1. Over the course of the reaction $3H_2(g) + N_2(g) \longrightarrow 2NH_3(g)$, the following data was obtained:

Time (min)	$[H_2] (mol/L)$	$[N_2]$ (mol/L)	$[NH_3] (mol/L)$
0	0.99	1.00	0.00
1	0.70	0.90	0.20
2	0.54	0.84	0.31
3	0.47	0.82	0.35

- (a) Calculate the average rates of change of [H₂], [N₂], and [NH₃] over the first 3.0 minutes of the reaction (include units).
- (b) Calculate the average reaction rate over the first 3.0 minutes of the reaction (include units).

$$\begin{aligned} \frac{\Delta[H_2]}{\Delta t} &= \frac{[H_2]_2 - [H_2]_1}{t_2 - t_1} = \frac{0.47 - 0.99 \ M}{3 - 0 \ min} = -0.17 M/min\\ \frac{\Delta[N_2]}{\Delta t} &= \frac{0.82 - 1.00 \ M}{3 - 0 \ min} = -0.058 \ M/min\\ \frac{\Delta[NH_3]}{\Delta t} &= \frac{0.35 - 0.00 \ M}{3 - 0 \ min} = 0.12 \ M/min\\ Rate &= -\frac{1}{3} \frac{\Delta[H_2]}{\Delta t} = -\frac{1}{3} (-0.17 \ M/min) = 0.058 \ M/min \end{aligned}$$

(Note: You could use the N₂ rate of change instead and you should get the same answer.)

2. What are the units of k for each type of reaction?

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(a) zero-order M/s
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- (b) first-order s^{-1}
- (c) second-order $M^{-1}s^{-1}$

$$rate = k \left[A \right]^n$$

- 3. Consider the reaction: $X + Y \longrightarrow Z$. From the following data, obtained at 360 K:
 - (a) Determine the order of the reaction.
 - (b) Determine the initial rate of change of [X] when the concentration of X is 0.30 M and that of Y is 0.40 M.

Initial rate of disappearance of X (M/s)	[X] (M)	[Y] (M)
-0.053	0.10	0.50
-0.127	0.20	0.30
-1.02	0.40	0.60
-0.254	0.20	0.60
-0.509	0.40	0.30

General rate expression: $Rate = k[X]^a[Y]^b = -\frac{\Delta[X]}{\Delta t}$

We will use the method of initial rates. To determine the order for X, find two measurements where X varies, but Y stays the same. Use the 2nd and 5th.

 $\frac{Rate_5}{Rate_2} = \frac{k[X]^a[Y]^b}{k[X]^a[Y]^b}$ Lots of terms cancel and you can plug in values: $\frac{0.509 \ M/s}{0.127 \ M/s} = \frac{(0.40 \ M)^a}{(0.20 \ M)^a} \Rightarrow 4 = 2^a \Rightarrow a = 2$

Now get the order for Y. Use the 2nd and 4th rates, because [X] does not vary.

 $\frac{Rate_4}{Rate_2} = \frac{0.254 \ M/s}{0.127 \ M} = \frac{(0.60 \ M)^b}{(0.30 \ M)^b} \Rightarrow 2 = 2^b \Rightarrow b = 1$

So the rate expression is $Rate = k[X]^2[Y]$ (2nd order in X, 1st order in Y, 3rd order overall)

For part b:

 $Rate = k[X]^{2}[Y] = -\frac{\Delta[X]}{\Delta t}$

From the first rate: $0.053 M/s = k(0.10 M)^2(0.50 M)$

Solve for k: $k = 10.6 M^{-2} s^{-1}$

Then answer the question: $Rate = (10.6 \ M^{-2} s^{-1})(0.30 \ M)^2(0.40 \ M)$

$$Rate = 0.38 \ M/s = -\frac{\Delta[X]}{\Delta t}$$
$$\frac{\Delta[X]}{\Delta t} = -0.38 \ M/s$$

4. This reaction is first order in N₂O₅ with a rate constant (at a given temperature) of $k = 0.053 \ s^{-1}$.

 $N_2O_5(g) \longrightarrow NO_3(g) + NO_2(g)$

- (a) Calculate the rate of the reaction when $[N_2O_5] = 0.055$ M.
- (b) What would the rate of the reaction be at the concentration indicated in part a if the reaction were second order? What about zero order? (Assume the same numerical value for *k*, but the units would be different, but you knew that already).

It is first order, so $Rate = k[N_2O_5]$

 $Rate = (0.053 \ s^{-1})(0.055 \ M) = 0.0029 \ M/s$

If it were 2nd order: $Rate = k[N_2O_5]^2 = (0.053 \ M^{-1}s^{-1})(0.055 \ M)^2 = 0.00016 \ M/s$

If it were 0 order: Rate = k = 0.053 M/s

5. The rate constant for the second-order reaction

$$2 \operatorname{NOBr}(g) \longrightarrow 2 \operatorname{NO}(g) + \operatorname{Br}_2(g)$$

is 0.80 $M^{-1}s^{-1}$ at 10 °C.

- (a) Starting with a concentration of 0.086 M, calculate the concentration of NOBr after 22 s.
- (b) Calculate the half-lives when $[NOBr]_0 = 0.072 \text{ M}$ and $[NOBr]_0 = 0.054 \text{ M}$.

It is 2nd order, and we need the integrated rate law, which means

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$
$$\frac{1}{[A]_t} = (0.80 \ M^{-1} s^{-1})(22 \ s) + \frac{1}{0.086 \ M}$$

Practice your algebra: $[A]_t = 0.034 M$

For 2nd order: $t_{1/2} = \frac{1}{k[A]_0}$ For first case: NOBr: $t_{1/2} = \frac{1}{(0.80M^{-1}s^{-1})(0.072 M)} = 17. s$ For second case: NOBr: $t_{1/2} = 23. s$ 6. This reaction was monitored as a function of time:

 $A \longrightarrow B + C$

A plot of ln[A] versus time yields a straight line with slope of $-0.0045 \ s^{-1}$.

- (a) What is the value of the rate constant, *k*, for this reaction at this temperature?
- (b) Write the rate law for the reaction.
- (c) What is the half-life?
- (d) If the initial concentration of A is 0.250 M, what is the concentration after 225 s?

If a plot of ln[A] vs. t yields a straight line, the reaction is first order.

The slope is -k, so $k = 0.0045 \ s^{-1}$

$$Rate = k[A] = (0.0045 \ s^{-1})[A]$$

$$t_{1/2} = \frac{0.693}{k} = 150 \ s$$

For 1st order: $ln[A]_t = -kt + ln[A]_0$ $ln[A]_t = -(0.0045 \ s^{-1})(225 \ s) + ln(0.250 \ M)$ $ln[A]_t = -2.40$ $[A]_t = e^{-2.40}$ $[A]_t = 0.0908 \ M$