78 \times 10^{-5})t + (-0.770) \qquad r^2 = 0.971$$

- Graph for second order:  $[\text{NO}_2]^{-1}$  vs. time [y vs. x;  $y = ax + b$ ]

$$\text{slope} = 2.10 \times 10^{-4} \qquad \text{y-intercept} = 2.01 \qquad r^2 = 0.999 - \text{best so}$$

order is 2

$$\text{General integrated rate law: } [A]^{-1} = kt + [A]_0^{-1}$$

$$\text{This reaction's integrated rate law: } [\text{NO}_2]^{-1} = 2.10 \times 10^{-4}t + 2.01 \qquad r^2 = 0.999$$

- Graph with the greatest  $r^2$  value:  $[\text{NO}_2]^{-1}$  vs. time, so the order is second order

a. Order with respect to  $\text{NO}_2$ :

$$\underline{\underline{2}}$$

b. Rate law for this reaction:

$$\underline{\underline{\text{rate} = k[\text{NO}_2]^2}}$$

c.  $[\text{NO}_2]$  at  $2.7 \times 10^4$  s after the start of the rxn.  
+ 2.01"

$$\text{Subbing } 2.7 \times 10^4 \text{ s for time in } "[\text{NO}_2]^{-1} = 2.10 \times 10^{-4}t$$

$$[\text{NO}_2] = 0.130 \text{ mol/L}$$

5.

- Graph for zeroth order:  $[\text{N}_2\text{O}_5]$  vs. time [y vs. x;  $y = ax + b$ ]

$$\text{slope} = -4.54 \times 10^{-4} \qquad \text{y-intercept} = 1.31 \qquad r^2 = 0.947$$

$$\text{General integrated rate law: } [A] = -kt + [A]_0$$

$$\text{This reaction's integrated rate law: } [\text{N}_2\text{O}_5] = (-4.54 \times 10^{-4})t + 1.31 \qquad r^2 = 0.947$$

- Graph for first order:  $\ln[\text{N}_2\text{O}_5]$  vs. time [y vs. x;  $y = ax + b$ ]

$$\text{slope} = -6.05 \times 10^{-4} \qquad \text{y-intercept} = 0.353 \qquad r^2 = 0.999$$

$$\text{General integrated rate law: } \ln[A] = -kt + \ln[A]_0$$

$$\text{This reaction's integrated rate law: } \ln[\text{N}_2\text{O}_5] = (-6.05 \times 10^{-4})t + 0.353 \qquad r^2 = 0.999 - \text{best so}$$

order is 1



## ***KINETICS Practice Problems and Solutions***

- Graph for second order:  $[\text{N}_2\text{O}_5]^{-1}$  vs. time [y vs. x;  $y = ax + b$ ]

slope =  $9.18 \times 10^{-4}$                       y-intercept =  $0.517$                        $r^2 = 0.971$

General integrated rate law:                       $[A]^{-1} = kt + [A]_0^{-1}$

This reaction's integrated rate law:                       $[\text{N}_2\text{O}_5]^{-1} = 9.18 \times 10^{-4}t + 0.517$                        $r^2 = 0.971$

- Graph with the greatest  $r^2$  value:                       $\ln [\text{N}_2\text{O}_5]$  vs. time, *so the order is first order*

Order with respect to  $\text{N}_2\text{O}_5$ :

Rate law for this reaction:

a. Order with respect to  $\text{N}_2\text{O}_5$ :

\_\_\_\_\_1\_\_\_\_\_

b. Rate law for this reaction:

\_\_\_\_\_rate =  $k[\text{N}_2\text{O}_5]^1$ \_\_\_\_\_

c.  $[\text{N}_2\text{O}_5]$  at  $3.5 \times 10^3$  s after the start of the rxn.                      Subbing  $3.5 \times 10^3$  s for time in " $\ln[\text{N}_2\text{O}_5] = (-6.05 \times 10^{-4}t + 1.31$ "

$[\text{N}_2\text{O}_5] = 0.171 \text{ mol/L}$