# KINETICS Practice Problems and Solutions 

Name:
Period: $\qquad$

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.
6. Consider the reaction: $\mathrm{P}_{4}+6 \mathrm{H}_{2} \rightarrow 4 \mathrm{PH}_{3}$. A rate study of this reaction was conducted at 298 K . The data that were obtained are shown in the table.

| $\left[\mathrm{P}_{4}\right], \mathrm{mol} / \mathrm{L}$ | $\left[\mathrm{H}_{2}\right], \mathrm{mol} / \mathrm{L}$ | Initial Rate, $\mathrm{mol} /(\mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: |
| 0.0110 | 0.0075 | $3.20 \times 10^{-4}$ |
| 0.0110 | 0.0150 | $6.40 \times 10^{-4}$ |
| 0.0220 | 0.0150 | $6.39 \times 10^{-4}$ |

a. What is the order with respect to:

$$
\mathrm{P}_{4} \quad-0 \_ \text {. }
$$ .

$\mathrm{H}_{2} \quad{ }^{-1}$ $\qquad$ .
b. Write the rate law for this reaction. rate $=\mathrm{k}\left[\mathrm{H}_{2}\right]$
c. 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 $\mathrm{k}=0.0427 \mathrm{~s}^{-1}$
7. Consider the reaction: $\mathrm{SO}_{2}+\mathrm{O}_{3} \rightarrow \mathrm{SO}_{3}+\mathrm{O}_{2}$. A rate study of this reaction was conducted at 298 K . The data that were obtained are shown in the table.

| $\left[\mathrm{SO}_{2}\right], \mathrm{mol} / \mathrm{L}$ | $\left[\mathrm{O}_{3}\right], \mathrm{mol} / \mathrm{L}$ | Initial Rate, $\mathrm{mol} /(\mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: |
| 0.25 | 0.40 | 0.118 |
| 0.25 | 0.20 | 0.118 |
| 0.75 | 0.20 | 1.062 |

a. What is the order with respect to: $\qquad$ 2_.
$\mathrm{O}_{3} \quad 0_{-}$ $\qquad$
b. Write the rate law for this reaction. rate $=\mathrm{k}\left[\mathrm{SO}_{2}\right]^{2}\left[\mathrm{O}_{3}\right]^{0}$
c. 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 $\mathrm{k}=2.36 \mathrm{~mol}^{-1} \mathrm{~L}^{-1} \cdot \mathrm{~s}^{-1}$
8. Consider the following mechanism. $\quad \mathrm{A}_{2}+\mathrm{B}_{2} \rightarrow \mathrm{R}+\mathrm{C}$ (slow)

$$
\mathrm{A}_{2}+\mathrm{R} \rightarrow \mathrm{C} \quad \text { (fast) }
$$

a. Write the overall balanced chemical equation. $2 \mathrm{~A}_{2}+\mathrm{B}_{2} \rightarrow 2 \mathrm{C}$
b. Identify any intermediates within the mechanism. R
c. What is the order with respect to each reactant? $\mathrm{A}_{2} 1^{\text {st. }} ; \mathrm{B}_{2} \quad 1^{\text {st }}$
d. Write the rate law for the overall reaction. rate $=k\left[\mathrm{~A}_{2}\right]\left[\mathrm{B}_{2}\right]$
9. Consider the following mechanism. $\mathrm{O}_{3} \rightarrow \mathrm{O}_{2}+\mathrm{O}$
$\mathrm{O}_{3}+\mathrm{O} \rightarrow 2 \mathrm{O}_{2}$
(slow)
a. Write the overall balanced chemical equation. $2 \mathrm{O}_{3} \rightarrow 3 \mathrm{O}_{2}$

## KINETICS Practice Problems and Solutions

b. Identify any intermediates within the mechanism. O
c. What is the order with respect to each reactant? $\mathrm{O}_{3} 2^{\text {nd }}$ (once in rds, then once when sub for intermediate)
d. Write the rate law for the overall reaction. rate $=\mathrm{k}\left[\mathrm{O}_{3}\right]^{2}$
10. Consider the reaction: $2 \mathrm{~B} \rightarrow \mathrm{C}+3 \mathrm{D}$. In one experiment it was found that at 300 K the rate constant is 0.134 $\mathrm{L} /(\mathrm{mol} \cdot \mathrm{s})$. A second experiment showed that at 450 K , the rate constant was $0.569 \mathrm{~L} /(\mathrm{mol} \cdot \mathrm{s})$. Determine the activation energy for the reaction.
at $300 \mathrm{~K}: \quad k_{300}=A e^{\frac{-E a}{R T}}$
at $450 \mathrm{~K}: \quad k_{450}=A e^{\frac{-E a}{R T}}$
$\ln \left(\frac{k_{450}}{A}\right)=\frac{-E_{a}}{R T}$
$\ln \left(k_{450}\right)-\ln (A)=\frac{-E_{a}}{R T} \quad$ where $\ln (A)=\ln \left(k_{300}\right)-\frac{-E_{a}}{R T}$
so that
$\ln \left(k_{450}\right)-\left[\ln \left(k_{300}\right)-\frac{-E_{a}}{R T}\right]=\frac{-E_{a}}{R T}$
$\ln \left(\frac{k_{450}}{k_{300}}\right)=\frac{E_{a}}{R}\left(\frac{1}{T_{300}}-\frac{1}{T_{450}}\right)$
plug and solve for $\mathrm{Ea}, \mathrm{Ea}=10.8 \mathrm{~kJ}$

## 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:

| $\mathrm{O}_{3}$ | +NO | $\rightarrow$ | $\mathrm{NO}_{2}+$ | $\mathrm{O}_{2}$ | (slow) |
| :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{NO}_{2}$ | +O | $\rightarrow$ | $\mathrm{NO}+\mathrm{O}_{2}$ | (fast) |  |

overall rxn $\mathrm{O}_{3}+\mathrm{O} \quad \rightarrow \quad 2 \mathrm{O}_{2}$
a. Which species is an intermediate?
b. Which species is a catalyst?
c. Which is the rate-determining step (rds)?
d. Number of times each reactant is used in the rds?
e. Write the rate law for the reaction.

## KINETICS Practice Problems and Solutions

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: $2 \mathrm{ClO}_{2}+2 \mathrm{OH}^{1-} \rightarrow \mathrm{ClO}_{3}{ }^{1-}+\mathrm{ClO}_{2}{ }^{1-}+\mathrm{H}_{2} \mathrm{O}$.

| Experiment | $\left[\mathrm{ClO}_{2}\right]_{\mathrm{o}}, \mathrm{mol} / \mathrm{L}$ | $\left[\mathrm{OH}^{1-}\right]_{\mathrm{o}}, \mathrm{mol} / \mathrm{L}$ | Initial Rate, $\mathrm{mol} /(\mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: | :---: |
| 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 $\mathrm{ClO}_{2}$ :
b. Order with respect to $\mathrm{OH}^{1-}$ :
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 $(\mathrm{Hb})$ and carbon monoxide.

| Experiment | $[\mathrm{HB}]_{\mathrm{o}}, \mu \mathrm{mol} / \mathrm{L}$ | $[\mathrm{CO}]_{\mathrm{o}}, \mu \mathrm{mol} / \mathrm{L}$ | Initial Rate, $\mu \mathrm{mol} /(\mathrm{L} \cdot \mathrm{s})$ |
| :---: | :---: | :---: | :---: |
| 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: $\qquad$
d. Value and units for the rate constant: $\qquad$

## KINETICS Practice Problems and Solutions

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 $\mathrm{NO}_{2}: \quad \mathrm{NO}_{2}+\mathrm{CO} \rightarrow \mathrm{NO}+\mathrm{CO}_{2}$.

The following data were collected.

| Time (s) | $\left[\mathbf{N O}_{2}\right](\mathrm{mol} / \mathrm{L})$ |
| :---: | :---: |
| 0 | 0.500 |
| 1200. | 0.444 |
| 3000. | 0.381 |
| 4500. | 0.340 |
| 9000. | 0.250 |
| 18000. | 0.174 |

a. Order with respect to $\mathrm{NO}_{2}$ :
b. Rate law for this reaction: $\qquad$
c. $\left[\mathrm{NO}_{2}\right]$ at $2.7 \times 10^{4} \mathrm{~s}$ after the start of the rxn.
5. The following data were obtained for the decomposition of $\mathrm{N}_{2} \mathrm{O}_{5}$ in $\mathrm{CCl}_{4}$.

The following data were collected.

| Time (s) | $\left[\mathbf{N}_{\mathbf{2}} \mathbf{O}_{\mathbf{5}}\right](\mathrm{mol} / \mathrm{L})$ |
| :---: | :---: |
| 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 $\mathrm{N}_{2} \mathrm{O}_{5}$ :
b. Rate law for this reaction: $\qquad$
c. $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ at $3.5 \times 10^{3} \mathrm{~s}$ after the start of the rxn.

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

1. 

a. Which species is an intermediate?
$\mathrm{NO}_{2}$
b. Which species is a catalyst?

NO
c. Which is the rate-determining step (rds)?
slow step
d. Number of times each reactant is used in the rds?
e. Write the rate law for the reaction.
$\mathrm{O}_{3}$ is used once so order is 1 O is used zero times, so order is 0
rate $=\mathrm{k}\left[\mathrm{O}_{3}\right]^{1}$

## 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. $\frac{\text { rate }_{2}}{\text { rate }_{1}}=\frac{k\left[\mathrm{ClO}_{2}\right]_{2}^{n}\left[\mathrm{OH}^{-}\right]_{2}^{n}}{k\left[\mathrm{ClO}_{2}\right]_{1}^{n}\left[\mathrm{OH}^{-}\right]_{1}^{n}}$

$$
\frac{\text { rate }_{2}}{\text { rate }_{3}}=\frac{k\left[\mathrm{ClO}_{2}\right]_{2}^{n}\left[\mathrm{OH}^{-}\right]_{2}^{n}}{k\left[\mathrm{ClO}_{2}\right]_{3}^{n}\left[\mathrm{OH}^{-}\right]_{3}^{n}}
$$

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

$$
4=2^{m}
$$

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

a. Order with respect to $\mathrm{ClO}_{2}$ :

2
b. Order with respect to $\mathrm{OH}^{1-}$ :

1
c. Rate law for this reaction:
so, rate $=\mathrm{k}\left[\mathrm{ClO}_{2}\right]^{2}\left[\mathrm{OH}^{1-}\right]^{1}$
d. Value and units for the rate constant:
$\mathrm{k}=230 \frac{L^{2}}{\mathrm{~mol}{ }^{2} \cdot \mathrm{~s}}$
get the value by subbing the data for exp't 1 into the rate law and solving for k
3. $\frac{\text { rate }_{2}}{\text { rate }_{1}}=\frac{k[\mathrm{HB}]_{2}^{m}[\mathrm{CO}]_{2}^{n}}{k[\mathrm{HB}]_{1}^{m}[\mathrm{CO}]_{1}^{n}}$

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

$$
\begin{aligned}
& \frac{\text { rate }_{3}}{\text { rate }_{1}}=\frac{k[\mathrm{HB}]_{3}^{m}[\mathrm{CO}]_{3}^{n}}{k[\mathrm{HB}]_{1}^{m}[\mathrm{CO}]_{1}^{n}} \\
& \frac{2.26}{0.619}=\frac{(3.36)^{1}}{(2.21)^{1}} \frac{(2.41)^{n}}{(1.00)^{n}}
\end{aligned}
$$

$$
2=2^{m}
$$

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

$$
\begin{aligned}
2.4 & =2.4^{n} \\
1 & =\mathrm{n} \text {, so the order is } 1
\end{aligned}
$$

a. Order with respect to HB :

1
b. Order with respect to CO:

1
c. Rate law for this reaction:

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

d. Value and units for the rate constant:

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

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

## KINETICS Practice Problems and Solutions

4. 

- Graph for zeroeth order: $\left[\mathrm{NO}_{2}\right]$ vs. time [y vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}$ ]
slope $=-1.72 \times 10^{-5} \quad y$-intercept $=0.451 \quad \mathrm{r}^{2}=0.901$

General integrated rate law:
$[\mathrm{A}]=-\mathrm{kt}+[\mathrm{A}] \mathrm{o}$
This reaction's integrated rate law:
$\left[\mathrm{H}_{2} \mathrm{O}_{2}\right]=\left(-1.72 \times 10^{-5}\right) \mathrm{t}+0.451$ $\mathrm{r}^{2}=0.901$

- Graph for first order: $\ln \left[\mathrm{NO}_{2}\right]$ vs. time [y vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}$ ]
slope $=-5.78 \times 10^{-5} \quad y$-intercept $=-0.770 \quad r^{2}=0.971$
General integrated rate law: $\quad \ln [A]=-k t+\ln [A]_{0}$
This reaction's integrated rate law: $\quad \ln \left[\mathrm{NO}_{2}\right]=\left(-5.78 \times 10^{-5}\right) \mathrm{t}+(-0.770) \quad \mathrm{r}^{2}=0.971$
- Graph for second order: $\left[\mathrm{NO}_{2}\right]^{-1}$ vs. time [y vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}$ ]
slope $=2.10 \times 10^{-4} \quad y$-intercept $=2.01 \quad r^{2}=0.999$ - best so
order is 2
General integrated rate law: $\quad[A]^{-1}=\mathrm{kt}+[A]_{o}^{-1}$
This reaction's integrated rate law: $\quad\left[\mathrm{NO}_{2}\right]^{-1}=2.10 \times 10^{-4} \mathrm{t}+2.01 \mathrm{r}^{2}=0.999$
- Graph with the greatest $\mathrm{r}^{2}$ value: $\left[\mathrm{NO}_{2}\right]^{-1}$ vs. time, so the order is second order
a. Order with respect to $\mathrm{NO}_{2}$ :
b. Rate law for this reaction:
c. $\left[\mathrm{NO}_{2}\right]$ at $2.7 \times 10^{4} \mathrm{~s}$ after the start of the rxn.
+2.01 "
$\frac{2}{\text { rate }=\mathrm{k}\left[\mathrm{NO}_{2}\right]^{2}}$

Subbing $2.7 \times 10^{4} \mathrm{~s}$ for time in " $\left[\mathrm{NO}_{2}\right]^{-1}=2.10 \times 10^{-4} \mathrm{t}$

$$
\left[\mathrm{NO}_{2}\right]=0.130 \mathrm{~mol} / \mathrm{L}
$$

5. 

- Graph for zeroeth order: $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right.$ ] vs. time [y vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}$ ]
slope $=-4.54 \times 10^{-4} \quad y$-intercept $=1.31$
$r^{2}=0.947$
General integrated rate law:
$[\mathrm{A}]=-\mathrm{kt}+[\mathrm{A}] \mathrm{o}$
This reaction's integrated rate law:
$\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=\left(-4.54 \times 10^{-4}\right) \mathrm{t}+1.31 \mathrm{r}^{2}=0.947$
- Graph for first order: $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ vs. time [y vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}$ ]
slope $=-6.05 \times 10^{-4}$
General integrated rate law:
This reaction's integrated rate law: $\quad \ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=\left(-6.05 \times 10^{-4} \mathrm{t}+0.353 \quad \mathrm{r}^{2}=0.999\right.$ - best so


## KINETICS Practice Problems and Solutions

- Graph for second order: $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]^{-1}$ vs. time $[\mathrm{y}$ vs. $\mathrm{x} ; \mathrm{y}=\mathrm{ax}+\mathrm{b}]$
slope $=9.18 \times 10^{-4} \quad y$-intercept $=0.517 \quad r^{2}=0.971 \mathrm{~s}$
General integrated rate law:
$[A]^{-1}=\mathrm{kt}-+[A]_{o}^{-1}$
This reaction's integrated rate law:
$\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]^{-1}=9.18 \times 10^{-4} \mathrm{t}+0.517 \mathrm{r}^{2}=0.971$
- Graph with the greatest $\mathrm{r}^{2}$ value: $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ vs. time, so the order is first order

Order with respect to $\mathrm{N}_{2} \mathrm{O}_{5}$ :
Rate law for this reaction:
a. Order with respect to $\mathrm{N}_{2} \mathrm{O}_{5}$ :
b. Rate law for this reaction:
$\qquad$
1

$$
\text { rate }=\mathrm{k}\left[\mathrm{~N}_{2} \mathrm{O}_{5}\right]^{1} .
$$

$\qquad$
c. $\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]$ at $3.5 \times 10^{3} \mathrm{~s}$ after the start of the rxn. Subbing $3.5 \times 10^{3} \mathrm{~s}$ for time in " $\ln \left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=(-6.05 \times 10-$ ${ }^{4} \mathrm{t}+1.31$ "

$$
\left[\mathrm{N}_{2} \mathrm{O}_{5}\right]=0.171 \mathrm{~mol} / \mathrm{L}
$$

