

# SOLUTIONS

## L1: KINETICS PROBLEMS

Differential Rate Law: rate of change over time

Integrated Rate Law: concentration as function of time

Order	Diff. Rate Law	Int. Rate Law
0 <sup>th</sup>	$\frac{dA}{dt} = k$	$A(t) = A_0 - kt$
1 <sup>st</sup>	$\frac{dA}{dt} = k[A]$	$A(t) = A_0 e^{-kt}$
2 <sup>nd</sup>	$\frac{dA}{dt} = k[A]^2$	$A(t) = \frac{A_0}{1 + ktA_0}$

① Show that:

- $[A] \propto t$  if 0<sup>th</sup> order.
- $\ln [A] \propto t$  if 1<sup>st</sup> order.
- $\frac{1}{[A]} \propto t$  if 2<sup>nd</sup> order.

using the Integrated Rate Laws.

When 0<sup>th</sup> order,  $A(t) = A_0 - kt$  ;  $A(t) = [A]$

$\therefore [A] \propto t$  because  $A(t) = -kt + A_0$  is a linear relationship with slope  $m = -k$  and y-intercept  $(A_0)$ .

When 1<sup>st</sup> order,  $A(t) = A_0 e^{-kt}$

$$\ln [A(t)] = \ln [A] = A_0 \ln e^{-kt} = A_0 (-kt)$$

$$\ln [A] = (-A_0 k) t$$

$\therefore \ln [A] \propto t$  because there is a linear relationship

w/ slope  $m = -A_0 k$  and y-intercept  $(0, 0)$ .

When 2<sup>nd</sup> order,  $A(t) = \frac{A_0}{1 + ktA_0}$

$$A(t) = \frac{\frac{A_0}{A_0}}{\frac{1}{A_0} + \frac{ktA_0}{A_0}} = \frac{1}{\frac{1}{A_0} + kt} = [A]$$

$$\frac{1}{A_0} + kt = \frac{1}{[A]}$$

$\therefore \frac{1}{[A]} \propto t$  because  $\frac{1}{A_0} + kt = \frac{1}{[A]}$  is a linear relationship with slope  $m = k$  and y-intercept  $(0, \frac{1}{A_0})$ .

② The half-life of a 1st order reaction is  $\frac{\ln 2}{k}$ . Prove this using the integrated rate law.

1st order integrated rate law:  $A(t) = A_0 e^{-kt}$

let  $t_{1/2}$  = half-life of reaction

then  $A(t_{1/2}) = \frac{1}{2} A_0$

substituting, we have

$$\frac{1}{2} A_0 = A_0 e^{-kt_{1/2}}$$

$$\frac{1}{2} = e^{-kt_{1/2}}$$

$$\ln \frac{1}{2} = -kt_{1/2}$$

$$kt_{1/2} = -\ln \frac{1}{2} = \ln \left(\frac{1}{2}\right)^{-1} = \ln 2$$

$$\boxed{t_{1/2} = \frac{\ln 2}{k}}$$

This means that half-life is not dependent on initial concentration for first-order reactions!

③ If half-life of a reaction increases as initial reactant concentration increases, reaction order is

A. zero  
B. first

C. second  
D. third

0th order:

$$A(t_{1/2}) = \frac{1}{2} A_0$$

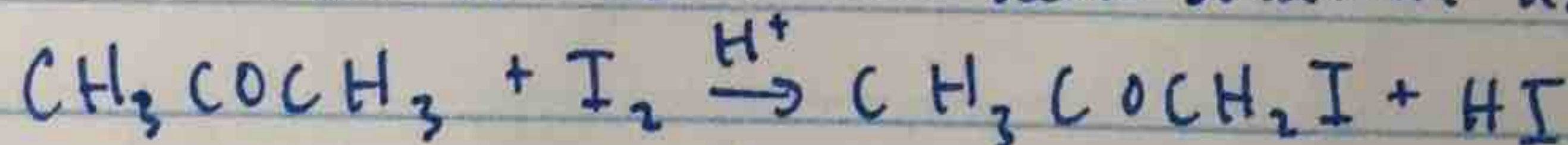
$$\frac{1}{2} A_0 = A_0 - kt_{1/2}$$

$$-\frac{1}{2} A_0 = -kt_{1/2}$$

$$t_{1/2} = \frac{A_0}{2k}$$

$$\boxed{t_{1/2} \propto A_0}$$

④ Propanone reacts with iodine in an acid solution as shown:



These data were obtained when this reaction was studied:

$[\text{CH}_3\text{COCH}_3]$ (M)	$[\text{I}_2]$ (M)	$[\text{H}^+]$ (M)	Relative Rate
0.010	0.010	0.010	1
0.020	0.010	0.010	2
0.020	0.020	0.010	2
0.020	0.010	0.020	4

What is the rate equation (differential) for this reaction?

Answer:  $\frac{d[\text{CH}_3\text{COCH}_2\text{I}]}{dt} = k[\text{CH}_3\text{COCH}_3][\text{H}^+]$

let  $a = \text{order of } [\text{CH}_3\text{COCH}_3]$ ,  $b = \text{order of } [\text{I}_2]$ ,  $c = [\text{H}^+]$

1. Divide Trial 2 ~~by~~ by Trial 1.

$$\frac{0.020^a 0.010^b 0.010^c = 2}{0.010^a 0.010^b 0.010^c = 1} \rightarrow 2^a = 2 \rightarrow \underline{\underline{a=1}}$$

2. Divide Trial 3 by Trial 2.

$$\frac{0.020^a 0.020^b 0.010^c = 2}{0.020^a 0.010^b 0.010^c = 2} \rightarrow 2^b = 1 \rightarrow \underline{\underline{b=0}}$$

3. Divide Trial 4 by Trial 2.

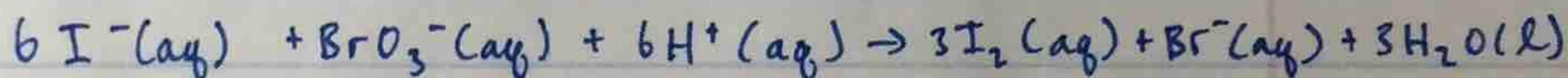
$$\frac{0.020^a 0.010^b 0.020^c = 4}{0.020^a 0.010^b 0.010^c = 2} \rightarrow 2^c = 2 \rightarrow \underline{\underline{c=1}}$$

Hence,

$$\text{Rate} = k [\text{CH}_3\text{COCH}_3] [\text{I}_2] [\text{H}^+]$$

Bromate ion

⑤ ~~Propose~~ reacts with iodine in acid solution:



This data was obtained when this reaction was studied:

$[\text{I}^-] (\text{M})$	$[\text{BrO}_3^-] (\text{M})$	$[\text{H}^+] (\text{M})$	Rate ( $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$ )
0.0010	0.0020	0.010	$8.0 \times 10^{-5}$
0.0020	0.0020	0.010	$1.6 \times 10^{-4}$
0.0020	0.0040	0.010	$1.6 \times 10^{-4}$
0.0010	0.0040	0.020	$1.6 \times 10^{-4}$

What are the units of the rate constant for this reaction?

A.  $\text{s}^{-1}$

B.  $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$

C.  $\text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

D.  $\text{L}^2 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

Rate Law:  $\frac{d[\text{Br}^-]}{dt} = k [\text{I}^-] [\text{H}^+]$

⑥ For reaction  $\text{A} \rightarrow \text{B}$ , rate law is rate =  $k[\text{A}]$  (first order).

If the reaction is 40.0% complete after 50.0 min,

what is the rate constant,  $k$ ?

A.  $8.00 \times 10^{-3} \text{ min}^{-1}$

C.  $1.39 \times 10^{-2} \text{ min}^{-1}$

B.  $1.02 \times 10^{-2} \text{ min}^{-1}$

D.  $1.83 \times 10^{-2} \text{ min}^{-1}$

First order reaction  $\rightarrow$  convert to integrated Rate Law.

$$A(t) = A_0 e^{-kt}$$

Given:  $A(50 \text{ min}) = 0.600 A_0 = A_0 e^{-k(50 \text{ min})}$

$$\ln 0.600 = -k(50 \text{ min}) \rightarrow k = \frac{-\ln 0.600}{50.0 \text{ min}} = 1.02 \times 10^{-2} \text{ min}^{-1}$$

① CHALLENGE PROBLEM:

Given generic reaction:



and experimental data:

[A] (M)	[B] (M)	Relative Rate
a	b	c
d	e	f

② Derive a rate equation  $k = [A]^m [B]^n$  for constants  $m$  and  $n$  written as functions of  $a, b, c, d, e$ , and/or  $f$ .

Assume that conditions  $a = qd$ ,  $b = qe$ , and  $c = qf$  are not all satisfied for any  $q \in \mathbb{R}$ .

Multiply Trial 2 data by  $\frac{a}{d}$ . Divide Trial 1 by (Trial 2)  $(\frac{a}{d})$ .

$$\frac{k a^m b^n = c}{k a^m (\frac{ae}{d})^n = (\frac{af}{d})} \rightarrow \left(\frac{bd}{ae}\right)^n = \frac{cd}{af} \rightarrow n = \frac{\ln \frac{cd}{af}}{\ln \frac{bd}{ae}}$$

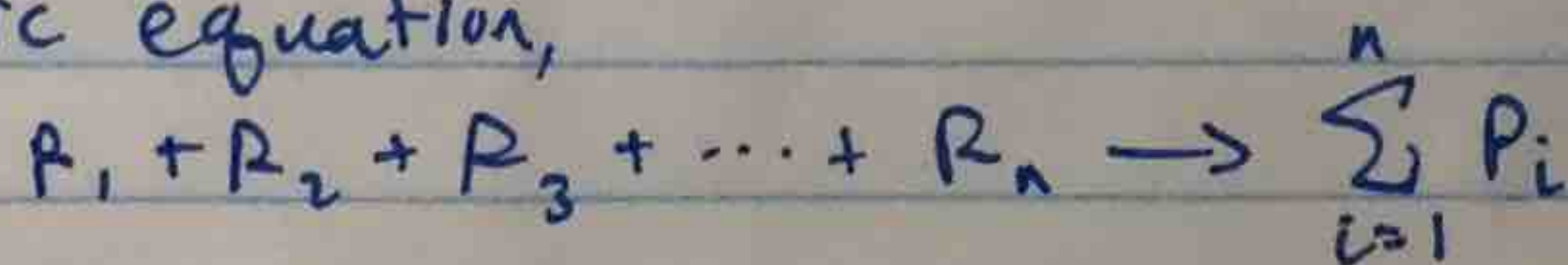
$$n = \ln c + \ln d - \ln a - \ln f - \ln b - \ln d + \ln a + \ln e = \ln \frac{ce}{bf}$$

Similarly, by multiplying Trial 2 data by  $\frac{b}{e}$ , and then dividing Trial 1 by (Trial 2)  $(\frac{b}{e})$ , we have  $m = \ln \frac{cd}{af}$ .

Hence, we have  $\boxed{\text{Rate} = k [A]^{\ln \frac{cd}{af}} [B]^{\ln \frac{ce}{bf}}}$ .

③ Let  $R_n =$  reactants and  $\sum_{i=1}^n P_i =$  all of the products  
let  $m_n =$  order of reaction with respect to reactant  $R_n$

Given generic equation,



how many unique experimental trials using unique initial reactant concentrations do you need to determine

$m_n$  for all  $R_n$  in this reaction?

Assuming unique trials are not multiples of each other, we ~~have~~ need at least  $\boxed{n \text{ unique trials}}$  to determine all  $m_n$

in this reaction. (Can you solve a system of equations with  $n$  variables provided only  $n-1$  equations?)