

If anybody cares

The homework page is #66-not 166

The scores HW and Quizzes have been updated and are current-please let me know if there's anything wrong

A major update of the lecture help download has been posted. It should make your file current if it installs properly.

Exam 2/26 covers thru this evening's discussion. You should expect an exam of typical length/challenge.

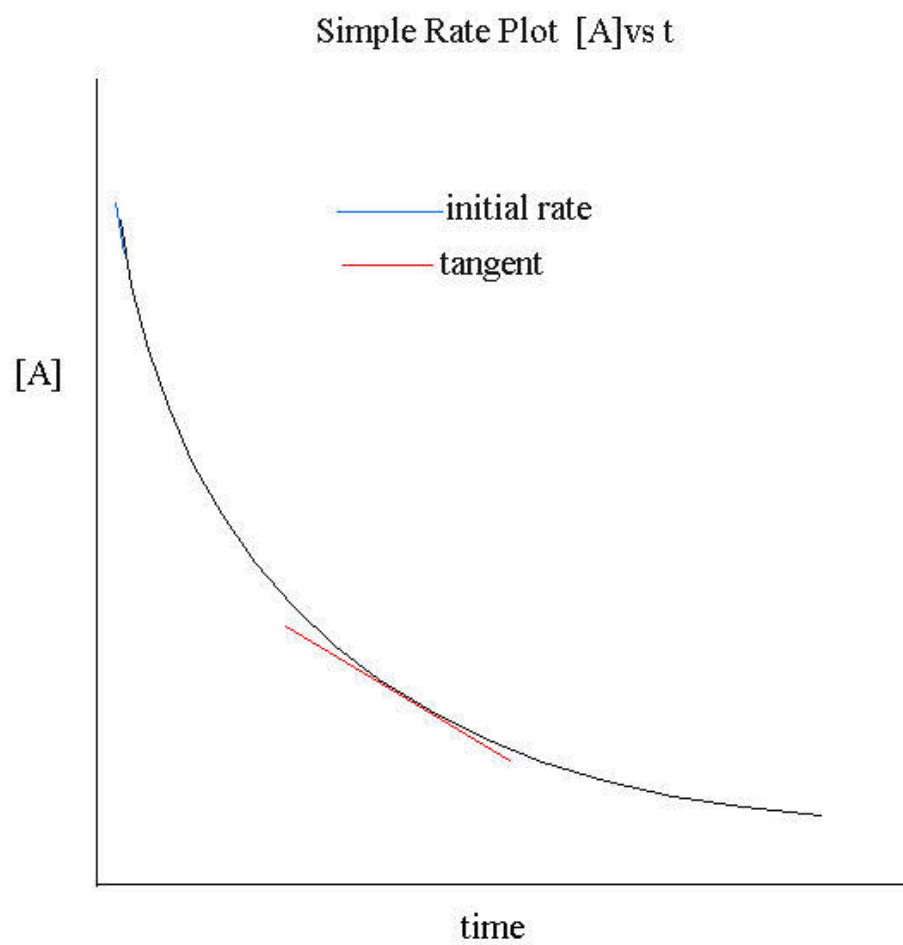
Of Things to Come

- In evaluating the true “impact” of any change, there are two universal factors-how large is it and how fast does it occur. This is true whether one is speaking of global warming, changes in interest rates or chemical reactions.
- How the issues of degree and speed are applied to chemical change are the central points for much of the remainder of the year.
- The study of the extent to which a chemical reaction occurs is called equilibrium.
- The study of how quickly (or slowly) a reaction occurs is called kinetics

Kinetics

- You are well aware that not all chemical changes occur at the same rate.
- Kinetics is an experimental area. Little if any information about the kinetics of a reaction can be gleaned from the balanced equation.
- Some parameters
- Recall that many reactions can occur in either direction. In kinetics, reactant and products are strictly defined: the reaction is always written in the direction in which it is occurring.
- Reaction rates are defined as $\Delta[\]/\Delta t$ (should actually be a derivative) with dimensions Msec^{-1} . However, the time dimension varies a little (hours, years) and in gas systems, as usual, pressures are sometimes used
- Reaction rates are always positive by convention. However, the rate of change for a given compound can be positive or negative.
- For the reaction $2\text{A} + \text{B} \Rightarrow 3\text{C}$
 - if we define the rate as: $\text{rate} = \Delta[\text{C}]/\Delta t$
 - then $\text{rate} = -3 \cdot \Delta[\text{B}]/\Delta t$ or
 - $\text{rate} = -3/2 \cdot \Delta[\text{A}]/\Delta t$
- the – sign is needed to produce a positive number since the concentrations of A and B will be decreasing with time, the coefficient is required due to the stoichiometry. Everytime a B reacts, 3 Cs are produced, thus the rate for C is 3x that of B.

Following a reaction



The key to everything-the rate law

- The defining kinetic property of a chemical reaction is the rate law: a statement of what chemical species affect the reaction rate and how fast the reaction is.
- For reasons that will be presented later, not all reactants necessarily affect the rate of a reaction. This is a major reason why experiments are critical in kinetics.
- For a reaction $2A + B \Rightarrow 3C$, one begins by writing the “general rate law” $\text{rate} = k[A]^a[B]^b$ where k is the rate constant (more on that later) and a, b are the reaction orders which show how the rate is affected by the chemical species. The most common values for orders are 0 and 1 with 2 occasionally appearing. Other values, including fractions and negatives are known.
- The process of determining whether a reactant affects the rate is very straightforward. If the concentration of the species is changed, does the rate change?

Experimental Design-initial rates and integral changes

- It seems logical (with one very rare exception) that a reaction will slow down as the reagents are consumed and that the rate is certainly not likely to be linear.
- Given the above, how is a rate actually measured?
 - The tangent to the line of $[]$ vs t will give $d[]/dt$
 - If the reaction is studied at the start and over a period of time when $[]$ vs t is relatively linear, the rate can be approximated with fairly good precision as $([]_o - []_t)/t$. This is called an initial rate study and is a common approach.
 - Regardless of the method chosen, measuring rates is relatively simple in principle, collect $[]$ vs t data.
- To determine a reaction order, one does two rate measurements where the reaction systems vary due to a change in a single concentration. Thus, any rate change can be ascribed to the species whose concentration was changed. If the experiment is designed for easy interpretation, then the data analysis requires little math, most of it mental.
- Assume you wanted the order in A, You do a first rate measurement. Then you double the concentration of A while leaving everything else the same.
 - $\text{Rate}_2/\text{Rate}_1 = ([A]_2/[A]_1)^a$
 - no change in the rate (Run 1 vs Run 2)-rate doesn't depend on A \Rightarrow zero order
 $\text{Rate}_2/\text{Rate}_1 = 1 = (2)^0$
 - rate doubles-first order $\text{Rate}_2/\text{Rate}_1 = 2 = (2)^1$
 - rate quadruples-second order $\text{Rate}_2/\text{Rate}_1 = 4 = (2)^2$

- This operation is repeated until orders for all of the reactants have been obtained.
- Assume the study yielded the rate law: $\text{rate} = k[A][B]^2$
- the rate constant can now be determined by taking any one of the runs $\Rightarrow k = \text{rate}/([A][B]^2)$
- k
 - the value of k gives you the actual reaction rate.
 - k has variable dimensions-remember that the rate is always Msec^{-1} , but the concentration terms will vary with the reaction system. The dimensions of k are set by the overall reaction order or the sum of the individual orders. For the example above, that's 3.
 - What would the dimensions of k be in that case?
- dimension of k and overall order-if the overall order is n then the dimensions of k are $\text{M}^{-(n-1)}\text{sec}^{-1}$ or $\text{M}^{-(n-1)}\text{sec}^{-1}$

Using the Rate Law

- Assuming that the rate law and constant have been determined (or provided), what can be done with that information?
- Relative rates
- Determination of rates for different reaction mixtures

Integrated Rate Laws

- The rate should actually be $d[A]/dt$
- For a 1st order reaction $-d[A]/dt=k[A]$
- If this equation is rearranged to the form
 - 1) $d[A]/[A]=-kdt$
 - and then integrated, you get
 - 2) $\ln([A]_t/[A]_0)=-kt$
 - 3) $\ln[A]_t=-kt+\ln[A]_0$
- The key meaning of this is that a plot of $\ln[A]$ vs t will give a straightline whose slope $=-k$ (p.483)
- Integrated rate laws are known for all the possible reaction orders, but first order reactions are of particular interest.
- If you examine equation 2) above, you should see that first order processes lend themselves to considerable analysis if only two things are known: the rate constant and the concentration at any time.

Half-lives of 1st order reactions

- $\ln([A]_t/[A]_0) = -kt$
- If $\frac{1}{2}$ of the reactant has been consumed $t = t_{1/2}$ and $\ln([A]_t/[A]_0) = \ln(1/2) = -.693$.
- Thus $t_{1/2} = 0.693/k$ (does the structure of this seem reasonable? What does it say about the relationship between k and $t_{1/2}$?)
- For first order reactions, the half-life is constant, depending only on k . For all other reaction orders, the half life varies with time, as it is concentration dependent. Why is that such a big deal?

Strategies for dealing with ln

- A first order reaction has $k=0.034\text{sec}^{-1}$. In what directions can you go from this point?
- What is $t_{1/2}$?
- General reaction progress analysis
- How long will it take until.....
- After 18secs, how.....
- With the exception of calculating $t_{1/2}$, all such problems require pressing that “ln” key on your calculator that you may be wondering about. The key issue is to use the ln and e key properly and at the correct stage in the problem.