

## Spring 2009 CH302: Kinetics Worksheet Answer Key

1. What factors determine the rate of a reaction? How does each of them affect the rate?

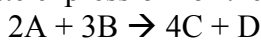
Answer:  $\text{Rate} = [ ]^x A e^{-E_a/RT}$ . Shown in this equation, the factors affecting rate of reaction are: concentration and order of reactants and products ( $[ ]^x$ , which increases as rate increases), the activation energy ( $E_a$ , which decreases as rate increases), the temperature ( $T$ , which increases as rate increases), and pre-exponential factor ( $A$ , which increases as rate increases).

2. To minimize the rate of a reaction, would you minimize or maximize each of the above terms you listed in (1)? Can you think of a spontaneous reaction that has a slow rate?

Answer:  $[ ]^x$ , minimize  
 $E_a$ , maximize  
 $T$ : minimize  
 $A$ : minimize

The process of diamond turning into graphite is slow, but spontaneous. The half-life of the process is about 5700 years.

3. Write the rate expression for the following reaction:



Answer:  $\text{Rate} = -\Delta [A]/(2\Delta t) = -\Delta [B]/(3\Delta t) = \Delta [C]/(4\Delta t) = \Delta [D]/\Delta t$

4. Define activation energy. How does a catalyst change the activation energy? What is its effect on the equilibrium?

Answer: Activation energy is the energy barrier to get to the transition state. A catalyst lowers this barrier (thereby increases reaction rate) but has absolutely no effect on the state of equilibrium.

5. What is the rate constant  $k$ , and what is the order of reaction if  $k = 4 \text{ M}^{-1}\text{sec}^{-1}$

Answer:  $k$  is the  $A e^{-E_a/RT}$  part of the rate law. The reaction has to be second order, since  $\text{rate (M/sec)} = k (\text{M}^{-1}\text{sec}^{-1}) [ ]^2 (\text{M}^2)$ .

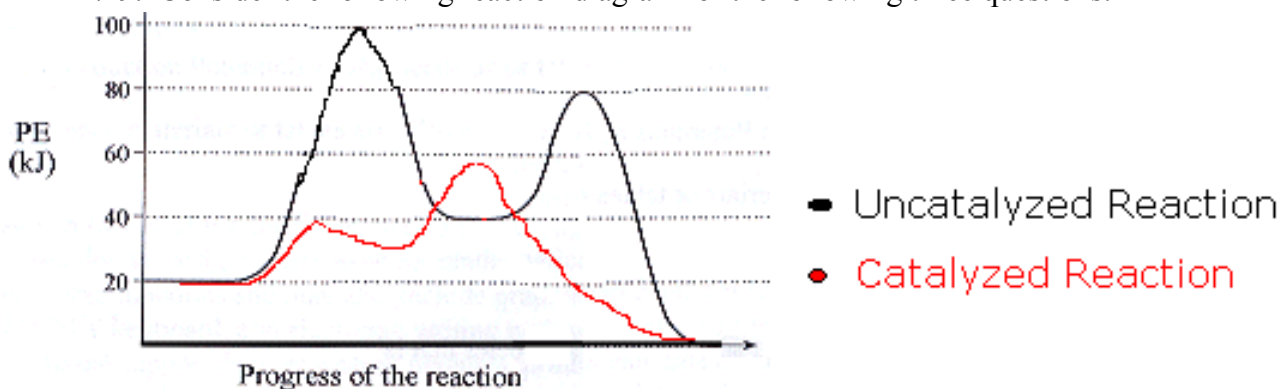
6. Consider the reaction  $A \rightarrow B$ , what is the order of the reaction and what is the rate expression?

	[A]	[B]	Rate
Experiment 1	1 M	1M	0.1
Experiment 2	1M	3M	0.1
Experiment 3	2M	1M	0.2

Answer:  $\text{Rate} = 0.1 \text{ sec}^{-1} [A]$ . First-order.

Using Experiments 1 and 2, you should be able to figure out that the rate is independent of  $[B]$  ( $B$  tripled, rate did not change). Using Experiments 1 and 5, you should see that the rate doubled when  $[A]$  doubled. Thus the rate expression is  $\text{Rate} = k [A]^1 [B]^0$ . To figure out  $k$ , plug this into experiment 1 to obtain:  $0.1 = k (1M)$ , thus  $k = 0.1 \text{ sec}^{-1}$ .

7-9. Consider the following reaction diagram for the following three questions:



7. What is the overall  $\Delta H$  for the reaction?  $\Delta H = -20 \text{ kJ}$

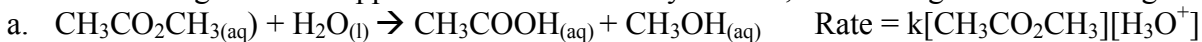
8. What is the  $E_a$  for each step in the uncatalyzed reaction? In the catalyzed reaction? Which step is the rate-determining step?  $E_{a1\text{uncat.}} = 80 \text{ kJ}$ ,  $E_{a2\text{uncat.}} = 40 \text{ kJ}$ ,  $E_{a1\text{cat.}} = 20 \text{ kJ}$ ,  $E_{a2\text{cat.}} = 30 \text{ kJ}$ . In the uncatalyzed reaction, the first step is rate-determining because it has the highest activation barrier. The second step in the catalyzed reaction is rate-determining.

9. Is this reaction endo or exothermic? exothermic

10. Which of the following statements is true? If any are false, correct them to make them true.

- A catalyst is always consumed in the overall reaction. False. The catalyst is never consumed in the reaction. It reacts over and over with the substrates to produce products. Only a small amount of catalyst is needed since it is frequently turned over in the reaction.
- A catalyst must always be in the same phase as the reactants. False. Heterogenous (different phase) and Homogenous (same phase) catalysts are known and used industrially.
- A catalyst can change the course of a reaction and allow different products to be produced. True. A catalyst lowers the activation barrier of a reaction by changing the reaction course (aka different mechanism). This also allows that different reaction products (or byproducts) may be produced.

11. Which of the following reactions appears to involve a catalyst? If so, is it homogenous or heterogenous?



Yes, homogenous ( $\text{H}_3\text{O}^+$ )



No



Yes, heterogenous (Pt metal)

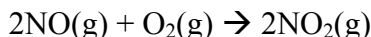


No

12. Which of the following regarding catalysts is false?

- The concentration of a catalyst can appear in the rate law. true
- A catalyst increases reaction rate by lowering  $\Delta H_{\text{rxn}}$ . false
- A catalyst promotes a reaction by orienting the reacting partners in favorable positions. true
- The  $E_a$  for a reaction never changes. false
- Catalysts are usually very specific in the substrates they work with and the reactions they promote. true
- Enzymes, radicals (photons), acids, bases and metals are all famous catalysts. true

13. For the reaction of NO and  $\text{O}_2$  at 660K,

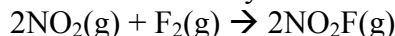


[NO] mol/L	[O <sub>2</sub> ] mol/L	Rate disappearance of NO (mol/L*s)
0.010	0.010	$2.5 \times 10^{-5}$
0.020	0.010	$1.0 \times 10^{-4}$
0.010	0.020	$5.0 \times 10^{-5}$

- Determine the order of reaction for each reactant. NO = second order,  $\text{O}_2$  = first order

- b. Write the rate equation for the reaction. Rate =  $k[\text{NO}]^2[\text{O}_2]$   
 c. What is the rate constant?  $k = 25 \text{ L}^2/\text{mol}^2\cdot\text{s}$   
 d. What is the rate when  $[\text{NO}] = 0.025 \text{ M}$  and  $[\text{O}_2] = 0.05 \text{ M}$ ? rate =  $7.8 \times 10^{-4} \text{ mol/L}\cdot\text{s}$

14. Nitryl fluoride is an explosive compound that is made by the oxidation of nitrogen dioxide with fluorine.



$[\text{NO}_2]$ mol/L	$[\text{F}_2]$ mol/L	$[\text{NO}_2\text{F}]$ mol/L	Rate disappearance of NO (mol/L*s)
0.0010	0.0050	0.0020	$2.0 \times 10^{-4}$
0.0020	0.0050	0.0020	$4.0 \times 10^{-4}$
0.0020	0.0020	0.0020	$1.6 \times 10^{-4}$
0.0020	0.0020	0.0010	$1.6 \times 10^{-4}$

- a. What is the rate law for the reaction? Rate =  $k[\text{NO}_2] [\text{F}_2]$   
 b. What is the order of the reaction with respect to each reactant and product?  $\text{NO}_2 = 1, \text{F}_2 = 1, \text{NO}_2\text{F} = 0$ .  
 c. Calculate the rate constant k.  $k = 40 \text{ L}^2/\text{mol}^2\cdot\text{s}$

15. Which of the following factors will affect the rate of a reaction?

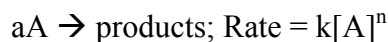
2. Concentration of reactants
3. temperature
4. catalyst
5. physical phase
  - i. I, II, III, IV
  - ii. I, II only
  - iii. I, II, II only
  - iv. None of above

Answer/Explanation: All of the following will affect reaction rate:

$k = A \exp[-E_a/RT]$ ; temperature dependence is obvious, and catalysts will lower activation energy, which will increase the rate of reaction. The Arrhenius prefactor is affected by the physical state (S,L or G) of the reactants. The general rate equation shows the dependence on reactant concentration.

16. Which of the following statements regarding kinetics is true?

- I. Reaction orders must be integer values
- II. Zeroth order processes are dependent on reactant concentration
- III. The power n in the following rate expression has no direct relation to the coefficient in the balanced chemical equation:



- a. I only
- b. II and III
- c. III only
- d. None are true

Answer/Explanation: It is very important to remember that rates are experimentally determined, and reaction orders cannot be determined just using stoichiometric ratios. Reaction orders in some cases can be non-integer values, and zeroth order processes are independent of reactant concentration, since  $[\text{A}]^0 = 1$ .

17. Given the following reaction:

What is the rate constant  $k$  for the first order decomposition of  $\text{N}_2\text{O}_5$  (g) at room temperature if the half life at room temperature is  $4.03 \times 10^{-4}$  s?

Answer/Explanation: Since you were told the kinetics were first order, employ the following relation:

$$t_{1/2} = \ln 2/k = 4.03 \times 10^{-4} \text{ s}$$

Algebraically rearrange to find  $k = 1.72 \times 10^{-5}/\text{s}$

18. After one day, what percentage of  $\text{N}_2\text{O}_5$  (g) molecules will NOT have reacted?

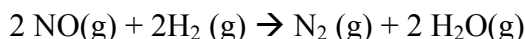
Answer/Explanation: Solve for time,  $t$ , in terms of seconds; 1 day =  $8.64 \times 10^4$  s.

First order:  $\ln([A]/[A_0]) = -kt$

Solve for  $[A]/[A_0] = \exp[-kt] = 0.226$ .

Thus, 22.6 % of molecules will remain unreacted after one day.

19. For the reaction



it is observed that when the concentration of hydrogen gas is cut in half, the rate of the reaction is also cut in half. When the concentration of NO is multiplied by 10, the rate of the reaction increases by a factor of 100.

Write the rate expression for this reaction.

a) Rate =  $k[\text{NO}]^2[\text{H}_2]^2$

b) Rate =  $k[\text{NO}]^2[\text{H}_2]$

c) Rate =  $k[\text{NO}][\text{H}_2]$

Answer/explanation: You can use the initial rates method by employing arbitrary concentrations for the reactants, or you can recognize the linear dependence of the rate on hydrogen and the 'square' rate dependence on NO. Also, remember that reactants belong in the rate equation, not products. Rate =  $k[\text{NO}]^2[\text{H}_2]$

20. The reaction  $\text{FCIO}_2 \rightarrow \text{FCIO}(\text{g}) + \text{O}(\text{g})$  is first order with a rate constant of  $6.76 \times 10^{-4}/\text{s}$  at 322 C.

What is the half life of the reaction at 322 C?

a)  $3.03 \times 10^3$  s.

b)  $1.03 \times 10^{-3}$  s.

c)  $1.03 \times 10^3$  s.

Answer/explanation:

Half life (first order) =  $\ln 2/k = 0.693/6.76 \times 10^{-4}/\text{s} = 1.03 \times 10^3$  s.

21. For the reaction in question 20: If the initial partial pressure of  $\text{FCIO}_2$  (g) in a container at 322 C is 0.040 atm, how long will it take to fall to 0.010 atm?

a)  $2.06 \times 10^3$  s

b)  $1.06 \times 10^6$  s

c)  $103 \times 10^3$  s

Answer/Explanation: By noting that the final pressure is one-fourth the initial pressure, the answer comes quickly. The pressure drops to half its original value in the first half life, and half of that in the second half life.

Thus, the answer is two half lives,  $2(t_{1/2}) = 2.06 \times 10^3$  s.