14.27 a) Since this particular reaction is zero order in A, doubling the concentration of A will not change the rate of the reaction.

b) The reaction is zero order in A, second order in B and second order overall.

c) $M^{-1}s^{-1}$

14.28 a) rate = $k[A][C]^2$

b) Doubling[A] will double the rate.

c) Tripling [B] will not change the rate.

d) Tripling [C] will increase the rate by a factor of nine

e) Since the reaction is third order overall, tripling the concentration of all reactants with increase the rate by a factor of 27.

f) Similarly, when the concentration is cut in half the rate decreases by a factor of 1/8.

14.29 a) rate = $k[N_2O_5]$

b) rate = $k[N_2O_5] = 4.82\text{x}10^{-3}\text{s}^{-1}[0.0240M] = 1.16\text{x}10^{-4}\ M/\text{s}$

c) Because this reaction is first order in N_2O_5, doubling the concentration of this reactant will double the rate, making it $2.32\text{x}10^{-4}M/\text{s}$.

d) Because this reaction is first order in N_2O_5, halving the concentration of this reactant will halve the rate, making it $0.58\text{x}10^{-4}M/\text{s}$. ($5.8\text{x}10^{-5}M/\text{s}$).

14.33 a) Comparing the 1st and 2nd trials, we see that doubling the concentration of OCl^- while the concentration of I^- remains constant causes the rate to double, indicating that the reaction is first order in OCl^-. Comparing the 1st and 3rd trials, we see that doubling the concentration of I^- while the concentration of OCl^- remains constant causes the rate to double, indicating that the reaction is first order in I^-. As a result, the rate law for this reaction is rate=$k[OCl^-][I^-]$

14.33 b) First, we must determine the value of *k*. Using trail 1:

$$\text{rate} = k[OCl^-][I^-]$$

$$1.36 \times 10^{-4} M/\text{s} = k[1.5\text{x}10^{-3} M][1.5\text{x}10^{-3} M]$$

$$k = 60 M^{-1}\text{s}^{-1}$$

Next, we solve the rate law equation at these new concentrations:

$$\text{rate} = k[OCl^-][I^-]$$

$$\text{rate} = 60 M^{-1}\text{s}^{-1}[2.0\text{x}10^{-3} M][5.0\text{x}10^{-4} M]$$

$$\text{rate} = 6.0\text{x}10^{-5} M/\text{s}$$

14.35 a) Comparing the 1st and 2nd trials, we see that halving the concentration of NH_3 while the concentration of BF_3 remains constant causes the rate to halve, indicating that the reaction is first order in NH_3. Comparing the 3rd and 4th trials, we see that increasing the concentration of BF_3 by a factor of 1.75 while the concentration of NH_3 remains constant causes the rate to increase by a factor of 1.75, indicating that the reaction is first order in BF_3. As a result, the rate law for this reaction is rate=$k[NH_3][BF_3]$

b) This reaction is second order overall

c) Referencing trail 1:

$$\text{rate} = k[NH_3][BF_3]$$

$$0.2130M/\text{s} = k[0.250M][0.250M]$$

$$k = 3.41M^{-1}\text{s}^{-1}$$

d)

$$\text{rate} = k[NH_3][BF_3]$$

$$\text{rate} = 3.41M^{-1}\text{s}^{-1}[0.500M][0.100M]$$

$$\text{rate} = 0.171M/\text{s}$$

14.37 a) Comparing the 1st and 2nd trials, we see that increasing the concentration of NO by a factor of 2.5 while the concentration of Br_2 remains constant causes the rate to increase by a factor of 6.25, indicating that the reaction is second order in NO. Comparing the 1st and 3rd trials, we see that increasing the concentration of Br_2 by a factor of 2.5 while the concentration of NO remains constant causes the rate to increase by a factor of 2.5, indicating that the reaction is first order in Br_2. As a result, the rate law for this reaction is rate=$k[NO]^2[Br_2]$

b) rate=$k[NO]^2[Br_2]$

$24M/s = k[.10M]^2[0.20M]$ $k = 12000M^{-2}s^{-1}$

$150M/s = k[.25M]^2[0.20M]$ $k = 12000M^{-2}s^{-1}$ Ave $k = 12000M^{-2}s^{-1}$

$60M/s = k[.10M]^2[0.50M]$ $k = 12000M^{-2}s^{-1}$

$735M/s = k[.35M]^2[0.50M]$ $k = 12000M^{-2}s^{-1}$

c) From the balanced equation, we see that the rate of appearance of NOBr will be twice the rate of disappearance of Br_2.

14.37 d) rate = $k[NO]^2[Br_2]$

rate = $12000 M^{-2}s^{-1}[0.075M]^2[0.25M]$

rate = $16.9M/s$

This calculated rate is the rate of appearance of NOBr. We determined in the previous question that the rate of disappearance of Br_2 will be half this rate or $8.45M/s$.