

Problems from Atkins and other practice problems on Chemical Kinetics

Chemistry BC3252y

Steps in obtaining rate laws and rate constants from experimental data (concentration measurements as a function of time)

1. Unless already suggested, propose possible rate laws. If there is one reactant A, two common possibilities are first and second order in A: $v = -d[A]/dt = k[A]^n$ where $n = 1$ or 2 . If there are two reactants A and B, then a likely candidate is $v = k[A][B]$.
2. Look up or determine the **integrated** form of the rate law, and decide what function of [A] (and [B]) will give a linear plot to verify the rate law.
3. Look at the data. Often what is not given is [A], but rather something from which you can calculate [A], based on stoichiometry or other facts.
4. Set up an Excel spreadsheet. Calculate [A] (and [B] if relevant), then calculate the function you need to plot. Plot the points and LOOK at the graph: do the points fall on a straight line?
5. If the plot appears to be linear, add a trendline, showing the equation, and then use the slope to determine k. Report k **with units!**
6. If it is curved, a trendline may be used to help see the curvature, but DO NOT show the equation: it is meaningless. Try a different rate law.



The above reaction was studied at 67°C. One atmosphere of pure $\text{N}_2\text{O}_5(\text{g})$ was placed in a closed container. The total pressure was monitored as a function of time, with the results below. What is the rate law and the rate constant?

Key preliminary question: For proposed rate law, what function of p do you plot in order to get a straight line?

t (min)	1.00	2.00	3.00	5.00
p (atm)	1.443	1.755	1.977	2.241

Problem 26.6 (reworded)



In 1898, Bodenstein observed the following rate law:

$$v = d[\text{HI}]/dt = k [\text{H}_2][\text{I}_2]$$

Is this consistent with this being an elementary reaction?

Does this prove that the reaction is elementary?

In 1967, Sullivan proposed a mechanism for the reaction:

- 1) $\text{I}_2(\text{g}) \rightleftharpoons 2 \text{I}(\text{g})$ **rate constants k_1, k_{-1}**
- 2) $\text{H}_2(\text{g}) + \text{I}(\text{g}) + \text{I}(\text{g}) \rightarrow 2 \text{HI}(\text{g})$ **rate constant k_2**

Use the steady state approximation to determine the overall rate of formation of product. Show how certain conditions yield the rate law observed by Bodenstein.