

# Chapter 14

## Chemical Kinetics

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### Chapter 14 suggested problems

10th Ed. - 14.x: 27, 29, 33, 35, 39, 45, 48, 49, 51, 53, 55, 57, 61, 65, 67, 69, 84, 94

11th Ed. - 14.x: 29, 31, 35, 37, 41, 47, 50, 51, 53, 55, 57, 59, 63, 67, 69, 71, 86, 99

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## Chapter Objectives

After completing this chapter, you should, *at a minimum*, be able to do the following. This information can be found in my lecture notes for this and other chapters and also in your text.

1. Correctly answer all of the questions suggested above and in the quiz for this chapter.
  2. Define basic terms such as thermodynamics, kinetics, reaction rate, rate law, initial rates method, reactant order, overall reaction order, integrated rate law, half-life, collision theory, activation energy, Arrhenius equation, activated complex, transition state, transition state theory, Boltzman's distribution, frequency factor, reaction mechanism, elementary step, reaction intermediate, molecularity, unimolecular, bimolecular, termolecular, catalyst, homogeneous catalyst, heterogeneous catalyst.
  3. Describe the basic factors that affect reaction rates.
  4. Be able to describe the relationship between a reaction's stoichiometry and its rate.
  5. Write the rate law for a reaction.
  6. Use the initial rates method to determine reactant orders and rate constants.
  7. Explain the relationship between the reactant order of a reactant and its effect on the reaction rate.
  8. Be able to use integrated rate laws to determine reactant concentrations as functions of time and reaction half-lives.
  9. Be able to use integrated rate laws graphically to determine reaction orders and rate constants from experimental data.
  10. Be able to articulate the basic concepts of collision theory.
  11. Describe basic transition state theory.
  12. Explain the role of activation energy in both exothermic and endothermic reactions.
  13. Be able to graphically determine activation energy and frequency factors from experimental data.
  14. Be able to use the Arrhenius equation to find such things as the activation energy of a reaction or the fraction of particles with sufficient energy to react.
  15. Be able to assess the plausibility of simple reaction mechanisms.
  16. Explain the fundamental concepts of catalysis.
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## Class Notes

### I. Factors that affect reaction rates

#### A. General

1. What is thermodynamics?
2. What is kinetics?
3. Examples of fast and slow reactions

#### B. Factors that affect reaction rates

1. Reactant concentration
2. Temperature
3. Surface area (esp. of solids)
4. Catalysts

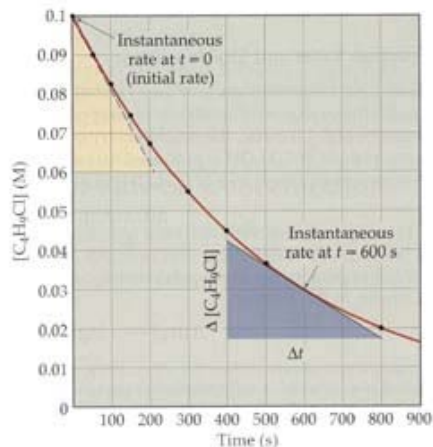
### II. Reaction rates

A. Reaction rates can be measured in terms of changes in concentration as a function of changes in time.

1.  $\text{C}_4\text{H}_9\text{Cl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_4\text{H}_9\text{OH}(\text{aq}) + \text{HCl}(\text{aq})$
2. (image source: BLB Table 14.1)

Time, $t$ (s)	$[\text{C}_4\text{H}_9\text{Cl}]$ (M)	Average Rate (M/s)
0.0	0.1000	$1.9 \times 10^{-4}$
50.0	0.0905	$1.7 \times 10^{-4}$
100.0	0.0820	$1.6 \times 10^{-4}$
150.0	0.0741	$1.4 \times 10^{-4}$
200.0	0.0671	$1.22 \times 10^{-4}$
300.0	0.0549	$1.01 \times 10^{-4}$
400.0	0.0448	$0.80 \times 10^{-4}$
500.0	0.0368	$0.560 \times 10^{-4}$
800.0	0.0200	
10,000	0	

3. (image source: BLB Figure 14.4)



Concentration of butyl chloride,  $\text{C}_4\text{H}_9\text{Cl}$ , as a function of time. The dots represent the experimental data from the first two columns of Table 14.2, and the red curve is drawn to smoothly connect the data points. Lines are drawn that are tangent to the curve at  $t = 0$  and  $t = 600$  s. The slope of each of these tangents is defined as the vertical change divided by the horizontal change, that is,  $\Delta[\text{C}_4\text{H}_9\text{Cl}]/\Delta t$ . The reaction rate at any time is related to the slope of the tangent to the curve at that time. Because  $\text{C}_4\text{H}_9\text{Cl}$  is disappearing, the rate is equal to the negative of the slope.

4. For any reaction at  $t = 0$ ,  $[\text{prod}] = 0$ ,  $[\text{rxt}] = x$
5. As the reaction proceeds,  $[\text{prod}]$  increases as  $[\text{rxt}]$  decreases
6. Reaction rate: the decrease in molar concentration of a reactant (or, the increase in molar concentration of a product) per unit time

- a. Rate =  $\Delta [\text{rxt}] / \Delta t$
- b. Units: mol/L·s or M/s
- c. Sign conventions: reactants: -; products: +

#### B. Instantaneous vs. average reaction rates

1. The distinction between average and instantaneous rates
  - a. Instantaneous rate =  $\Delta[\text{rxt}]/\Delta t$  averaged over a very small interval
  - b. Average rate =  $\Delta [\text{rxt}] / \Delta t$  averaged over a larger interval
2. Usually in kinetics the instantaneous rate is being discussed

#### C. Rates and stoichiometry

1. Because of the relationship between the stoichiometry of a reaction and the rate of reaction, the rate of a reaction can be correctly expressed as a function of the changing concentration of any reactant or product
2. Given the reaction  $aA + bB \rightarrow cC + dD$
3. Rate =  $-1/a \Delta[A]/\Delta t = -1/b \Delta[B]/\Delta t = +1/c \Delta[C]/\Delta t = +1/d \Delta[D]/\Delta t$

#### D. Reaction rates must be determined experimentally by measuring [rxt] and [prod] at various times during the reaction, which may be done using the following techniques

1. Real time: in situ analysis using MS or spectroscopy or by withdrawing small samples for analysis (laser techniques capable of ps observations)
2. Reaction quenching
3. Flow techniques

### III. Concentration and rate

#### A. A rate law is an equation based on observation of experimental results that relates reaction rate to the concentration of reactants and catalysts

1. Given:  $wA + xB \rightarrow yC + zD$
2. rate =  $k [A]^m [B]^n$
3.  $k$  = rate constant, depends on particular reaction and temperature
4.  $m, n$  are the reaction order w.r.t. to particular reactants
  - a. These are not tied to the stoichiometric coefficients
  - b. Usually but not always integers
  - c. Usually but not always positive
  - d. 0th order ( $m=0$ ): reactant must be present but no relationship between reactant concentration and reaction rate
  - e. 1st order ( $m=1$ ): linear relationship between reactant concentration and reactant rate

f. 2nd order (m=2): exponential relationship between reactant concentration and reactant rate

g. Overall order of the reaction is equal to the sum of the orders of the reactants

#### B. Most common method of data treatment: initial rate method

1. rate 1 =  $k[\text{rxt}]_1^m$  and rate 2 =  $k[\text{rxt}]_2^m$
2.  $\ln \text{rate 1} = \ln k + m \ln [\text{rxt}]_1$  and  $\ln \text{rate 2} = \ln k + m \ln [\text{rxt}]_2$
3.  $\ln \text{rate 1} - \ln k + m \ln [\text{rxt}]_1 = \ln \text{rate 2} - \ln k + m \ln [\text{rxt}]_2$
4.  $\ln \text{rate 1} - \ln \text{rate 2} = m \ln [\text{rxt}]_1 - m \ln [\text{rxt}]_2 = m (\ln [\text{rxt}]_1 - \ln [\text{rxt}]_2)$
5.  $m = (\ln \text{rate 1} - \ln \text{rate 2}) / (\ln [\text{rxt}]_1 - \ln [\text{rxt}]_2)$
6. Alternatively you can often evaluate m by inspection

#### C. Examples

1. The following data were measured for the reaction of nitric oxide and oxygen. Determine the rate law, the orders of the reactants, the overall order of the reaction, and the rate constant (rate =  $k[\text{NO}]^2[\text{O}_2]$ ;  $k_{\text{avg}} = 7.11 \times 10^3 \text{ M}^{-2}\text{s}^{-1}$ )

2 NO(g) + O <sub>2</sub> (g) → 2 NO <sub>2</sub> (g)			
experiment	[NO] (M)	[O <sub>2</sub> ] (M)	initial rate (M/s)
1	0.0126	0.0125	1.41 × 10 <sup>-2</sup>
2	0.0252	0.0250	1.13 × 10 <sup>-1</sup>
3	0.0252	0.0125	5.64 × 10 <sup>-2</sup>

2. The following data were measured for the reaction of nitric oxide and bromine. Determine the rate law, the orders of the reactants, the overall order of the reaction, and the rate constant. How are the rates of appearance of NOBr and disappearance of bromine related? (rate =  $k[\text{NO}]^2[\text{O}_2]$ ;  $k_{\text{avg}} = 1.2 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$ ; -1/2)

2 NO(g) + Br <sub>2</sub> (g) → 2 NOBr(g)			
experiment	[NO] (M)	[Br <sub>2</sub> ] (M)	initial rate (M/s)
1	0.10	0.20	24
2	0.25	0.20	150
3	0.10	0.50	60
4	0.35	0.50	735

D. Once a rate law is known, it can be used to predict reaction rates as a function of reactant concentration

1. Carbon monoxide and nitrogen dioxide react to form carbon dioxide and nitric oxide  
 $\text{CO(g)} + \text{NO}_2(\text{g}) \Rightarrow \text{CO}_2(\text{g}) + \text{NO(g)}$   
 The reaction was studied at 540 K. The reaction is first order in each of the reactants, and the rate constant was determined to be 1.9 L/mol·hr. Determine the initial rate of the reaction if the starting concentrations of carbon monoxide and nitrogen dioxide are  $3.8 \times 10^{-4} \text{ M}$  and  $0.600 \times 10^{-4} \text{ M}$  respectively. ( $4.7 \times 10^{-8} \text{ mol/L}\cdot\text{hr}$ )

#### IV. Changes of concentration with time: integrated rate laws

## A. General

1. Rate laws permit us to predict the rate of reaction at any time based on  $[rxt]$
2. Alternatively, if the rate law is known can also predict  $[rxt]$  at any time (i.e.,  $[rxt]$  as a function of time)

## B. Integrated rate laws: derived by integrating the rate laws of equations

## 1. 0th order

- a.  $-d[rxt]/dt = k[rxt]^0$

- b.  $[rxt]_t - [rxt]_0 = -kt$

## 2. 1st order

- a.  $-d[rxt]/dt = k[rxt]^1$

- b.  $-d[rxt]/[rxt] = kdt$

- c. integration from  $t=0$  to  $t=t$

- d.  $\ln\{[rxt]_t / [rxt]_0\} = -kt$

## 3. 2nd order

- a.  $-d[rxt]/dt = k[rxt]^2$

- b.  $-d[rxt]/[rxt]^2 = kdt$

- c. integration from  $t=0$  to  $t=t$

- d.  $1/[rxt]_t - 1/[rxt]_0 = +kt$

## C. Graphing and kinetics experiments

1. By plotting time and concentration information the rate constant and reaction order can be derived
2. 0th order:  $m = k$ ,  $b = [rxt]_0$
3. 1st order:  $m = k$ ,  $b = \ln [rxt]_0$
4. 2nd order:  $m = k$ ,  $b = 1/[rxt]_0$

## D. Half-life: the time required for a reactant concentration to decrease to one-half of its original value

1. Correlation between half-life and reaction rate: usually the longer the half-life the slower the reaction
2. Usually half-life is only discussed for 1st order processes
3.  $\ln\{[rxt]_t / [rxt]_0\} = \ln(0.50) = -kt$
4. By rearranging the equation and given that ( $\ln 2 = 0.693$ ),  $t_{1/2} = 0.693/k$
5. Note that  $t_{1/2}$  depends on  $k$  (and thus is temperature dependent) but that it is independent of reactant concentration

## 6. Examples

- a. The decomposition of hydrogen peroxide in dilute sodium hydroxide solution at 20°C follows first order kinetics and behaves thusly:  

$$2 \text{H}_2\text{O}_2 (\text{aq}) \Rightarrow 2 \text{H}_2\text{O} (\text{l}) + \text{O}_2 (\text{g}) \quad k = 1.06 \times 10^{-3} \text{ min}^{-1}$$
 If the initial  $[\text{H}_2\text{O}_2] = 0.020 \text{ M}$ , what is it at 100 minutes? ( $t_{1/2} = 653.4 \text{ min}$ ; at 100 min  $[\text{H}_2\text{O}_2] = 0.018 \text{ M}$ )
- b. The decomposition of gaseous nitrogen dioxide to nitric oxide gas and oxygen gas at 300°C is a first order reaction ( $k = 3.6 \times 10^{-3} \text{ sec}^{-1}$ ). If a sample of nitrogen dioxide is heated at this temperature for 150 seconds, how much of the initial sample will be left? (58.28%) How long must the sample be heated until 99% of the sample has decomposed? (1279 sec)
- c. The hydrolysis of sucrose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) to fructose and glucose in acidic solution follows the rate law {rate =  $k[\text{sucrose}]$ } where  $k = 0.208 \text{ hr}^{-1}$  at 25°C. What is the half-life of sucrose in acidic solution? (3.33 hr) How long will it take for 63% of the sucrose to hydrolyze? (4.78 hrs) How many half-lives does this correspond to? (1.435 half-lives)

## V. Chemical reactions at a molecular level

- A. Given the reaction  $\text{NO} (\text{g}) + \text{O}_3 (\text{g}) \rightarrow \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$  (rate law: rate =  $k[\text{NO}][\text{O}_3]$ ), what things must happen for a reaction to occur?
- B. Collision theory
  1. Reacting molecules must collide
  2. The collisions must possess sufficient energy to result in the breakage of chemical bonds
  3. Molecular orientation must be correct
- C. Molecules must collide for a reaction to occur
  1. As  $[\text{rxt}]$  increases the number of collisions increases
  2. As temperature increases, molecular velocity increases and the number of collisions increases
- D. Temperature effects on reaction rates
  1. At a given temperature molecules have a variety of energies described by Boltzmann's distribution
  2. As temperature increases, molecular velocity increases and the number of collisions increases
  3. The KE of the molecules increases with increasing T
  4. Energy of activation ( $E_a$ ) - an energy barrier to reactions
    - a. Chemical reactions involve the formation of a high energy reaction intermediate (activated complex) in the transition state between reactants and products
    - b. The higher the temperature the greater the fraction of molecules with sufficient energy to surmount the energy barrier when they collide

## E. Arrhenius equation

- The dependence of reaction rate on  $E_a$  is described by the Arrhenius equation
- $k = A \exp(-E_a/RT)$ 
  - A: frequency factor (with units of  $L/mol \cdot s$ ) is related to both the number of collisions and to the fraction with correct orientation at a reactant concentration of 1 M
  - The term  $\exp(-E_a/RT)$  is always less than 1 and describes the fraction of molecules possessing the necessary minimum energy at a given temperature
- By conducting experiments at various temperatures, determining  $k$  at those temperatures, and plotting  $(\ln k)$  vs  $1/T$   $E_a$  can be determined
  - $\ln k = \ln A - (E_a/RT)$
- Graphic determination
  - Given the reaction  $2 N_2O(g) \rightarrow 2 N_2(g) + O_2(g)$  and the following experimental data calculate the activation energy for the reaction

temp (K)	1/T (K <sup>-1</sup> )	k (L/mol·s)	ln k
1125	$8.889 \times 10^{-4}$	11.59	2.4501
1053	$9.497 \times 10^{-4}$	1.67	0.513
1001	$9.990 \times 10^{-4}$	0.380	-0.968
838	$11.9 \times 10^{-4}$	0.0011	-6.81
$E_a = 250 \text{ kJ/mol}$			

- Algebraic determination or two-step Arrhenius equation
  - At any two temperatures  $\ln k_1 = \ln A - (E_a/RT_1)$  and  $\ln k_2 = \ln A - (E_a/RT_2)$
  - $\ln(k_1/k_2) = +E_a/R [1/T_2 - 1/T_1]$
  - When heated to a high temperature, cyclobutane decomposes to form ethylene.  
 $C_4H_8 \Rightarrow 2 C_2H_4$   
 The activation energy for this reaction is 260. kJ/mol. At 800. K the rate constant is  $0.0315 \text{ s}^{-1}$ . Determine the rate constant at 850. K. ( $0.3 \text{ s}^{-1}$ ; source: Kotz/Treichel/Weaver, 6th Ed. p. 748, #43.)

## VI. Reaction mechanisms

- Many reactions occur in more than one step; the overall reaction is the sum of the individual steps
  - Simple (single step) reaction:  $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$
  - Two-step reaction:  $Br_2(g) + 2 NO(g) \rightarrow 2 BrNO(g)$ 
    - $Br_2(g) + NO(g) \rightarrow Br_2NO(g)$
    - $Br_2NO(g) + NO(g) \rightarrow 2 BrNO(g)$
  - NOBr: Nitrosyl Bromide;  $Br_2NO$ : ???

4. The sequence of bond-breaking and bond-making steps is called a reaction mechanism
  5. Each step in the sequence is called an elementary step (elementary reaction)
  6. Species that occur as products in one elementary step and that are completely consumed as reactants in another elementary step are called reaction intermediates
    - a. Reaction intermediates do not appear in the net (overall) equation
    - b. Reaction intermediates are not the same as activated complexes
  7. Each elementary step is a single event in a reaction, such as a decomposition, rearrangement, collision, etc.
  8. The overall reaction mechanism and the contributing elementary steps are based on the rate law, experimental evidence of transitory species that cannot be isolated, and intuition and common sense
- B. Molecularity: categorization of elementary steps by the number of participating reactant "particles" (i.e. atoms, molecules, ions or radicals)
1. While reaction orders can be non-integer and zero or negative, molecularities are always positive whole numbers
  2. Example reaction:  $2 \text{O}_3 (\text{g}) \rightarrow 3 \text{O}_2 (\text{g})$
  3. Unimolecular: one reactant particle, typically a rearrangement or decomposition
    - a.  $^* \text{O}_3 (\text{g}) \rightarrow \text{O}_2 (\text{g}) + \text{O}(\text{g})$
  4. Bimolecular: two reactant particles; very common; usually a collision step
    - a.  $\text{O}_3 (\text{g}) + \text{O}(\text{g}) \rightarrow 2 \text{O}_2 (\text{g})$
    - b. Net reaction:  $2 \text{O}_3 (\text{g}) \rightarrow 3 \text{O}_2 (\text{g})$
  5. Termolecular: three reactant molecules; occur but are not common since the simultaneous collision of three molecules with the correct orientation is required
  6. Greater than termolecular: rare
- C. Rate equations for elementary steps
1. The rate law for an overall (net) reaction must be determined experimentally
  2. The rate law for any elementary step is directly related to the stoichiometry of the elementary step
  3. The molecularity of an elementary step and its reaction order are the same

elementary step	rate law	molecularity	reaction order
$\text{A} \rightarrow \text{P}$	$\text{rate} = k[\text{A}]$	unimolecular	1st
$\text{A} + \text{A} \rightarrow \text{P}$	$\text{rate} = k[\text{A}]^2$	bimolecular	2nd
$\text{A} + \text{B} \rightarrow \text{P}$	$\text{rate} = k[\text{A}][\text{B}]$	bimolecular	2nd
$\text{A} + \text{A} + \text{A} \rightarrow \text{P}$	$\text{rate} = k[\text{A}]^3$	termolecular	3rd
$\text{A} + \text{A} + \text{B} \rightarrow \text{P}$	$\text{rate} = k[\text{A}]^2[\text{B}]$	termolecular	3rd

$A + B + C \rightarrow P$	rate = $k[A][B][C]$	termolecular	3rd
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#### D. Reaction mechanisms and rate equations

1. The rates of the elementary steps are seldom the same and depend on the stability (or instability) of the transition state, i.e., elementary steps with low activation energies (less unstable transition states) occur more rapidly than elementary steps with high activation energies (more unstable transition states)
2. The slowest elementary step is called the rate-determining step (analogy: driving from Elk Ridge to the "U")
3. First step is rate-determining
  - a.  $\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$ , experimentally determined that 2nd order in  $\text{NO}_2$ , 0th order in  $\text{CO}$ ; rate law: rate =  $k[\text{NO}_2]^2$
  - b. First step:  $\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{NO}(\text{g})$  (rate constant =  $k_1$ , slow)
  - c. Second step:  $\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{CO}_2(\text{g})$  (rate constant =  $k_2$ , fast)
  - d. Rate law for the rate-determining step: rate =  $k[\text{NO}_2]^2$
  - e. Is a one-step mechanism plausible for this reaction?
    - i. rate =  $k[\text{NO}_2][\text{CO}]$ , but this does not agree with experimental observations
4. If the first step is not the slow (rate-determining) step, faster steps produce intermediates that accumulate before they are consumed in the slow step; in addition, the rate law for the slow (rate-determining) step contains reaction intermediates which are transitory and present in low concentration
  - a.  $\text{Br}_2(\text{g}) + 2 \text{NO}(\text{g}) \rightarrow 2 \text{BrNO}(\text{g})$  (net), experimentally determined that 2nd order in  $\text{NO}$ , 1st order in  $\text{Br}_2$ ; overall rate law: rate =  $k[\text{NO}]^2[\text{Br}_2]$
  - b. Could this reaction be termolecular? According the rate law, it's possible but statistically it's unlikely
  - c. Proposed two step mechanism with two bimolecular elementary steps
    - i. Step 1:  $\text{Br}_2(\text{g}) + \text{NO}(\text{g}) \rightarrow \text{Br}_2\text{NO}(\text{g})$  (fast); rate =  $k_1[\text{Br}_2][\text{NO}]$
    - ii. Step 2:  $\text{Br}_2\text{NO}(\text{g}) + \text{NO}(\text{g}) \rightarrow 2 \text{BrNO}(\text{g})$  (slow); rate =  $k_2[\text{Br}_2\text{NO}][\text{NO}]$
  - d. Dynamic equilibrium in fast step results in decomposition of much of the reaction intermediate (which is unstable and does not accumulate) before it has a chance to participate in the slow step; express  $[\text{Br}_2\text{NO}]$  in terms of other species
    - i. Forward reaction for step 1: rate =  $k_1[\text{Br}_2][\text{NO}]$
    - ii. Reverse reaction for step 1: rate =  $k_{-1}[\text{Br}_2\text{NO}]$
    - iii. At eqb forward rate equals the reverse rate, therefore:  $k_1[\text{Br}_2][\text{NO}] = k_{-1}[\text{Br}_2\text{NO}]$
    - iv.  $(k_1/k_{-1})[\text{Br}_2][\text{NO}] = [\text{Br}_2\text{NO}]$

$$\text{v. rate} = k_2[\text{Br}_2\text{NO}][\text{NO}] = k_2(k_1/k_{-1})[\text{Br}_2][\text{NO}][\text{NO}] = k[\text{NO}]^2[\text{Br}_2] \text{ where } k = (k_2k_1/k_{-1})$$

- e. This is more probable than a single termolecular step mechanism because it involves two bimolecular steps
5. An alternative reaction mechanism for the reaction is as follows
- Proposed mechanism
    - Step 1:  $\text{NO}_{(g)} + \text{NO}_{(g)} \rightarrow \text{N}_2\text{O}_2_{(g)}$  (fast); rate =  $k_1[\text{NO}]^2$
    - Step 2:  $\text{N}_2\text{O}_2_{(g)} + \text{Br}_2_{(g)} \rightarrow 2 \text{BrNO}_{(g)}$  (slow); rate =  $k_2[\text{N}_2\text{O}_2][\text{Br}_2]$
  - Will this proposed mechanism provide the same overall rate law? (overall rate law: rate =  $k[\text{NO}]^2[\text{Br}_2]$ )
  - Rate law for the rate-limiting step: rate =  $k_2[\text{N}_2\text{O}_2][\text{Br}_2]$
  - Express  $[\text{N}_2\text{O}_2]$  in terms of other species based on assumption that a dynamic equilibrium exists between the forward and reverse reactions in the first step
  - rate forward = rate reverse =  $k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$
  - $k_1/k_{-1}[\text{NO}]^2 = [\text{N}_2\text{O}_2]$
  - rate =  $k_2[\text{N}_2\text{O}_2][\text{Br}_2] = k_2k_1/k_{-1}[\text{NO}]^2[\text{Br}_2] = k[\text{NO}]^2[\text{Br}_2]$  where  $k = (k_2k_1/k_{-1})$

## VII. Catalysis

- Catalysts change the speed of chemical reactions without undergoing permanent chemical changes in the process
- Catalysts work either by affecting the A or the  $E_a$  terms in the Arrhenius equation, but most commonly and conspicuously influence the latter
- Homogeneous catalysts: catalyst present in the same phase as the reactants
  - For example, acid and base-catalyzed organic reactions
  - Homogeneous catalysts serve to lower the  $E_a$  by providing a different reaction mechanism with lower  $E_a$  than the uncatalyzed reaction
- Heterogeneous catalysts: catalyst and reactants are in different phases
  - Reactants adsorb to active sites on the catalyst and are activated, i.e., bonds are pre-stretched or broken, the catalyst may donate or withdraw electron density from the reactant, etc.
    - Adsorb: binding of molecules to a surface
    - Absorb: the uptake of molecules into the interior of another substance

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***[Chemistry 1220 Index Page]***

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