

During Class Invention

Name \_\_\_\_\_

Method of Initial Rates

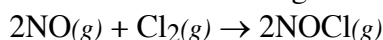
TA Name \_\_\_\_\_

Lab Section # \_\_\_\_\_

1. Define the terms; *rate equation* and *rate law* for a chemical reaction.

**Rate equation and rate law are synonymous. The rate equation is a mathematical equation that relates the instantaneous rate at a particular point in the progress of a chemical reaction to the concentration of the reacting specie(s).**

2. Write the general rate law for the following reaction;



$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

Identify the rate constant in the rate law. What are the exponents in the rate law called?

**k is the rate constant in the mathematical equation.**

**The exponents 'm' and 'n' represent the order of the reaction with respect to NO and Cl<sub>2</sub>, respectively.**

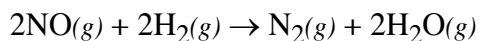
**“rate” generally refers to the initial rate. The initial rate is the fastest rate of the reaction and occurs at the very beginning of the reaction. At this point there are few competing reactions. It should be noted when using the initial rate the concentration of the reactants are initial concentrations.**

$$\text{rate} = k[\text{NO}]_0^m[\text{Cl}_2]_0^n$$

3. What experimental data is needed to determine the order of a chemical reaction?

**Since rate is defined as  $-\frac{\Delta[\text{reactant}]}{\text{time}}$ , the concentration of reacting species must be followed over time. (See the data in Exercise 5) Typically two experiments, each with different initial concentrations, are required. After collecting the experimental data, the initial rate is determined. The order of the reaction with respect to a particular reactant is obtained by comparing the ratio of the initial concentrations of the reactant with the ratio of their initial rates.**

- 4a. Consider the reaction



and the following initial rate data.

Experiment			
Number	P <sub>NO</sub> (mmHg)	P <sub>H<sub>2</sub></sub> (mmHg)	Initial Rate ( $\frac{\text{mmHg}}{\text{s}}$ )
1	400	150	0.66
2	400	300	1.34
3	150	400	0.25
4	300	400	1.03

i) Determine the reaction order for NO and H<sub>2</sub>.

**Selecting Exp. #1 and #2 the P<sub>NO</sub> is constant.**

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2(\text{PNO})_2^m(\text{PH}_2)_2^n}{k_1(\text{PNO})_1^m(\text{PH}_2)_1^n}$$

Because the P<sub>NO</sub> is constant and k is constant they can both be canceled from the ratio. Leaving

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{(\text{PH}_2)_2^n}{(\text{PH}_2)_1^n} \frac{1.34}{0.66} = \frac{(300)^n}{(150)^n}$$

$$2.03 = (2)^n \quad n = 1$$

To solve for 'm' we repeat the procedure only we need to select a pair of experiments in which P<sub>H<sub>2</sub></sub> is constant and P<sub>NO</sub> is changing. In this case we could select Exp. #3 and #4.

$$\frac{\text{rate}_4}{\text{rate}_3} = \frac{k_2(\text{PNO})_4^m(\text{PH}_2)_4^1}{k_1(\text{PNO})_3^m(\text{PH}_2)_3^1}$$

Because the P<sub>H<sub>2</sub></sub> is constant and k is constant they can both be canceled from the ratio. Leaving

$$\frac{\text{rate}_4}{\text{rate}_3} = \frac{(\text{PNO})_4^m}{(\text{PNO})_3^m} \quad \frac{1.03}{0.25} = \frac{(300)^m}{(150)^m}$$

$$4 = (2)^m \quad m = 2$$

ii) Determine the overall order of the reaction.

**The reaction is third order overall. Overall order = m + n = 3**

iii) Write the specific rate law for the reaction.

**The specific rate law is: rate = k(P<sub>NO</sub>)<sup>2</sup>(P<sub>H<sub>2</sub></sub>)<sup>1</sup>**

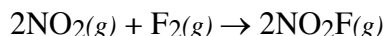
iv) Determine the rate constant for the reaction (include units).

**The rate constant for the reaction is**

$$k = \frac{\text{rate}}{(\text{PNO})^2(\text{PH}_2)^1} = \frac{6.6 \times 10^{-1} \frac{\text{mmHg}}{\text{s}}}{[400 \text{ mmHg}]^2[150 \text{ mmHg}]^1}$$

$$= 2.7 \times 10^{-8} \text{ mmHg}^{-2} \cdot \text{sec}^{-1}$$

b. The following initial rate data were collected for the reaction



at 100 °C. (Problems: BL 15.15 – 15.16)

Exp.	[NO <sub>2</sub> ]	[F <sub>2</sub> ]	initial rate (M/sec)
1	0.0482 M	0.0318 M	1.90 x 10 <sup>-3</sup>
2	0.0120 M	0.0315 M	4.69 x 10 <sup>-4</sup>
3	0.0480 M	0.127 M	7.57 x 10 <sup>-3</sup>

i) Determine the reaction order for NO<sub>2</sub> and F<sub>2</sub>.

To determine the order with respect to NO<sub>2</sub> experiments 1 and 2 will be used. Even though the concentration of F<sub>2</sub> is not exactly constant, it is to two significant figures.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1[\text{NO}_2]_1^m[\text{F}_2]_1^n}{k_2[\text{NO}_2]_2^m[\text{F}_2]_2^n}$$

the rate constant and [F<sub>2</sub>] are constant.

$$\frac{1.90 \times 10^{-3} \frac{\text{M}}{\text{s}}}{4.69 \times 10^{-4} \frac{\text{M}}{\text{s}}} = \left( \frac{.0482 \text{ M}}{0.0120 \text{ M}} \right)^m$$
$$4.05 = (4.02)^m$$
$$1 = m$$

To determine the order of the reaction with respect to F<sub>2</sub> experiments 1 and 3 can be used.

$$\frac{\text{rate}_3}{\text{rate}_1} = \frac{k_1[\text{NO}_2]_3^m[\text{F}_2]_3^n}{k_2[\text{NO}_2]_1^m[\text{F}_2]_1^n}$$
$$\frac{7.57 \times 10^{-3} \frac{\text{M}}{\text{s}}}{1.90 \times 10^{-3} \frac{\text{M}}{\text{s}}} = \left( \frac{0.127}{0.0318} \right)^n$$
$$3.98 = 3.99^n \quad n = 1$$

ii) Determine the overall order of the reaction.

**The reaction is second order overall. Overall order = m + n = 2**

iii) Write the specific rate law for the reaction.

**The specific rate law is: rate = k[NO<sub>2</sub>]<sup>1</sup>[F<sub>2</sub>]<sup>1</sup>**

iv) Determine the rate constant for the reaction (include units).

**The rate constant for the reaction is**

$$k = \frac{\text{rate}}{[\text{NO}_2]^1[\text{F}_2]^1}$$
$$= \frac{1.90 \times 10^{-3} \frac{\text{M}}{\text{s}}}{[0.0482 \text{ M}]^1[0.0318 \text{ M}]^1} = 1.24 \text{ M}^{-1}\cdot\text{sec}^{-1}$$