Pre-Health Post-Baccalaureate Program Study Guide and Practice Problems

Course: CHM2046

Textbook Chapter: 16 (Silberberg 6e)

Topics Covered: CHM2045 Review:

Reaction Rates
Rate Laws
Chemical Kinetics
Catalysts
Reaction Mechanisms

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1) Reaction Rates (16.1-16.2)

In chemical reactions, recall that we see reactants changing into products during chemical reactions.

A reaction rate, simply put, allows to think about how the concentration of reactant or product is changing as time moves forward.

A higher reaction rate means that the reaction is happening quickly, or that [reactants] is decreasing quickly and that [products] is increasing quickly as time passes.

Likewise, a lower reaction rate means that the reaction is happening slowly, or that [reactants] is decreasing slowly and the [products] is increasing slowly as time passes.

What affects the reaction rate?

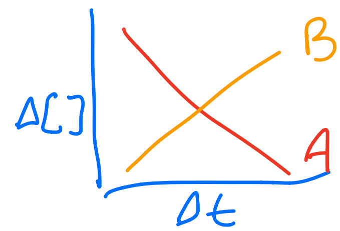
a. Concentration of reactants: Recall that molecules must collide with each other for the reaction to happen at all. If the concentrations of reactants are higher, the likelihood of collision increases, thus increasing the rate.
b. The temperature of the system: When the environment is warmer, molecules are energized and have higher frequencies, meaning that they collide more often.
c. Physical state of reactants: Molecules mix more easily when all reactants are liquids or aqueous.

Large solids do not mix into liquids or aqueous solutions well, because surface area is minimized. To maximize surface area of solids, it is best to first grind them into a powder.

d. Presence of a catalyst

What does this look like mathematically? Let’s use the example reaction:

$$A \longrightarrow B$$



The reaction rate is, of course, a rate. We want to express the “speed” of the reaction by showing changes in concentrations as the reaction proceeds. Thus, we can model this as:

$$\text{rate} = \frac{\Delta[B]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$$

Notice that there is a negative sign in front of the [A] term. This is because, according to our reaction, [A] decreases as [B] increases.

Now, let’s look at a reaction involving two reactants and two products:

$$aA + bB \rightarrow cC + dD$$

The general formula for the rate of this reaction is as follows:

$$rate = -\frac{\Delta[A]}{a\Delta t} = -\frac{\Delta[B]}{b\Delta t} = \frac{\Delta[C]}{c\Delta t} = \frac{\Delta[D]}{d\Delta t}$$

2. Rate Law (16.3)

Let's take a look at the rate law, which uses a constant *k* to describe rate in terms of concentration and temperature. Each reaction has its own rate constant.

For the reaction:

$$aA + bB \rightarrow cC + dD$$

The rate law is as follows (overall order = m + n):

$$rate = k[A]^m[B]^n$$

Reactions can have several different "orders."

Zero order: Rate does not change when [A] changes, that is, rate and [A] are independent.

$$rate = k[A]^0 = k(1) = k$$

First order: Rate and [A] change by the same factor. For example, for a first order reaction, doubling [A] would lead to the rate doubling as well.

$$rate = k[A]^1 = k[A]$$

Second order: Rate changes by a factor of [A]^2. For example, for a second order reaction, doubling [A] would lead to the rate quadrupling.

$$rate = K[A]^2$$

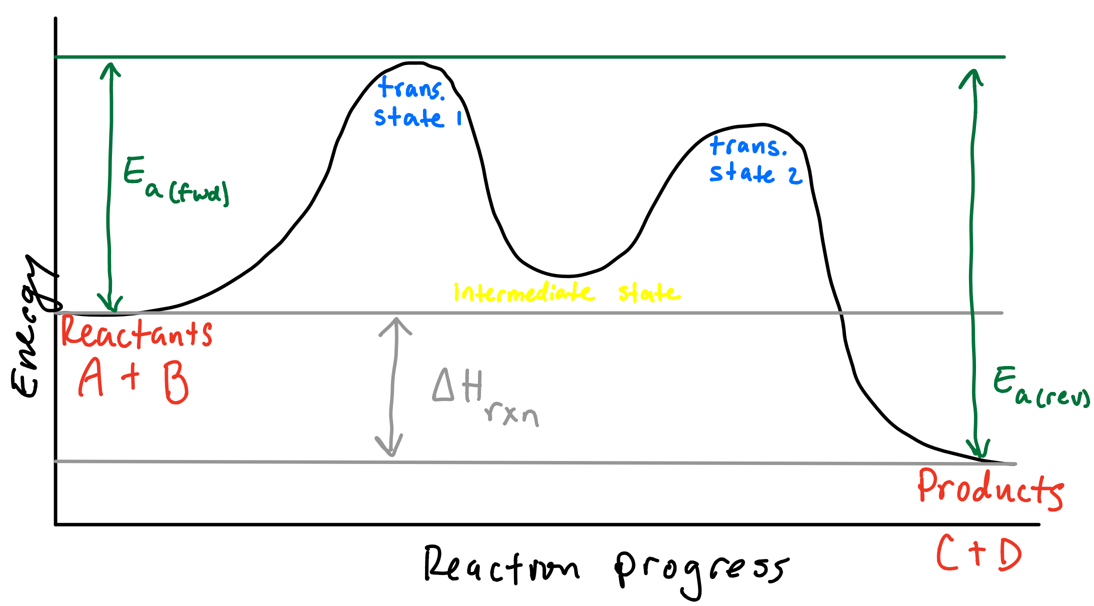
3. Chemical Kinetics (16.5)

According to the Arrhenius equation, as temperature increases, *k* increases, and the overall rate increases.

This is especially important for getting over the activation energy hump, which is the minimum energy that the reaction must have in order to proceed forward fully.

By increasing temperature, and therefore increasing the rate of reaction, we have enough energy to reach the “activated state” and get over the activation energy hump.

Let’s get a visual through a reaction energy diagram:



4. Catalysts (16.7)

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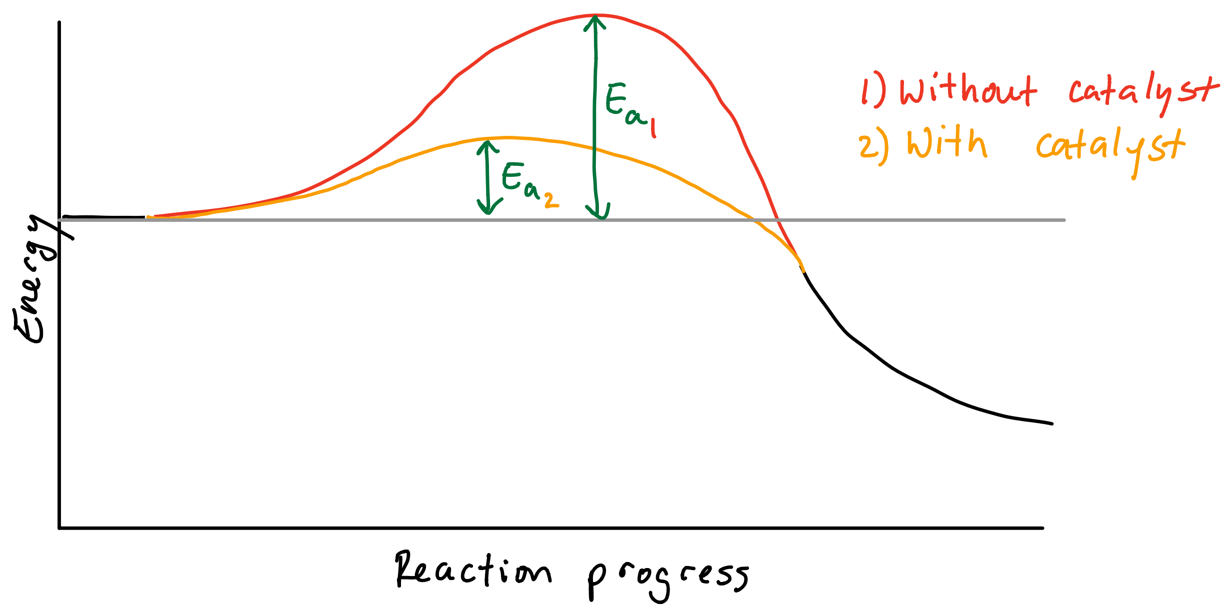
Another way of getting past the activation energy hump is to use a catalyst. A catalyst doesn't introduce more energy to the system, but instead lowers the activation energy.



By lowering the activation energy, we increase *k*, and increase the rate. This makes sense, because rate is all about how fast reactants are turning into products. By lowering the barrier to this change, we make product more quickly.

<u>5. Reaction Mechanisms (16.6)</u>

A mechanism is a proposed hypothesis of how a reaction likely occurs, and shows each step of the reaction.

If we know the individual steps, we can also work backwards by crossing out species that exist on both sides of the reaction arrow, and determine the chemical equation.

Let's look at the example from the textbook. If we are given the following steps, we can find the overall equation:

$$1)\quad A + B \rightarrow C$$

$$2)\quad C + A \rightarrow D$$

$$3)\quad D \rightarrow E + F$$

$$A + B + \cancel{C} + A + \cancel{D} \longrightarrow \cancel{C} + \cancel{D} + E + F$$

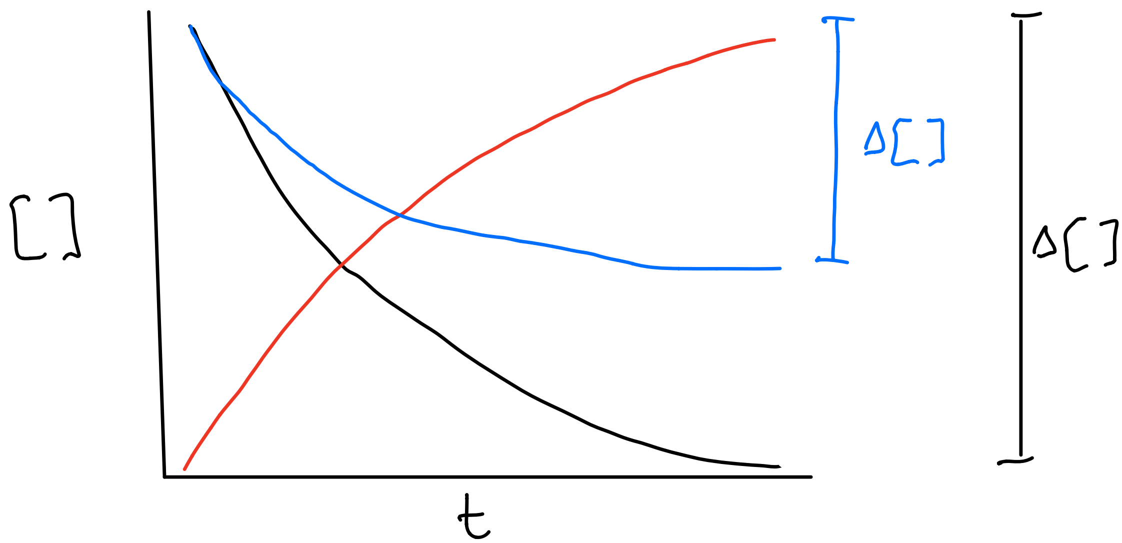
$$2A + B \longrightarrow E + F$$

Each step has its own rate, and the step with the slowest rate is called the "rate limiting step." A reaction overall, therefore, can only be as fast as the rate limiting step allows

Problems:

① For the below reaction, which curve represents hydrogen?

$$O_{2(g)} + 2H_{2(g)} \rightarrow 2H_2O_{(g)}$$



a) Red

b) Black

c) Blue

d) Either black or blue

e) Any of these could be hydrogen

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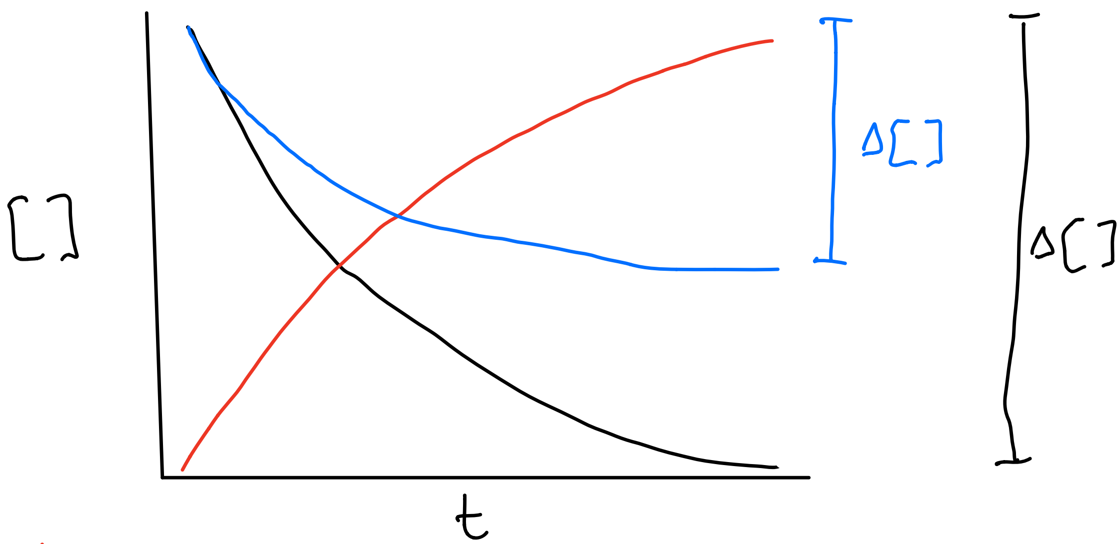

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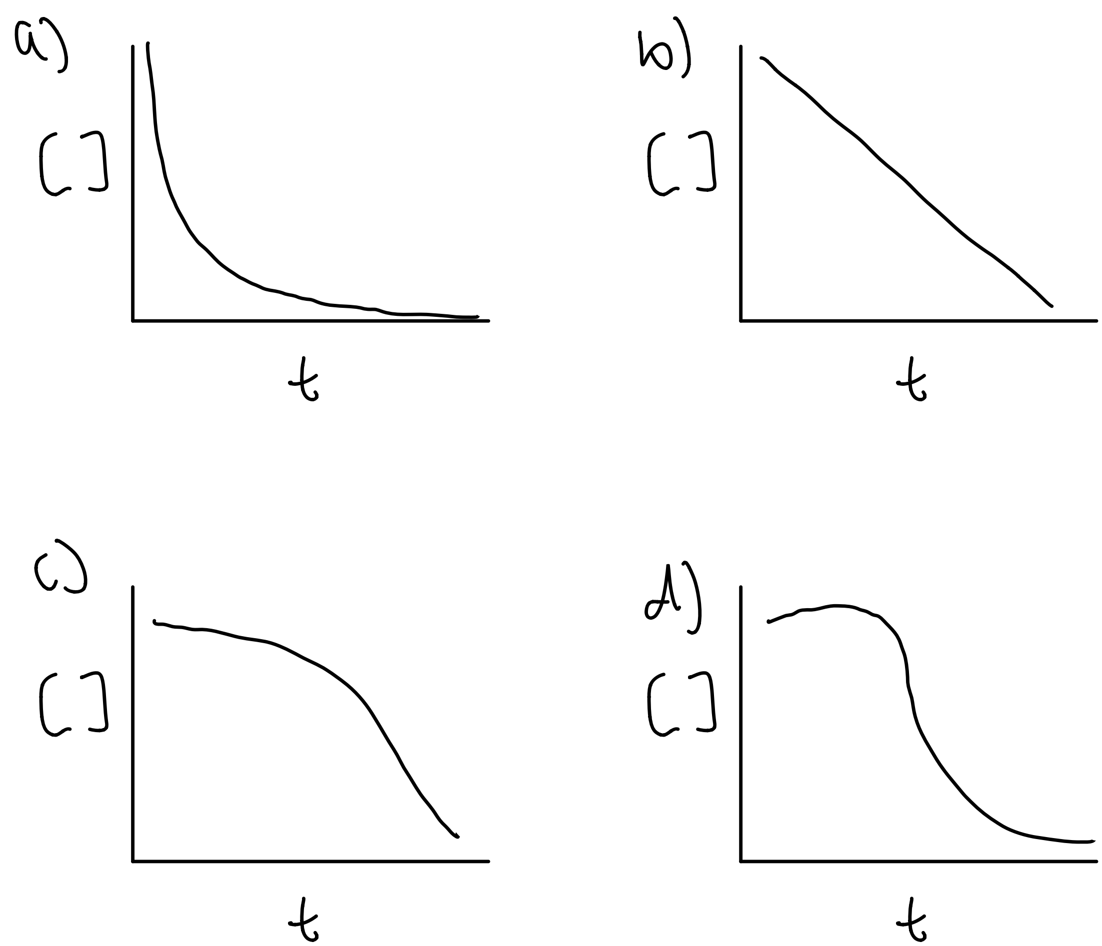
(2) Assuming that each graph has the same concentration and time axes, which graph has the greatest initial rate of disappearance of reactant?



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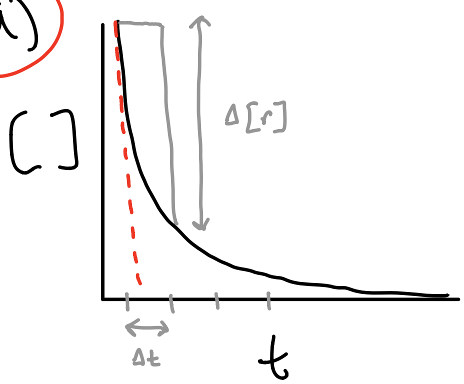
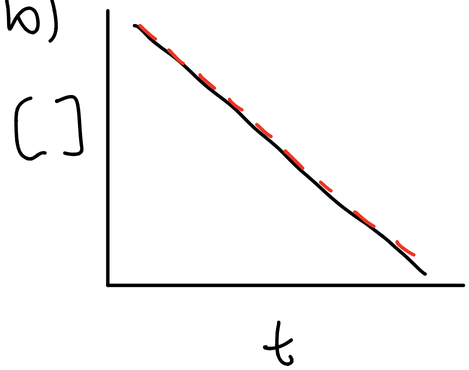
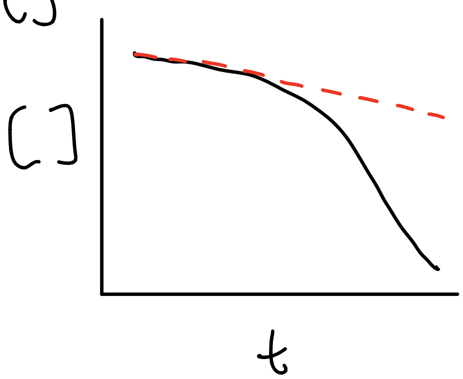
a)



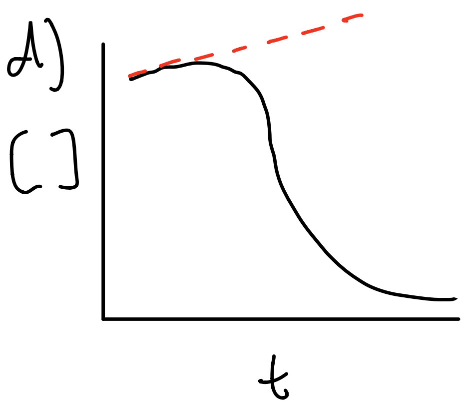
b)



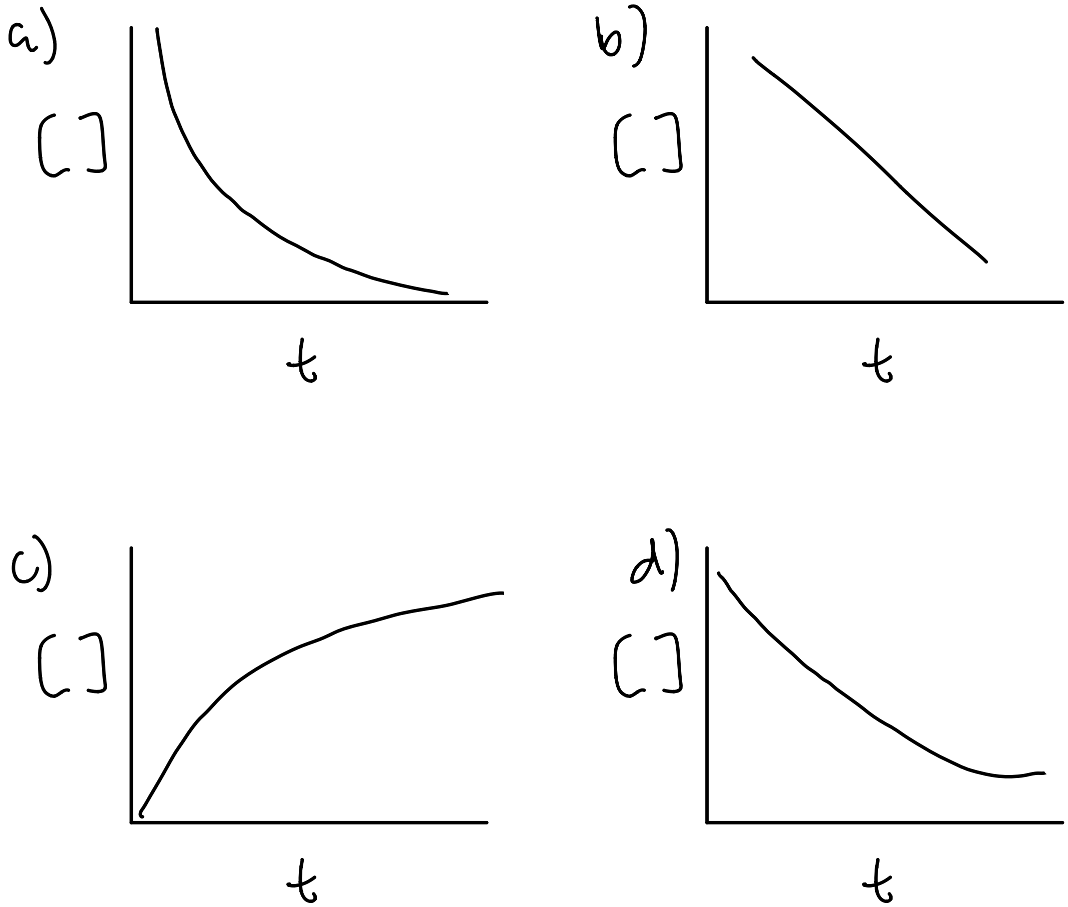
c)



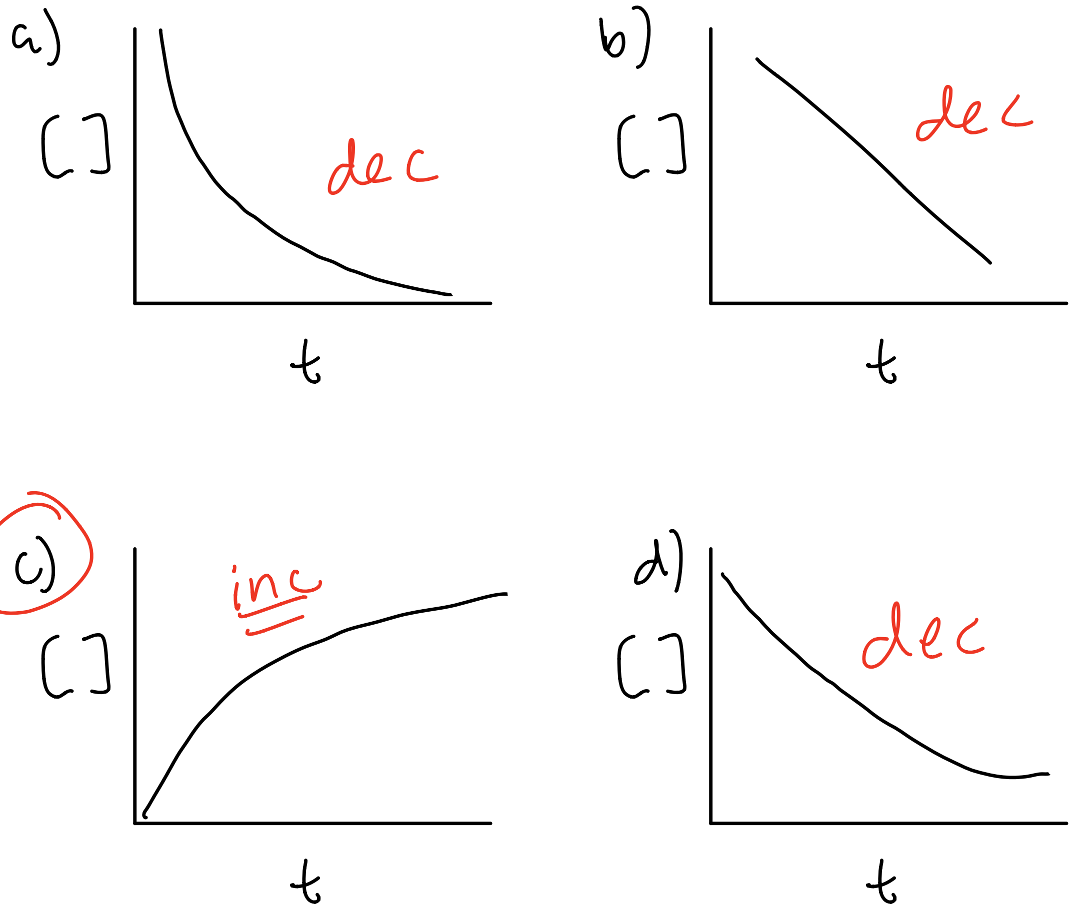
d)



③ Assuming the reaction proceeds forward, which of the following graphs is not a possible graph of concentration vs. time for a reactant?



(3) Assuming the reaction proceeds forward, which of the following graphs is not a possible graph of concentration vs. time for a reactant?



$$aA + bB \longrightarrow cC + dD$$

4 For the following reaction,

(a) express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with respect to time, and

(b) find the rate at which $[H_2O]$ is increasing when $[O_2]$ is decreasing at 0.23 mol/L·s.

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$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$$

(a) $$\text{Rate} = -\frac{\Delta[H_2]}{2\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = +\frac{\Delta[H_2O]}{2\Delta t}$$

(b) $$\frac{+\Delta[H_2O]}{2\Delta t} = -\frac{\Delta[O_2]}{\Delta t} = -\left(-0.23\ \frac{mol}{L\cdot s}\right)$$

$$\frac{\Delta[H_2O]}{\Delta t} = 2\left(0.23\ \frac{mol}{L\cdot s}\right) = 0.46\ \frac{mol}{L\cdot s}$$

⑤ Use the following reaction and data to determine the individual and overall reaction orders

$$NO_2 + CO \longrightarrow NO + CO_2$$

$$rate = k[NO_2]^m[CO]^n$$

Experiment	Initial rate (mol/L·s)	Initial $[NO_2]$ (mol/L)	Initial [CO] (mol/L)
1	0.0050	0.10	0.10
2	0.080	0.40	0.10
3	0.0050	0.10	0.20

$$\frac{\text{Rate } 2}{\text{Rate } 1} = \frac{\cancel{k}[NO_2]_2^m \cancel{[CO]_2^n}}{\cancel{k}[NO_2]_1^m \cancel{[CO]_1^n}}$$

$$\frac{\text{Rate } 2}{\text{Rate } 1} = \frac{[NO_2]_2^m}{[NO_2]_1^m}$$

$$\frac{0.08}{0.005} = \left(\frac{0.4}{0.1}\right)^m$$

$$16 = (4)^m \quad \therefore \quad m = 2$$

$$\frac{\text{Rate } 3}{\text{Rate } 1} = \frac{[CO]_3^n}{[CO]_1^n}$$

$$\frac{.0050}{.0050} = \left(\frac{.2}{.1}\right)^n$$

$$1 = (2)^n \quad \therefore \quad n = 0$$

order = 2