

CHEM 142 Exam Review Guide

CHAPTER 13: CHEMICAL KINETICS

Students must be able to accomplish the following in preparation for Exam 1

1. Differentiate between **kinetics** (rates of reaction) and **thermodynamics** (related to K_{eq} or simply K) - See beginning lecture notes
2. Explain how each of the following factors affect the rate of a reaction: Refer to lecture notes
 - ✚ Concentration of reactants
 - ✚ Temperature
 - ✚ Nature of reactants (state and type of reactants) - rusting of iron; 3 phases involved
 - ✚ Presence of a catalyst
3. *Importance of kinetics*: Give examples of everyday life reactions that we want to speed up (faster rate) - See lecture notes or think of your own examples
4. *Importance of kinetics*: Give examples of everyday life reactions that we want to slow down (faster rate) - See lecture notes or think of your own examples
5. Express the **rate** of a given chemical reaction (hence the word **rate expression**). See lecture notes, Tro Section 13-2 and Problem Set 4

Example: Given the following balanced equation, express the rate of reaction with respect to SO_2 .



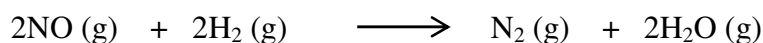
Note: You are asked to write the **rate expression w.r.t. SO_2** , a reactant. Since there are 2 moles of SO_2 in the balanced equation, and knowing that reactants are used up (declining concentration with time)

Answer:

$$\text{Rate} = \frac{-\Delta[\text{SO}_2]}{2 \Delta t}$$

For *more practice*, work on Problems 25a and 26a, p. 607 (Tro).

6. On a molecular level, be able to explain *why the rate of a reaction decreases with time*. HINT: Look into chances of collisions between reactant molecules as the reaction progresses.
7. Explain the difference between **average rate** and **instantaneous rate** of a chemical reaction. See lecture notes or Section 13.2 for definitions.
8. Calculate the **average rate** from a given *concentration vs. time* data. See lecture notes and Problem Set 4 for sample calculations; also read Section 13.2 (Tro) and work on Problems 25b, 26b, 29a and 30a.
9. Calculate the **instantaneous rate** from a given plot of *concentration vs. time* data. See lecture notes and Problem Set 4 (the last question is on instantaneous rate calc based on Tro, Problem 32b, p. 608)
10. Be able to express the **rate law** for a given reaction with or without the order of reaction w.r.t. reactants.
Example from Problem Set 4: Consider the following reaction:



The rate law for this reaction is first order in H₂ and second order in NO. Write the **rate law**.

Analysis: 1st order in H₂ means the second term of the equation will have [H₂]¹ or simply [H₂]; likewise, 2nd order in NO equates to [NO]². These numbers have nothing to do with the coefficients in the balanced equation, unless you are writing rate expressions.

Answer: **Rate = k [NO]² [H₂]** *NOTE: The order of reaction (e.g. 1st order, 2nd order) has nothing to do with the coefficients (number of moles) in the balanced equation.*

↑
Rate constant

11. Determine the **order of a reaction** from *initial rate vs. concentration* data. From this you can write the rate law for the given reaction. See lecture notes for sample calculations. I am also providing another example below.

Example: Determine the rate law and the **rate constant, k**, for the following reaction using the data provided.



Initial [N ₂ O ₅] (M)	Initial Rate (M ⁻¹ s ⁻¹)
0.093	4.84 x 10 ⁻⁴
0.186	9.67 x 10 ⁻⁴
0.745	38.67 x 10 ⁻⁴

Analysis: First, you must calculate the order of reaction w.r.t. the reactants. Since there is only one, you expect the general expression of rate law to be:

$$\text{Rate} = k [\text{N}_2\text{O}_5]^m \quad \text{where } m \text{ is the order of reaction w.r.t. the reactant N}_2\text{O}_5$$

First you must determine the value of m using the data above. This can be done by inspection, i.e.

Initial [N ₂ O ₅] (M)	Initial Rate (M ⁻¹ s ⁻¹)
0.093	4.84 x 10 ⁻⁴ = rate 1
0.186	9.67 x 10 ⁻⁴ = rate 2
0.745	38.67 x 10 ⁻⁴ = rate 3

Handwritten notes: Doubling this also doubles rate. } doubles also

Initial [N ₂ O ₅] (M)	Initial Rate (M ⁻¹ s ⁻¹)
0.093	4.84 x 10 ⁻⁴ = rate 1
0.186	9.67 x 10 ⁻⁴ = rate 2
0.745	38.67 x 10 ⁻⁴ = rate 3

Handwritten notes: (Quadruple) 4x increase here also increases (initial) rate 4x. } 4x increase also

A pattern like this ($n \times$ increase in reactant concentration also increases rate $n \times$ times, where $n = 1, 2, 3 \dots$) indicates first order reaction w.r.t. the reactant. Thus, you can conclude that the reaction is first order w.r.t. N_2O_5 , and the **rate law** is written as:

$$\text{Rate} = k [\text{N}_2\text{O}_5]^1 \quad \text{or simply} \quad \text{Rate} = k [\text{N}_2\text{O}_5]$$

In class, I showed you an alternative method of finding m , the order of reaction. The method of inspection is the quickest way to find m . The method I showed you uses simple algebra as shown below.

Step 1: Pick 2 sets of experiment to compare. In the above example, I marked their corresponding rates as rate 1, rate 2, etc. to indicate the results from experiments 1, 2, etc.

➤ Let's compare expts. 1 and 2, thus rates 1 and 2

Step 2: Write the rate law as ratio of the two experiments:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \frac{k [\text{N}_2\text{O}_5]_2^m}{k [\text{N}_2\text{O}_5]_1^m}$$

means concentration from expt. 2

concentration from expt. 1

k cancel @ other ; simplify $\frac{[]_2^m}{[]_1^m}$ as $\left(\frac{[]_2}{[]_1} \right)^m$

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \left(\frac{[\text{N}_2\text{O}_5]_2}{[\text{N}_2\text{O}_5]_1} \right)^m$$

Step 3: Calculate m , the order of reaction w.r.t. N_2O_5 reactant by substituting experimental data to the rate equation ratio above:

$$\frac{\text{Rate 2}}{\text{Rate 1}} = \left(\frac{[\text{N}_2\text{O}_5]_2}{[\text{N}_2\text{O}_5]_1} \right)^m$$

$$\frac{9.67 \times 10^{-4} \text{ M/s}}{4.84 \times 10^{-4} \text{ M/s}} = \left(\frac{0.186 \text{ M}}{0.093 \text{ M}} \right)^m$$

$$1.998 = (2)^m$$

$$2 = 2^m \quad \text{So} \quad m = 1 \quad \text{for the equation to be true}$$

Thus, the rate law is

$$\text{Rate} = k [\text{N}_2\text{O}_5]^1$$

Finally, to determine k , we can substitute any of the data from a given experiment to the rate law equation. Let's pick data from experiment 2:

Initial [N₂O₅] (M) Initial Rate (M⁻¹s⁻¹)

$[N_2O_5]$ from expt. 2 \rightarrow 0.186 $9.67 \times 10^{-4} = \text{rate 2}$

Since $\text{Rate} = k [N_2O_5]^1 \Rightarrow k = \frac{\text{Rate}}{[N_2O_5]^1}$

Note:

Unit: $M^{-1} s^{-1}$ equals $\frac{1}{M \cdot s}$
means inverse of

Unit cancellation for k :

$$\frac{1}{M \cdot s}$$

$$= \frac{1}{M \cdot (M \cdot s)} = \frac{1}{M^2 \cdot s}$$

$$k = \frac{\text{Rate 2}}{[N_2O_5]^1_{\text{expt. 2}}}$$

$$k = \frac{9.67 \times 10^{-4} / M \cdot s}{0.186 M}$$

$$k = 5.20 \times 10^{-3} / M^2 \cdot s$$

rate constant