CHEM 102 - Recitation Week 5 - Answer Key

- Ch. 14, 48. Indicate the order of reaction consistent with each observation. Explain your answers.
 - a) The half-life of the reaction gets shorter as the initial concentration of reactant increases,
 - b) A plot of the natural log of the concentration of the reactant versus time yields a straight line.
 - c) The half-life of the reaction gets longer as the initial concentration of reactant increases.

Concepts needed (see also Ch. 14, 41 solved in recitation last week):

- rate of reaction;
- rate law = experimentally determined equations that show the

"reactant concentration-reaction rate" dependence;

- reaction order with respect to one reactant (partial order) vs. overall reaction order;
- rate law equations based on reaction orders;
- half-life = = the time required for the reactant concentration to reduce to half of its initial value;
- integrated rate law equations = equations deduced mathematically, by integration of the experimentally determined rate law equations;
- Note: Rate law equations show the dependence of rate vs. concentration. Their graphical representation can be linear or not! Integrated rate law equations show the dependence of concentration vs. time as the reaction progresses. Their graphical representation is always linear!

Answer:

Notes:

See table 14.2/p. 605 in your textbook for a summary of rate laws and half-life expressions for zero, first, and second order reactions, respectively. Based on the table, statement a) indicates a second order reaction, statement b) indicates a first order reaction, and statement c) indicates a zero order reaction.

1) Since half-life is the time required for the reactant concentration to reduce to half of its initial value, use the integrated rate law equations to deduce the relationship between half life and the change in reactant concentration as the reaction progresses. An example of such calculations is shown below:

Integrated rate law for zero order reactions:

 $[A] = -kt + [A]_0$

If $t = t_{1/2}$ (half-life), then at that moment, $[A] = [A]_0/2$. So, we can re-write the equation as:

 $[A]_0/2 = -kt_{1/2} + [A_0]$

and then solve for $t_{1/2}$:

 $[A]_0/2 - [A_0] = -kt_{1/2}$ $- [A]_0/2 = -kt_{1/2}$ $- [A]_0/2k$

This expression shows that, when the numerator increases, so does t_{1/2}. Moreover, this is specific to zero order reactions, since similar calculations for the first- and second-order reactions yield different results. Try it see what you get for first- and second-order reactions!

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