

Solutions to the Extra Problems for Chapter 15

1. He measured it at t = 3.4 seconds. When using a reactant, the rate is defined as:

$$\text{Rate} = - \frac{\Delta[\text{Reactant}]}{\Delta t}$$

We know the rate and can get the change in concentration:

$$\Delta[\text{Reactant}] = \text{final concentration} - \text{initial concentration} = 2.15 \text{ M} - 8.01 \text{ M} = -5.86 \text{ M}$$

We now have enough information to solve for the change in time:

$$1.7 \frac{\text{M}}{\text{s}} = - \frac{-5.86 \text{ M}}{\Delta t}$$

$$\Delta t = \frac{5.86 \text{ M}}{1.7 \frac{\text{M}}{\text{s}}} = 3.4 \text{ s}$$

Now that we have the change in time, we can use it to get the final time at which the concentration was measured:

$$\Delta t = t_{\text{final}} - t_{\text{initial}}$$

$$3.4 \text{ s} = t_{\text{final}} - 0.0$$

$$t_{\text{final}} = 3.4 \text{ s}$$

2. a. The exponents indicate the order. Thus, this is first order with respect to HNO₃.

b. The exponents indicate the order. Thus, this is first order with respect to NH₃.

c. The overall order is the sum of the exponents, so this is second order overall.

d. The unit is 1/M·s. To figure out the units, we have to think of the rate equation:

$$\text{Rate} = k[\text{HNO}_3][\text{NH}_3]$$

We don't have numbers, but we can plug in the units, remembering that rate has units of M/s:

$$\frac{\text{M}}{\text{s}} = k[\text{M}][\text{M}]$$

Solving for k:

$$k = \frac{\cancel{\text{M}}}{[\text{M}][\cancel{\text{M}}] \cdot \text{s}} = \frac{1}{\text{M} \cdot \text{s}}$$

3. The reaction is third order overall. If you look at the final equation above, you will see that the M in the rate unit (M/s) will always cancel one M in the denominator. Thus, whatever survives in the units of the rate constant has one exponent less than the product of the concentrations raised to their exponents. If the unit for k is $\frac{1}{M^2 \cdot s}$, that means the product of the concentrations raised to their exponents must have resulted in M^3 , which means the sum of the exponents must be 3.

4. The rate equation is $\text{Rate} = (54,000 \text{ l}/M^3 \cdot s)[\text{NO}]^3[\text{H}_2]$. The rate equation takes the following form: $\text{Rate} = k[\text{NO}]^x[\text{H}_2]^y$. To determine one of the orders, we need two trials where the concentration of one reactant is the same. Trials 1 and 2 have the concentration of NO the same. Trial 1's rate equation is:

$$0.134 \frac{M}{s} = k[0.050 M]^x[0.020 M]^y$$

Trial 2's rate equation is:

$$0.268 \frac{M}{s} = k[0.050 M]^x[0.040 M]^y$$

We divide the equation with the higher rate by the equation with the lower rate:

$$\frac{0.268 \frac{M}{s}}{0.134 \frac{M}{s}} = \frac{k[0.050 M]^x[0.040 M]^y}{k[0.050 M]^x[0.020 M]^y}$$

$$2.00 = \frac{[0.040 M]^y}{[0.020 M]^y}$$

$$2.00 = \left(\frac{[0.040 \cancel{M}]}{[0.020 \cancel{M}]} \right)^y$$

$$2.00 = 2.0^y$$

This means $y = 1$. To find x, we do the same thing, but with two trials that have the same concentration of H_2 , so that the concentration of H_2 drops out. Trials 1 and 3 have that. Trial 1's rate equation is:

$$0.134 \frac{M}{s} = k[0.050 M]^x[0.020 M]^y$$

Trial 3's rate equation is:

$$1.072 \frac{M}{s} = k[0.100 M]^x[0.020 M]^y$$

Dividing the equation with the larger rate by the equation with the smaller rate:

$$\frac{1.072 \frac{\text{M}}{\text{s}}}{0.134 \frac{\text{M}}{\text{s}}} = \frac{k[0.100 \text{ M}]^x [0.020 \text{ M}]^y}{k[0.050 \text{ M}]^x [0.020 \text{ M}]^y}$$

$$8.00 = \frac{[0.100 \text{ M}]^x}{[0.050 \text{ M}]^x}$$

$$8.00 = \left(\frac{[0.100 \text{ M}]}{[0.050 \text{ M}]} \right)^x$$

$$8.00 = 2.0^x$$

The only way this equation works is if $x = 3$. We now have the rate equation:

$$\text{Rate} = k[\text{NO}]^3[\text{H}_2]$$

Now we can use the data from any trial (let's choose trial 1) to determine k :

$$0.134 \frac{\text{M}}{\text{s}} = k[0.050 \text{ M}]^3 [0.020 \text{ M}]$$

$$k = \frac{0.134 \frac{\text{M}}{\text{s}}}{[0.050 \text{ M}]^3 [0.020 \text{ M}]} = 54,000 \frac{1}{\text{M}^3 \cdot \text{s}}$$

5. The rate equation is $\text{Rate} = (1.7 \text{ 1/M}^2 \cdot \text{s}) \cdot [\text{Xe}]^2 [\text{F}_2]$ (The rate constant could also be $1.66 \text{ 1/M}^2 \cdot \text{s}$ if you used trial 2 or 3 to calculate k). The rate equation takes the following form: $\text{Rate} = k[\text{Xe}]^x [\text{F}_2]^y$. To determine one of the orders, we need two trials where the concentration of one reactant is the same. Trials 1 and 2 have the concentration of F_2 the same. Trial 1's rate equation is:

$$0.0056 \frac{\text{M}}{\text{s}} = k[0.150 \text{ M}]^x [0.150 \text{ M}]^y$$

Trial 2's rate equation is:

$$0.0224 \frac{\text{M}}{\text{s}} = k[0.300 \text{ M}]^x [0.150 \text{ M}]^y$$

We usually divide the equation with the higher rate by the equation with the lower rate:

$$\frac{0.0224 \frac{\text{M}}{\text{s}}}{0.0056 \frac{\text{M}}{\text{s}}} = \frac{k[0.300 \text{ M}]^x [0.150 \text{ M}]^y}{k[0.150 \text{ M}]^x [0.150 \text{ M}]^y}$$

$$4.0 = \frac{[0.300 \text{ M}]^x}{[0.150 \text{ M}]^x}$$

$$4.0 = \left(\frac{[0.300 \text{ M}]}{[0.150 \text{ M}]} \right)^x$$

$$4.0 = 2.00^x$$

The only way this works is if $x = 2$. To find y , we do the same thing, but with two trials that have the same concentration of Xe, so that the concentration of Xe drops out. Trials 1 and 3 have that. Trial 1's rate equation is:

$$0.0056 \frac{\text{M}}{\text{s}} = k[0.150 \text{ M}]^x [0.150 \text{ M}]^y$$

Trial 3's rate equation is:

$$0.0112 \frac{\text{M}}{\text{s}} = k[0.150 \text{ M}]^x [0.300 \text{ M}]^y$$

Dividing the equation with the larger rate by the equation with the smaller rate:

$$\frac{0.0112 \frac{\text{M}}{\text{s}}}{0.0056 \frac{\text{M}}{\text{s}}} = \frac{k[0.150 \text{ M}]^x [0.300 \text{ M}]^y}{k[0.150 \text{ M}]^x [0.150 \text{ M}]^y}$$

$$2.0 = \frac{[0.300 \text{ M}]^y}{[0.150 \text{ M}]^y}$$

$$2.0 = \left(\frac{[0.300 \text{ M}]}{[0.150 \text{ M}]} \right)^y$$

$$2.0 = 2.00^y$$

The only way this equation works is if $y = 1$. We now have the rate equation:

$$\text{Rate} = k[\text{Xe}]^2 [\text{F}_2]$$

Now we can use the data from any trial (let's choose trial 1) to determine k :

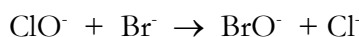
$$0.0056 \frac{\text{M}}{\text{s}} = k[0.150 \text{ M}]^2 [0.150 \text{ M}]$$

$$k = \frac{0.0056 \frac{\text{M}}{\text{s}}}{[0.150 \text{ M}]^2 [0.150 \text{ M}]} = 1.7 \frac{1}{\text{M}^2 \cdot \text{s}}$$

If we had used trial 2 or trial 3, we would have picked up one more significant figure, and the rate constant would have been 1.66 1/M²·s.

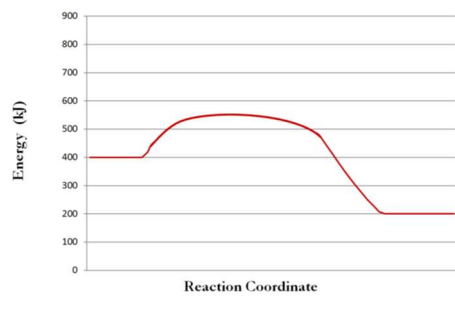
6. The reaction with the higher activation energy has the lower rate constant. The rate constant decreases with increasing activation energy.

7. H₂O is the catalyst, and the overall reaction is ClO⁻ + Br⁻ → BrO⁻ + Cl⁻. In step 1, ClO⁻ is used up but not remade, so it is a reactant in the overall equation. H₂O is used up in step 1 but then remade in step 3. Thus, it is the catalyst. HOCl is made in step 1 but then used up in step 2. OH⁻ is made in step 1 but used up in step 3. That means neither one is part of the overall reaction. Br⁻ is used up in step 2 and not remade, so it is a reactant in the overall reaction. HOBr is made in step 2 but used up in step 3, so it is not a part of the overall reaction. Cl⁻ is made in step 2 but not used up, so it is a product in the overall equation. The two reactants in step 3 were made in previous steps, and the H₂O product is the catalyst. However, BrO⁻ was not made in any previous steps, so it is also a product in the overall equation:



8. This is a homogeneous catalyst. Homogeneous catalysts change the reaction mechanism.

9. The reaction coordinate diagram needs to have a lower hill, because a catalyst lowers the activation energy:



10. It is in the solid phase. A heterogeneous catalyst must be in a different phase from the reactants.