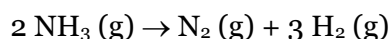
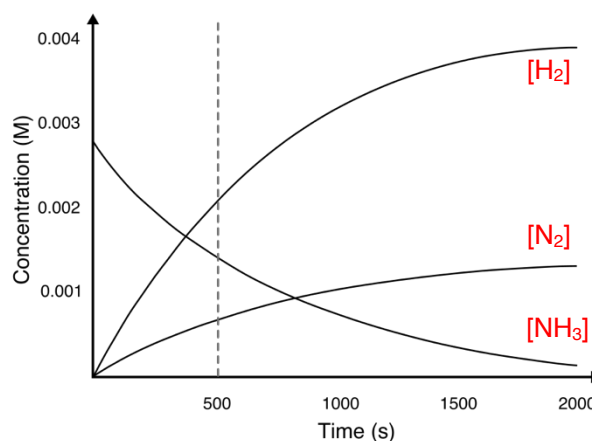


1. Consider the degradation of ammonia gas into nitrogen gas and hydrogen gas.



- A) For the concentration vs. time plot to the right, label each curve with the appropriate chemical species.



Discuss how you chose each curve.

$[\text{NH}_3]$  decreases over time.

$[\text{N}_2]$  and  $[\text{H}_2]$  increase over time.

$[\text{H}_2]$  increases more rapidly than  $[\text{N}_2]$ .

- B) At  $t = 500$  s, the slope of a line tangent to the  $\text{NH}_3$ -curve is  $-1.94 \times 10^{-6}$  M/s. What is the rate of the reaction at this instant?

Recall that the instantaneous relative rate of the reaction can be expressed as:

$$\text{Rate} = -\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t} = \frac{\Delta[\text{N}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2]}{\Delta t}$$

The slope of the line tangent to the  $\text{NH}_3$ -curve tells us how  $[\text{NH}_3]$  changes with time, so the rate is

$$\text{Rate} = -\frac{1}{2} \left( -1.94 \times 10^{-6} \frac{\text{M}}{\text{s}} \right) = 9.70 \times 10^{-7} \frac{\text{M}}{\text{s}}$$

- C) Compute the slopes of the tangent lines for the  $\text{N}_2$ - and  $\text{H}_2$ -curves at  $t = 500$  s.

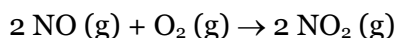
The instantaneous slopes will be related by the stoichiometry of the balanced chemical equation.

Therefore, the slopes of  $[\text{N}_2]$  and  $[\text{H}_2]$  can be related to  $[\text{NH}_3]$  by

$$\frac{\Delta[\text{N}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{NH}_3]}{\Delta t} = 9.70 \times 10^{-7} \frac{\text{M}}{\text{s}} \quad \frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{3}{2} \frac{\Delta[\text{NH}_3]}{\Delta t} = 2.91 \times 10^{-6} \frac{\text{M}}{\text{s}}$$

2. The overall stoichiometry in parts A and B below is the same, but the rate laws differ.

- A) Determine the rate law for the following reaction using the initial rates data.



Experiment	$[\text{NO}]_0$ (M)	$[\text{O}_2]_0$ (M)	Initial Rate (M/s)
1	0.100	0.100	1.24
2	0.100	0.050	0.62
3	0.050	0.100	0.31

Our rate law will have the form:  $\text{Rate} = k[\text{NO}]^a[\text{O}_2]^b$

Compare experiments 1 and 3 to find  $a$ , the order of the reaction with respect to  $[\text{NO}]$ .

Compare experiments 1 and 2 to find  $b$ , the order of the reaction with respect to  $[\text{O}_2]$ .

Plug in the values from any one experiment (I choose #1) to solve for  $k$ .

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k[\text{NO}]_1^a[\text{O}_2]_1^b}{k[\text{NO}]_3^a[\text{O}_2]_3^b}$$

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\text{NO}]_1^a}{[\text{NO}]_3^a}$$

$$\frac{1.24 \frac{\text{M}}{\text{s}}}{0.31 \frac{\text{M}}{\text{s}}} = \left( \frac{0.100 \text{ M}}{0.050 \text{ M}} \right)^a$$

$$4 = 2^a$$

$$a = 2$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k[\text{NO}]_1^a[\text{O}_2]_1^b}{k[\text{NO}]_2^a[\text{O}_2]_2^b}$$

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{O}_2]_1^b}{[\text{O}_2]_2^b}$$

$$\frac{1.24 \frac{\text{M}}{\text{s}}}{0.62 \frac{\text{M}}{\text{s}}} = \left( \frac{0.100 \text{ M}}{0.050 \text{ M}} \right)^b$$

$$2 = 2^b$$

$$b = 1$$

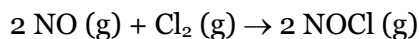
$$\text{Rate}_1 = k[\text{NO}]_1^2[\text{O}_2]_1^1$$

$$1.24 \frac{\text{M}}{\text{s}} = k(0.100 \text{ M})^2(0.100 \text{ M})^1$$

$$k = 1240 \text{ M}^{-2}\text{s}^{-1}$$

Therefore,  $\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1$ ;  $k = 1240 \text{ M}^{-2}\text{s}^{-1}$

B) Determine the rate law for the following reaction using the initial rates data.



Experiment	[NO] <sub>0</sub> (M)	[Cl <sub>2</sub> ] <sub>0</sub> (M)	Initial Rate (M/s)
1	0.200	0.100	0.63
2	0.200	0.300	5.70
3	0.800	0.100	2.58

Our rate law will have the form:  $\text{Rate} = k[\text{NO}]^a[\text{Cl}_2]^b$

Compare experiments 3 and 1 to find  $a$ , the order of the reaction with respect to [NO].

Compare experiments 2 and 1 to find  $b$ , the order of the reaction with respect to [Cl<sub>2</sub>].

Plug in the values from any one experiment (I choose #1) to solve for  $k$ .

$$\begin{aligned} \frac{\text{Rate}_3}{\text{Rate}_1} &= \frac{k[\text{NO}]_3^a[\text{Cl}_2]_3^b}{k[\text{NO}]_1^a[\text{Cl}_2]_1^b} & \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}]_2^a[\text{Cl}_2]_2^b}{k[\text{NO}]_1^a[\text{Cl}_2]_1^b} & \text{Rate}_1 &= k[\text{NO}]_1^1[\text{Cl}_2]_1^2 \\ \frac{\text{Rate}_3}{\text{Rate}_1} &= \frac{[\text{NO}]_3^a}{[\text{NO}]_1^a} & \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{[\text{Cl}_2]_2^b}{[\text{Cl}_2]_1^b} & 0.63 \frac{\text{M}}{\text{s}} &= k(0.200 \text{ M})^1(0.100 \text{ M})^2 \\ \frac{2.58 \frac{\text{M}}{\text{s}}}{0.63 \frac{\text{M}}{\text{s}}} &= \left(\frac{0.800 \text{ M}}{0.200 \text{ M}}\right)^a & \frac{5.70 \frac{\text{M}}{\text{s}}}{0.63 \frac{\text{M}}{\text{s}}} &= \left(\frac{0.300 \text{ M}}{0.100 \text{ M}}\right)^b & k &= 320 \text{ M}^{-2}\text{s}^{-1} \\ 4 &= 4^a & 9 &= 3^b & \text{If expt. 2 or 3:} & \\ a &= 1 & b &= 2 & k &= 315 \text{ M}^{-2}\text{s}^{-1} \end{aligned}$$

Therefore,  $\text{Rate} = k[\text{NO}]^1[\text{Cl}_2]^2$ ;  $k = 320 \text{ M}^{-2}\text{s}^{-1}$  or  $315 \text{ M}^{-2}\text{s}^{-1}$