

## **Chapter 15: Chemical Kinetics II**

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Low concentration = Few collisions



High concentration = More collisions



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## **Rate Laws**



- Experiments would allow you to determine the reaction order and rate constant, but what if you wanted to know [A] over time?
- Need to "integrate" the rate law (i.e., solve the above differential equation)



## **Zero Order Integrated Rate Law**



Note:  $[A] = [A]_t$  is a function of time.



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## **First Order Integrated Rate Law**

Rate = 
$$k[A] = -\frac{\Delta[A]}{\Delta t}$$
  
Solution to differential eq.:  
 $-\frac{d[A]}{dt} = k[A]$   
 $[A]_t = [A]_0 e^{-kt}$   
 $ln[A]_t = -kt + ln[A]_0$   
 $y = mx + b$   
Plot of ln[A] vs. time  
gives a straight line  
 $t$ 



## Second Order Integrated Rate Law





## **Experimental determination of reaction order**

Instead of measuring the initial rate, we could measure [A] as a function of time and then plot. Whichever curve gives a straight line (previous slides) must be the order.



(least squares fitting)



## 

## Half-life, $t_{1/2}$

Time required for the concentration of a reactant to fall to one-half of its initial value.

• To solve for  $t_{1/2}$  for first order reaction take the integrated rate law and plug in  $[A]_0 = 1$  and [A]= 0.5:

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

Substitute [A], in above: .....

$$(A)_{t} = \frac{1}{2}[A]_{0}$$
This gives directly:  

$$ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$t_{1/2} = \frac{0.693}{k}$$





#### Half-Life for a First-Order Reaction





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## Things to consider

$$t_{1/2} = \frac{0.693}{k}$$

- Higher k means faster (shorter) half-life, faster reaction
- Every half-life, concentration decreases by 1/2
- After x half-lives,  $[A] = (1/2)^{x} [A]_{0}$
- On your own: Solve for  $t_{1/2}$  for 0th and 2nd order reactions.



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## **Summary of Integrated Rate Laws**



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## Half-life example

- •C-14 produced in atmosphere
- Incorporated into plants through photosynthesis
- Incorporated into animals through food
- Relative amount of C-14 stays constant in living organisms until they die



14CO<sub>2</sub> + PHOTOSYNTHESIS → BIOLOGY

Willard F. Libby, 1946 Nobel Prize, Chemistry 1960

C-14 undergoes first order radioactive decay with *t*<sub>1/2</sub> = 5730 years



## Half-life example

Suppose a human bone found in a cave has 19.5% of the C-14 found in living organisms. How old is the bone?

1. 
$$t_{1/2} = \frac{0.693}{k}$$
  $k = \frac{0.693}{5730 \ yr} = 1.21 \times 10^{-4} \ yr^{-1}$ 

2. 
$$ln[A]_t = -kt + ln[A]_0$$

$$ln\left(\frac{[A]_t}{[A]_0}\right) = -kt$$

$$ln\left(\frac{0.195[A]_0}{[A]_0}\right) = -kt$$

 $t = 13,500 \ years \ old$ 

 $[A]_t = 0.195 [A]_0$ 



## **Temperature effects on kinetics**







- $2 H_2(\ell) + O_2(\ell) \rightarrow 2 H_2O(g)$
- Hydrogen and oxygen react slowly unless a spark is applied
- then, boom!
- Why? (activation energy)

## Effect of temperature on reaction rate

• Reaction rates are highly dependent on temperature:

$$Rate = k[A]^n = -\frac{\Delta[A]}{\Delta t}$$

 Arrhenius Equation (1889) says rate constant depends on temperature:

$$k = Ae^{\frac{-E_a}{RT}}$$

Svante Arrhenius 1859-1927 Uppsala/Stockholm, Sweden









## **Arrhenius Equation**

$$k = A e^{\frac{-E_a}{RT}}$$

- k = Rate constant
- A = Frequency factor (same units as *k*)
- *E*<sub>a</sub> = Activation energy
- *R* = Gas constant = 8.314 J / (mol K)
- Why? Collision theory & thermodynamics...







## **Chemical reaction energy diagram**

## **Recall from earlier:**

- Chemical reactions involve breaking and forming bonds
- These processes involve changes in (potential) energy





## **Reaction energy diagram** $A + B \rightarrow C + D$

Enthalpy (Heat of Reaction):  $\Delta H_{rxn}$ 



## **EXOTHERMIC**

- energy (heat) released
- $\Delta H_{rxn}$  is <u>negative</u>
- products at lower energy than reactants



## **Reaction energy diagram** $A + B \rightarrow C + D$

• Enthalpy (Heat of Reaction):  $\Delta H_{rxn}$ 



### **ENDOTHERMIC**

- Energy (heat) absorbed
- $\Delta H_{rxn}$  is positive
- products at higher energy than reactants



## **Collision theory**



Think about what must happen first in a reaction: collision!

```
O_3 + NO \rightarrow NO_2 + O_2
```



Both the kinetic energy of the molecules and their relative orientation determine the outcome.





## **Collision theory**

# $O_3 + NO \rightarrow NO_2 + O_2$ $\left[ \begin{array}{c} O \\ O \end{array} \right]^{\ddagger}$

(or "activated complex")

Molecules come together to form "transition" (‡) compound:

- distorted compared to "favored" configuration
- higher energy than both the reactants & products
- between reactants and products along the reaction path





## **Collision theory**



Products form:

Moving from transition state towards better configuration with a lower energy





## **Reaction coordinate**





## **Reaction coordinate**





## Activation energy (E<sub>a</sub>)

$$k = Ae^{\frac{-E_a}{RT}}$$

- *E*<sub>a</sub> is an energy barrier that the reactants must overcome to form the products
- Frequency factor (A): Rate of collisions (collisions / second)
- Not all collisions result in a reaction because some reactants do not have enough energy to overcome  $E_a$
- How could you increase rate constant?
  - Increase number of collisions per time (A)
  - Increase the number of collisions with enough energy to overcome the activation energy (exponential factor)
  - Decrease activation energy  $(E_a)$
- How do you give the reactants more (kinetic) energy? (temperature)

## Thermal energy

- In a given sample of molecules, the energy follows Boltzmann distribution
- Higher T: more molecules have enough energy to overcome activation energy





#### **Thermal Energy Distribution**

As temperature increases, the fraction of molecules with enough energy to surmount the activation energy barrier also increases.







## **Arrhenius Law**

- Experimentally determine *A*, *E*<sub>a</sub>, etc.
- Measure *k* at varying temperatures (must be expressed in Kelvin)
- Plot: ln(*k*) vs (1/*T*) "Arrhenius plot"
- slope =  $-E_a / R$
- intercept = ln(A)

$$k = Ae^{-\frac{E_a}{RT}}$$

$$ln \ k = ln(Ae^{-\frac{E_a}{RT}})$$

$$ln \ k = ln \ A + ln(e^{-\frac{E_a}{RT}})$$

$$ln \ k = ln \ A - \frac{E_a}{RT}$$

$$ln \ k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + ln \ A$$

y = m x + b(equation for straight line)





## **Arrhenius Law**





Note the axes in the graph!

*E<sub>a</sub>* = 93.1 kJ / mol *A* = 4.36 x 10<sup>11</sup> M<sup>-1</sup>s<sup>-1</sup>

Linear least squares fit using computer





## **Two-point form of Arrhenius Equation**

Make measurements at two temperatures only

$$ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Note: Not recommended unless the data is verified to be of Arrhenius form.

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## **Reaction mechanisms**

- Most reactions occur in multiple steps rather than in a single collision event!
- <u>Mechanism</u>: The <u>exact</u> molecular pathway that reactants follow to become products (i.e., multiple elementary steps)
- <u>Elementary reactions</u>: The individual steps in a reaction mechanism (cannot be broken down further). Takes place in a single collision.
- Add elementary reactions to get the overall reaction (reaction mechanism)







## **Example reaction**



Overall reaction:  $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$ but we know that N<sub>2</sub>O<sub>2</sub> is also detected during reaction Elementary Steps:

$$\begin{array}{rl} Step \ 1: & NO(g) + NO(g) \rightarrow N_2O_2(g) \\ \\ Step \ 2: & N_2O_2(g) + O_2(g) \rightarrow 2 \ NO_2(g) \\ \\ & 2 \ NO(g) + O_2(g) \rightarrow 2 \ NO_2(g) \end{array}$$

N<sub>2</sub>O<sub>2</sub> is an "intermediate": Species that appears in the mechanism, but not in overall reaction:

- formed in elementary step, then consumed
- usually short-lived and often difficult to detect



## **Rate laws for elementary reactions**

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- "Molecularity" = Number of reactants in an elementary step
- Rate law follows stoichiometry (molecularity)
   <u>For elementary reactions only!</u> (not overall reaction)
  - Unimolecular: $A \rightarrow Products$ Rate = k[A]Bimolecular: $A + A \rightarrow Products$ Rate = k[A]<sup>2</sup>Bimolecular: $A + B \rightarrow Products$ Rate = k[A][B]Termolecular: $A + A + A \rightarrow Products$ Rate = k[A]<sup>3</sup>Termolecular: $A + A + B \rightarrow Products$ Rate = k[A]<sup>2</sup>[B]Termolecular: $A + B + C \rightarrow Products$ Rate = k[A][B][C]

(No known reactions beyond this)





## **Example** $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$

## Step 1: $NO(g) + NO(g) \rightarrow N_2O_2(g)$ Rate = $k_1[NO]^2$ Step 2: $N_2O_2(g) + O_2(g) \rightarrow 2 NO_2(g)$ Rate = $k_2[N_2O_2][O_2]$

 $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$ 

What is the overall rate?? We will see in a bit...



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## **Kinetics for multi-step reactions**

- Often one step is fast and the other is slow
- The <u>slow step</u> will control the overall rate of the reaction ("rate-limiting" step)
- If first step is slow:







## **Kinetics for multi-step reactions**



- Often one step is fast and the other is slow
- The <u>slow step</u> will control the overall rate of the reaction ("rate-limiting" step)
- If last step is slow:
  - Intermediate will increase in concentration enough to drive the slow reaction
  - Steady state approximation







## **Example** $2 NO(g) + O_2(g) \rightarrow 2 NO_2(g)$





#### **Energy Diagram for a Two-Step Mechanism**



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## Catalysis

$$k = Ae^{-\frac{E_a}{RT}}$$



- Recall: One way to increase rate constant is to reduce the activation energy.
- A catalyst can alter the reaction mechanism such that the activation energy is reduced.







## **Example: Catalytic destruction of ozone**

- Ozone: O<sub>3</sub>
- Absorbs UV light in the stratosphere and prevents it from reaching the Earth's surface (skin cancer).





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**Example: Catalytic destruction of ozone** 

Chlorofluorocarbons (CFCs; refrigerant)

- Example:  $CFC-11 = CCI_3F$
- Very unreactive (inert) so they were used as coolants, propellants, etc.
- Stratosphere: ~20 km altitude, lots of UV light from sun





## **Example: Catalytic destruction of ozone**



 $\begin{array}{ccc} \mathsf{CCI}_3\mathsf{F} + \mathsf{h}\nu \to \mathsf{CI} + \mathsf{CCI}_3 & \mathsf{CI} + \mathsf{O}_3 \to \mathsf{CIO} + \mathsf{O}_2 \\ & & \underbrace{\mathsf{CIO} + \mathsf{O} \to \mathsf{CI} + \mathsf{O}_2} \\ \mathsf{O}_3 + \mathsf{h}\nu \to \mathsf{O} + \mathsf{O}_2 \\ & & \mathsf{O} + \mathsf{O}_2 \to \mathsf{O}_3 \end{array} \begin{array}{c} \mathsf{Overall:} & \mathsf{O} + \mathsf{O}_3 \to \mathsf{O}_2 + \mathsf{O}_2 \end{array}$ 

This should happen normally

Cl atom acts as a catalyst: Provides an alternative pathway for reaction to take place.

(cyclic reaction: Cl is re-formed)

## **Montreal Protocol**

- Banned CFCs in 1987
- Ozone hole will recover in ~100 years
- Fortunately alternative compounds available

http://cdiac.ornl.gov/ftp/oceans/CFC\_ATM\_Hist/CFC\_ATM\_Hist\_2015/Fig1.png





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## Homogeneous vs. heterogeneous catalysis





FIGHT

SMOG



## **Catalytic converters**



Smog in Hong Kong

LA smog protests of 1954

WE WANT

CLEAN SWEEP

SMOG

Supervisors

SEE

Unburned Hydrocarbons + NOx

PAN = Peroxyacetyl nitrate

→ O<sub>3</sub> +
PANs + more

(health hazard)



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## **Catalytic converters**



(downside: catalytic converters are expensive!)



## **Catalytic converters**



Despite more cars and more miles driven!





## Enzymes

- Biological catalysts which increase reaction rates for biochemical reactions.
- Enzyme (usually a protein) has an "active site" where reactants can bind.

## Example: Sucrase









## $E + S \rightleftharpoons ES$ (Fast) $ES \rightarrow E + P$ (Slow, rate limiting)

(Michaelis-Menten kinetics)



## **Tips for this section**

- Understand/Identify integrated rate laws:
  - Equations
  - Plots, slope, intercept, etc.
- Half-life
- Reaction order
- Reaction coordinate identify activation energy, enthalpy, transition state, etc.
- Elementary steps, rates
- Catalysis, how do catalysts increase reaction rate?
- Lots of calculations!