DR. SANDBLOM'S KINETICS EXAMPLES AND HOMEWORK

Average Rates Homework: Consider the following reaction and experimental data.

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_{2(g)}$$

t (s)	$[O_2]$ (M)	$[N_2O_5]$ (M)
600	0.0021	0.0124
1200	0.0036	0.0094
4200	0.0072	0.0022
4800	0.0075	0.0016

Calculate the average rate between 600 s and 1200 s for:

a. production of O_2
b. consumption of N_2O_5

Calculate the average rate for production of O_2 between 4200 s and 4800 s.

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ESSENTIAL STEPS for Rate Law Determination from Initial Rate Experimental Data:

1. Write down the **Rate Law** based on the reactants in the balanced chemical equation. **Warning!** Do not use stoichiometric coefficients in the Rate Law.
2. Consider the experimental data to compare **Initial Rate** to **Concentration** and determine **Order**.
   a. If there is only one reactant, compare 2 experiments and consider how a change in concentration affects the rate.
   b. If there is more than one reactant, choose 2 experiments where only one reactant changes concentration and consider how this change in concentration affects the rate.
3. Write the **Rate Law** including **Order**, and use a set of data to calculate the **Rate Constant**, k, including units.

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Initial Rate 1: Nitrogen dioxide decomposes in the gas phase according to the equation:

$$NO_{2(g)} \rightarrow NO_{(g)} + \frac{1}{2}O_{2(g)}$$

The following initial rate experiments were run at 300°C and, for each, the initial rate of consumption of NO_2 was determined. Find the rate law including the value of the rate constant. What is the overall order?

	$[NO_2]_0$ (M)	Initial Rate ($M\ s^{-1}$)
Expt 1	0.010	5.430×10^{-5}
Expt 2	0.020	2.172×10^{-4}
Expt 3	0.030	4.887×10^{-4}

Initial Rate 2: Consider the following reaction:

$$2NO_{(g)} + H_{2(g)} \rightarrow N_2O_{(g)} + H_2O_{(g)}$$

The following initial-rate experiments were run at the same temperature, and, for each, the initial rate of formation of water was determined. Find the rate law including the value of the rate constant. What is the overall order?

	$[NO]_0$ (M)	$[H_2]_0$ (M)	Initial Rate (M min^{-1})
Expt 1	0.10	0.80	0.26
Expt 2	0.20	0.40	0.52
Expt 3	0.30	0.80	2.34

Initial Rate Homework: Four experiments were conducted to discover how the initial rate of consumption of BrO_3^- ions varies as the as the concentration of the reactants are changed in the reaction below.

$$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$$

Use the experimental data in the table below to determine the order of the reaction with respect to each reactant and the overall order. Write the rate law for the reaction and determine the value of k.

	$[BrO_3^-]_0$ (M)	$[Br^-]_0$ (M)	$[H^+]_0$ (M)	Initial Rate (M s^{-1})
Expt 1	0.10	0.10	0.10	1.2
Expt 2	0.20	0.10	0.10	2.4
Expt 3	0.10	0.30	0.10	3.5
Expt 4	0.20	0.10	0.15	5.4

Integrated Rate 1: Decomposition of 1 mole of N_2O_5 is 1st order with a rate constant at 45°C of 4.8 x 10^{-4} s^{-1}.

(a) If the initial concentration is 1.65 x 10^{-2} M, what is the concentration after 825 s?

(b) How long would it take for the concentration to decrease to 1.00 x 10^{-2} M?

(c) What is the half life of the reaction?

Integrated Rate 2: The rate constant for a 1st order reaction is 2.5 x 10^{-4} s^{-1}. How long does it take for only 3.125% of the initial concentration to remain?

Integrated Rate 3: The rate constant for a 1st order reaction is 0.01680 s^{-1}. How long will it take for 90. % of the initial concentration to react?

Integrated Rate Homework 1: The decomposition of NO_2 has a rate constant of 2.8 x 10^{-10} M^{-1} s^{-1} at 25°C. If 3.00 mol of NO_2 are initially present in a sealed 2.00 L vessel at 25°C, what is the half life of the reaction in years?

Integrated Rate Homework 2: SO_2Cl_2 decomposes to SO_2 and Cl_2 in a first order gas-phase reaction. In an experiment, the initial concentration of SO_2Cl_2 was 0.248 M. If the rate constant for is 2.2 x 10^{-5} s^{-1}, what is the concentration of SO_2Cl_2 after 4.5 hours?

Arrhenius Homework: For the formation of HI from the elements, H_2 and I_2, the rate constant at 600 K is $2.7 \times 10^{-4}\ M^{-1}\ s^{-1}$ and the rate constant at 650 K is $3.5 \times 10^{-3}\ M^{-1}\ s^{-1}$. (a) What is the activation energy? (b) What is the rate constant at 700 K?

Essential STEPS for Evaluating a Mechanism

1. Check that the steps add up to the overall reaction
2. Write a rate law based on the slowest elementary step.
3. If the slowest step is not the first step, intermediates may appear in this rate law. In this case, use the previous fast equilibrium step to substitute the concentration of intermediate with concentrations of reactants and/or products.
4. Check to see if this predicted rate law matches the experimental one.

Mechanisms 1: For the following gas-phase reaction:

$$O_3 + 2NO_2 \rightarrow O_2 + N_2O_5$$

Which of the following proposed mechanisms match the following Experimental Rate Law?

Rate = k[O_3][NO_2]

Proposed Mechanism A:

$$NO_2 + NO_2 + O_3 \xrightarrow{k_1} O_2 + N_2O_5$$
$$2NO_2 + O_3 \rightarrow O_2 + N_2O_5$$

Proposed Mechanism B:

$$O_3 + NO_2 \xrightarrow{k_2} NO_3 + O_2 \quad \text{slow}$$
$$NO_3 + NO_2 \xrightarrow{k_3} N_2O_5 \quad \text{fast}$$
$$2NO_2 + O_3 \rightarrow O_2 + N_2O_5$$

Mechanisms 2: For the following gas-phase reaction:

$$NO_2 + CO \rightarrow NO + CO_2$$

Which of the following proposed mechanisms match the following Experimental Rate Law?

Rate = k[NO_2]^2

Proposed Mechanism A:

$$NO_2 + NO_2 \xrightarrow{k_1} N_2O_4 \quad \text{slow}$$
$$N_2O_4 + CO \xrightarrow{k_2} NO + CO_2 + NO_2 \quad \text{fast}$$
$$NO_2 + CO \rightarrow NO + CO_2$$

Proposed Mechanism B:

$$NO_2 + NO_2 \xrightarrow{k_3} NO_3 + NO \quad \text{slow}$$
$$NO_3 + CO \xrightarrow{k_4} NO_2 + CO_2 \quad \text{fast}$$
$$NO_2 + CO \rightarrow NO + CO_2$$

Mechanisms 3:
For the following gas-phase reaction:

$$2O_3 \rightarrow 3O_2$$

What is the rate law predicted by the following proposed mechanism?

$$O_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2 + O \quad \text{fast, equilibrium}$$

$$O_3 + O \xrightarrow{k_2} 2O_2 \quad \text{slow}$$

Mechanisms Homework 1:
For the following gas-phase reaction:

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

What is the rate law predicted by the following proposed mechanism?

$$2NO \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} N_2O_2 \quad \text{fast, equilibrium}$$

$$N_2O_2 + H_2 \xrightarrow{k_2} N_2O + H_2O \quad \text{slow}$$

$$N_2O + H_2 \xrightarrow{k_3} N_2 + H_2O \quad \text{fast}$$

Mechanisms Homework 2:
What would be the rate law for the following proposed mechanism?

$$H_2O_2 + I^- \xrightarrow{k_1} OH^- + HOI \quad \text{slow}$$

$$HOI + I^- \xrightarrow{k_2} OH^- + I_2 \quad \text{fast}$$

$$\underline{2OH^- + 2H_3O^+ \xrightarrow{k_3} 4H_2O \quad \text{fast}}$$

$$2I^- + \underset{*}{H_2O_2} + \underset{*}{2H_3O^+} \underset{*}{\rightarrow} I_2 + 4H_2O$$