Rate of Reaction, Part I: The Method of Initial Rates

Some chemical reactions are complete within the time it requires to mix the reactants, such as most acid-base reactions. Others may take place as we observe them, and we can see concentrations of reactants and products change by a variety of techniques. Some are so slow, that even though a reaction *ought* to proceed spontaneously, it is so slow under typical conditions that we never detect any change taking place. Wood, left to itself in air, does not burn. In the presence of certain bacteria and fungi, wood slowly decomposes. In the presence of a flame to start the process, wood will burn spontaneously.

Chemical reaction rates, or kinetics, provide a wealth of information not only about how fast reactions proceed, but also what concentrations are expected in the future or were present in the past, and how the reaction itself proceeds on a molecular level. Chemical reaction rates are fundamentally experimental; they may have explanations that come from theory, but the actual rates themselves are determined by experiments. The purpose of this experiment is to introduce you to chemical reaction rates through observation, rather than from a rigorous study of their theory.

A rate, by definition, is a change in a variable as time changes. Velocity is a rate; it is the change of distance (Δs) within a specific change of time (Δt). In finance, an interest rate is the change in money ($\Delta \$$) with respect to time (Δt). A chemical reaction rate is the change in concentration (Δc) with respect to time (Δt). (When the concentration is molar, it is expressed with square brackets, [C].) A rate is expressed as the change in the "dependent" variable (the result of the operation or experiment) divided by the change in the independent variable (time). Velocity could be expressed as (Δs) / (Δt), or a reaction rate as (Δc) / (Δt). You will recognize this form as the slope (Δy) / (Δx) of a line on a graph with time plotted along the x-axis. In chemical reactions, very few graphs of concentration vs. time are straight lines. It is still possible to obtain the rate from a graph that is a curve, either by estimating or by calculating the slope of the tangent at one specific point on a curve. It can be estimated by drawing the tangent with a ruler and calculating (Δc) / (Δt). If you are familiar with calculus, you know it also can be computed from the "first derivative" of the curve, which is possible with many computers.

Concentration vs. time data are rarely linear, but some exponential relationship. However, in the early phase of most reactions the changes are nearly linear, thus the rate ($\Delta[C] / \Delta t$) can be obtained as the slope of the line (or the slope of the tangent drawn to the origin). This technique is known as the "Method of Initial Rates," and uses experiments in which concentrations of some reactants are deliberately held constant, and large changes are made in the others. The initial rates might be proportional to the initial concentration (rate = k [C]) or they may have an exponential relationship (rate = k [C]^n , where n is the "order"). For example, if doubling the initial concentration quadrupled the rate, the order is 2. If doubling the concentration doubled the rate, the order is 1. We will explore this method in the first part of the experiment.

Part I: The Bleaching of Phenolphthalein

Phenolphthalein is a compound that is used in titration analyses and in some forensic work. Its most familiar use is its color change from clear to a purplish pink color with small amounts of excess hydroxide ion above a pH of about 8.5. However, in more concentrated hydroxide solutions, the phenolphthalein anion decomposes and its color fades. This color change does not occur instantaneously, and the rate of its bleaching depends on the hydroxide concentration. In this experiment we will observe the change in color intensity of phenolphthalein solutions as they react with hydroxide by monitoring their absorbance with a spectrophotometer. Absorbance is proportional to concentration, as expressed in Beer's Law, A = a b c (where a and b are constants).

(**Note**: The Prelaboratory Assignment is the last page of this document, which must be completed and turned in at the start of lab.)

Procedure:

1. Turn on a spectrophotometer and set it to a wavelength of 550 nm. Select Absorbance.

2. Materials:

      5.2×10^{-3} M Phenolphthalein solution in ethanol (dispense with an Eppendorf pipet)

      1.0 M NaOH solution   (dispense with a 2.00 mL measuring pipet)

      Deionized water   (dispense with a 10.00 mL measuring pipet)

      Dropper pipet, 30 mL beaker, cuvet, spectrophotometer

You will be assigned to start with either experiment A or B. However <u>read all of step 4 before preparing your solutions</u>. In all cases we will assume volumes add quantitatively to 10.0 mL.

Expt.	μL 5.2×10^{-3}M Phenolphthalein solution	mL Deionized water	mL 1.0 M NaOH	M Phenolphthalein	M NaOH
A	50	9.20	0.80	2.6×10^{-5}	0.080
B	50	9.00	1.00	2.6×10^{-5}	0.10
C	50	8.40	1.60	2.6×10^{-5}	0.16
D	50	8.00	2.00	2.6×10^{-5}	0.20

3. After a 10 minute warm-up period, calibrate your spectrophotometer at 0.000 Absorbance using deionized water. Then empty and dry the cuvet.

4. Have all three pipets, the dropper, the beaker, the cuvet, and a timing device ready. Read ALL the following before starting:

    a) Add the appropriate amount of 1.0 M NaOH to the beaker.

    b) Add the appropriate amount of deionized water to the beaker.

    c) With the timer ready, add the phenolphthalein solution to the 30 mL beaker with the Eppendorf pipet, starting the timer when the first phenolphthalein hits the beaker's solution.

    d) Immediately draw part of the beaker solution up into a plastic dropper and flush back into the beaker; repeat once. This accomplishes mixing. Then fill the cuvet to the mark with the dropper.

    e) Record the absorbance at 30 seconds (if possible), then every 30 seconds for 240 seconds total.

5. Dispose of the solutions in the beaker and cuvet into a waste container, rinse the beaker, the dropper, and the cuvet thoroughly with deionized water, and dry the beaker and cuvet.

6. Conduct a second experiment (C or D) in which the NaOH molarity is twice the first experiment you ran; details are in the table above.

Name _____

Partner _____

Report:

Data:

First run: Letter _____   Second run: Letter _____

$[OH^-]$ = _____ $[OH^-]$ = _____

Time (sec)	A, first run	A, second run
30		
60		
90		
120		
150		
180		
210		
240		

Make a graph showing all data from both runs with two symbols on one set of axes; clearly indicate which run each symbol corresponds to. Using a ruler, place a straight line through each set of data for 30 to 120 seconds <u>only</u>, and extend the line to the y-axis intercept (at t = 0).
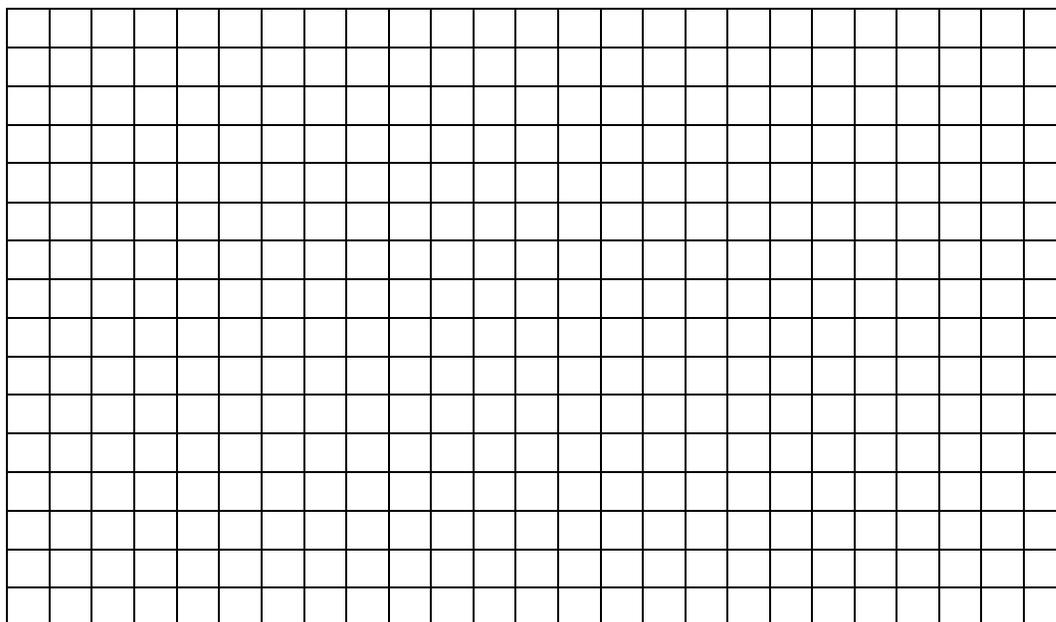
Critical Thinking Questions:

Over the time period of 0 to 120 seconds, are these data approximately straight or curved?

Are <u>all</u> the data for a single run straight or curved?

Calculations (using Absorbance in place of [C] throughout)

Using regression (or the straight line on the graph), determine the slope ($\Delta A / \Delta t$) for <u>only</u> the data between 30 and 120 seconds, which is the initial rate. Include units.

  Initial slope (initial rate), first run:

  Initial slope (initial rate) second run:

  Would these slopes be the same or different if you picked a later time interval?
    "Faster" or "slower"?

  Determination of Order:
    Qualitative: When comparing runs where [OH⁻] doubled, did the rate remain the same (zero order), approximately double (first order), or increase approximately four times (second order)?

    Quantitative: Set up two equations for the rate, using the format rate = k [OH⁻]^n. Substitute known experimental values for rate and [OH⁻]. Divide the equation with the faster rate by the equation with the slower rate, cancel k, and solve for n. Show both the decimal value and the closest integer value for n.

  Determination of the rate constant, "k":

Substitute your experimental values of rate (using their absolute values), [OH⁻], and your unrounded, experimental n in each of the two rate equations. Solve for k in each; include units.

      Is k constant or not constant (considering appropriate significant figures)?

  In this experiment, we did not study the influence of the phenolphthalein concentration. How could an experiment be designed to find out its influence? Give specific quantities.

Name _____

Rate of Reaction
Prelaboratory Assignment

1. In a graph of the concentration of a reactant vs. time, what parameter gives the rate?

2. Write Beer's Law as an equation. Show how absorbance can be used to monitor concentration.

3.   A rate equation could be written as $(\Delta c/\Delta t) = - k [c]^n$. Define (name) the following as they pertain to the rate equation:

    a) $(\Delta c/\Delta t)$

    b) k

    c) [c]

    d) n

4. Assume n in #3 is not zero.

    a) Does $(\Delta c/\Delta t)$ change or remain constant as a reaction progresses in time?

    b) Does k change or remain constant as a reaction progresses?

5. Why can we use absorbance in place of [c] in this experiment?