AP CHEMISTRY

TOPIC 8: KINETICS, MUCH MORE PRACTICE

Day 107:

1. Answer the following questions related to the kinetics of chemical reactions.

$$2\ NO(g) + 2\ H_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$$

Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

Experiment	Initial Concentration (mol/L) [NO]	[H_2]	Initial Rate of Formation of N_2 (mol/L·min)
1	0.0060	0.0010	1.8×10^{-4}
2	0.0060	0.0020	3.6×10^{-4}
3	0.0010	0.0060	0.30×10^{-4}
4	0.0020	0.0060	1.2×10^{-4}

(a) (i) Determine the order for each of the reactants, NO and H_2

Answers:

$$\text{Rate} = k\,[\,NO\,]^m\,[\,H_2\,]^n$$

$$\frac{Rate_{Exp\ 2}}{Rate_{Exp\ 1}} = \frac{3.6\times10^{-4}}{1.8\times10^{-4}} = 2$$

$$\frac{Rate_{Exp\ 2}}{Rate_{Exp\ 1}} = \frac{\cancel{k\,[\,0.0060\ M\,]^m}\,[\,0.20\ M\,]^n}{\cancel{k\,[\,0.0060\ M\,]^m}\,[\,0.10\ M\,]^n} = 2^n \;\;;\;\; \frac{[\,0.20\ M\,]^n}{[\,0.10\ M\,]^n} = 2^n \;\;;\;\; 2^n = 2$$

$$\boldsymbol{n = 1} = [\,H_2\,]^1$$

$$\frac{Rate_{Exp\ 4}}{Rate_{Exp\ 3}} = \frac{1.2\times10^{-4}}{0.30\times10^{-4}} = 4$$

$$\frac{Rate_{Exp\ 4}}{Rate_{Exp\ 3}} = \frac{k\,[\,0.0020\ M\,]^m\,\cancel{[\,0.0060\ M\,]^1}}{k\,[\,0.0010\ M\,]^m\,\cancel{[\,0.0060\ M\,]^1}} = 2^m \;\;;\;\; \frac{[\,0.0020\ M\,]^m}{[\,0.0010\ M\,]^m} = 2^m \;\;;\;\; 2^m = 4$$

$$\boldsymbol{m = 2} = [\,NO\,]^2$$

(ii) Write the overall rate law for the reaction.

Answers:

$$\text{Rate} = k\,[\,NO\,]^m\,[\,H_2\,]^n$$

$$\text{Rate} = k\,[\,NO\,]^2\,[\,H_2\,]^1$$

(b) Calculate the value of the rate constant, *k*, for the reaction. Include units.

Answers:

$$k = \frac{Rate}{[NO]^2[H_2]^1} = \frac{1.8\times10^{-4}\ M}{(0.0060\ M)^2(0.0010\ M)(\mathrm{min})} = 5000\ \frac{1}{M^2\cdot\mathrm{min}}$$

(c) For experiment 2, calculate the concentration of NO remaining when exactly one-half of the original amount of H_2 had been consumed.

Answers:

$$[\ H_2\ ]_0 = \text{initial concentration} = 0.0020\ M$$

$$[\ H_2\ ]_t = \text{half original concentration} = 0.0010\ M$$

$$\frac{0.0010\ mol\ H_2}{L}\times\frac{2\ mol\ NO}{2\ mol\ H_2} = \frac{0.0010\ mol\ NO}{L} = 0.0010\ M\ NO\ \ reacted$$

$$[\ NO\ ]_t = 0.0060\ M - 0.0010\ M = 0.0050\ M$$

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. $NO + NO \leftrightarrow N_2O_2$
II. $N_2O_2 + H_2 \rightarrow H_2O + N_2O$
III. $N_2O + H_2 \rightarrow N_2 + H_2O$

Based on the data presented, which of the above is the rate-determining step?

Answers:

Based on the calculated rate law… Rate = $k\,[\ NO\ ]^2\,[\ H_2\ ]^1$

Step II is the "Slow Step". Step I & II include all the reactants in the rate law.

Step III is NOT the slow step because hydrogen gas is only FIRST order.

2. The reaction between NO and H_2 is believed to occur in the following three-step process.

$$NO + NO \rightarrow N_2O_2 \qquad \text{(fast)}$$
$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \qquad \text{(slow)}$$
$$N_2O + H_2 \rightarrow N_2 + H_2O \qquad \text{(fast)}$$

(a) Write a balanced equation for the overall reaction.

Answers:

$$NO + NO \rightarrow \cancel{N_2O_2}$$
$$\cancel{N_2O_2} + H_2 \rightarrow \cancel{N_2O} + H_2O$$
$$\cancel{N_2O} + H_2 \rightarrow N_2 + H_2O$$

$$\boldsymbol{2\ NO + 2\ H_2 \rightarrow N_2 + 2\ H_2O}$$

(b) Identify the intermediates in the reaction. Justify your answer.

Answers:

$$\boldsymbol{N_2O_2\ \ \&\ \ N_2O}$$

Justification: Intermediates are "things" that are produced and LATER used as a reactant.

(c) From the mechanism represented above, a student correctly deduces that the rate law for the reaction is Rate = $k\,[NO]^2\,[H_2]$. The student then concludes that (1) the reaction is third-order and (2) the mechanism involves the simultaneous collision of two NO molecules and an H_2 molecule. Are conclusions (1) and (2) correct? Explain.

Answers:

Conclusion (1) is correct; the sum of the orders (exponents) in the rate law (2 + 1) = 3 is equal to the REACTION order. Conclusion (2) is NOT correct. According to the elementary steps two NO molecules collide to form N_2O_2 (forming an intermediate) and the N_2O_2 THEN collides with the H_2 molecule. It is VERY DIFFICULT (but not impossible) for three different molecules (particles) to collide correctly at the same time to form a new molecule(s).

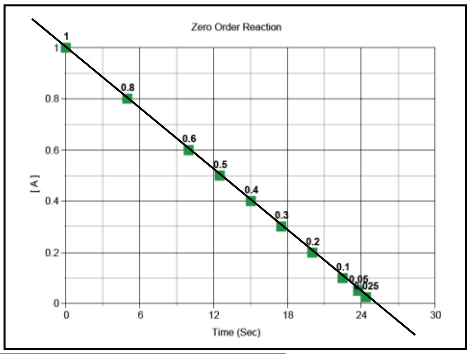
(d) Explain why an increase in temperature increases the rate constant, *k*, given the rate law in (c).

Answers:

This is NOT a trick question. Also, recall that constants (Kinetics and Equilibrium) are constant as long as the TEMPERATURE remains the same. Temperature is an amazing variable that can change a lot of "things" when discussing chemistry. So, to answer the question, increasing the temperature increases the constant, k, because the temperature increase allows the particles to move more rapidly allowing more possible collisions. Collisions equal reactions!

3. Draw the following graphs for each condition:

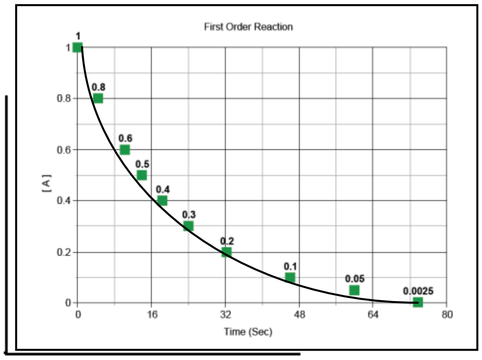
[A]



time

zero order

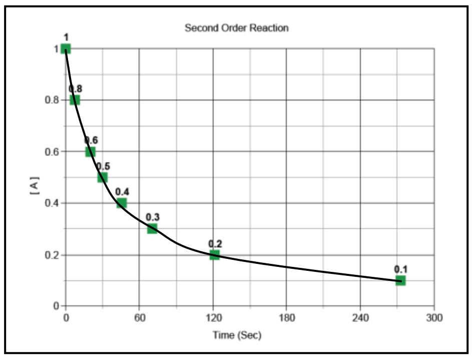
[A]



time

first order

[A]



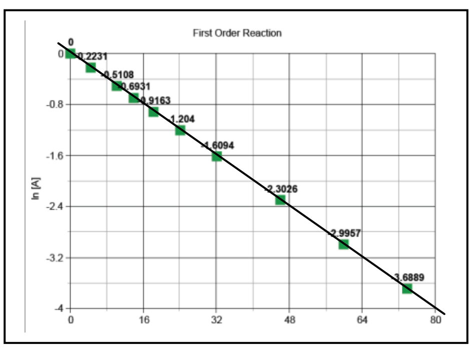
time

second order

To view the data and these graphs (a little more closely), go to:

www.avon-chemistry.com/graph.html

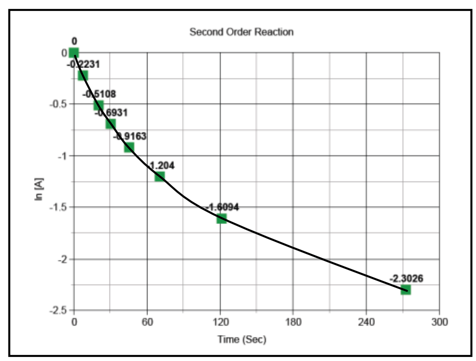
ln [A]



time

first order

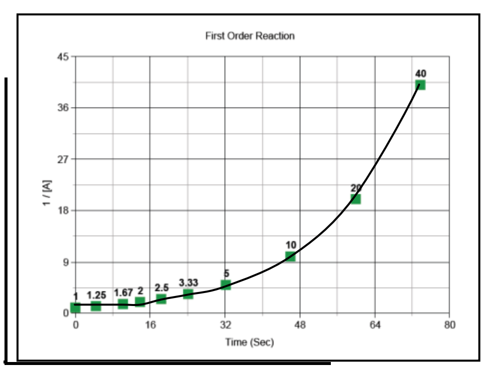
ln [A]



time

second order

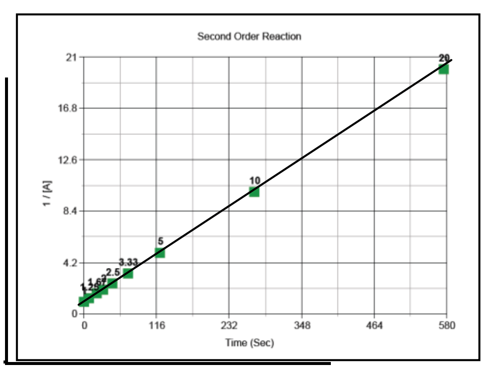
$\frac{1}{[\ A\ ]}$



time

first order

$\frac{1}{[\ A\ ]}$



time

second order

4. A certain second-order reaction is 22.3 % complete in 177 seconds. Calculate the rate constant and the half-life for this process.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt, \quad \frac{1}{0.777\ M} - \frac{1}{1\ M} = k(177\ \text{sec}) \ ; \ \left(\frac{1.287001}{M} - \frac{1}{M}\right) = k(177\ \text{sec})$$

$$k = \frac{0.287001}{177\ M \cdot \text{sec}} = 0.0016215\ \frac{1}{M \cdot \text{sec}}$$

$$\textit{Half-life:}\ \left(\frac{1}{0.50\ M} - \frac{1}{1\ M}\right) = \left(0.0016215\ \frac{1}{M \cdot \text{sec}}\right) t_{1/2}\ ;\ \left(\frac{2-1}{M}\right) = \left(0.0016215\ \frac{1}{M \cdot \text{sec}}\right) t_{1/2}$$

$$t_{1/2} = \frac{1\ (M \cdot \text{sec})}{0.0016215\ M} = 617\ \text{sec}$$

5. Information for the chemical reaction was collected by measuring the concentration of A, [A], at a particular temperature. Concentration versus time data were collected for this reaction and a plot of $\frac{1}{[A]}$ versus time resulted in a straight line with a slope value of $+0.230622\ M^{-1} \bullet \text{sec}^{-1}$. Calculate the time required for this reaction to be 84.6 % complete. Also, calculate the half-life time.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt, \quad \frac{1}{0.154\ M} - \frac{1}{1\ M} = \left(\frac{0.230622}{M \cdot \text{sec}}\right) t$$

$$\left(\frac{6.493506 - 1}{M}\right) = \left(\frac{0.230622}{M \cdot \text{sec}}\right) t\ ;\ \left(\frac{5.493506}{M}\right) = \left(\frac{0.230622}{M \cdot \text{sec}}\right) t$$

$$t = \frac{5.493506\ (M \cdot \text{sec})}{0.230622\ M} = 23.8\ \text{sec}$$

$$\textit{Half-life:}\quad t_{1/2} = \frac{1\ (M \cdot \text{sec})}{0.230622\ M} = 4.34\ \text{sec}$$

6. Information for the chemical reaction was collected by measuring the concentration of A, [A], at a particular temperature. Concentration versus time data were collected for this reaction and a plot of ln [A] versus time resulted in a straight line with a slope value of - 0.00930622 sec^{-1}. Calculate the time required for this reaction to be 26.6 % complete. Also, calculate the half-life time.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{0.734}{1.00}\right) = -\left(\ 0.00930622\ \ \text{sec}^{-1}\ \right)\ t$$

$$t\ =\ \frac{\ln(0.734)\ (\text{sec})}{-0.00930622}\ =\ 33.2\ \ \text{sec}$$

$$\textit{Half-life:}\qquad t_{1/2}\ =\ \frac{\ln(0.50)\ (\text{sec})}{-0.00930622}\ =\ 74.5\ \ \text{sec}$$

7. A certain first-order reaction has 63.3 % concentration remaining after 403 seconds. Calculate the rate constant and the half-life for this process.

$$\ln\left(\frac{[A]}{[A]_0}\right) = -kt, \quad \ln\left(\frac{0.633}{1.00}\right) = -k\left(\ 403\ \ \text{sec}\ \right)$$

$$k\ =\ \frac{\ln(0.633)}{-\ 403\ \ \text{sec}}\ =\ 0.0011347\ \ \text{sec}^{-1}$$

$$\textit{Half-life:}\qquad t_{1/2}\ =\ \frac{\ln(0.50)\ (\text{sec})}{-0.0011347}\ =\ 611\ \ \text{sec}$$