Kinetics: Mechanisms and Rates of Reactions

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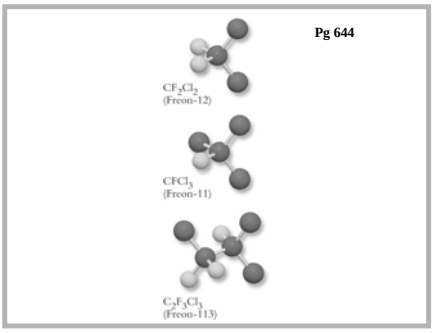
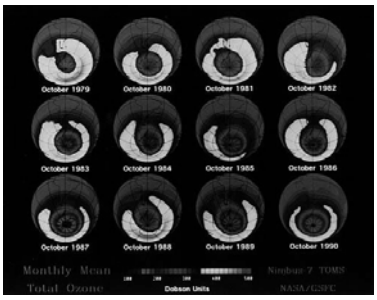


Chlorofluorocarbons (CFCs) pose a large threat to the ozone layer because of the tendencies of the CFCs to break down the ozone molecules.

Chlorofluorocarbons are composed of <u>fluorine, carbon, and chlorine</u>. When the CFCs enter the stratosphere, the ultraviolet radiation causes one of the chlorine atoms to break away. When this free single atom of Chlorine strikes an ozone molecule (O_3), one atom of oxygen (O_2) and one atom of chlorine monoxide (ClO) is formed. Therefore the ozone molecule has been destroyed. The problem is that once an atom of atomic oxygen collides with the chlorine monoxide, a new oxygen atom (O_2) is formed and a single chlorine atom remains. This lone chlorine atom is free to destroy more ozone molecules many times over.



Chemical Kinetics

a study of the rates of chemical reactions

Basically….How fast does a chemical reaction occur?

Rates of Chemical Reactions

Rate of a chemical reaction refers to the change in concentration of a substance per unit of time

Let's consider the rate at which you give me 3 dollars…

your 3 dollars → my 3 dollars

Let's say that it took you 5 seconds to give it to me.

reactants **products**

your 3 dollars → my 3 dollars

What is the rate of the reaction with respect to me [products]?

$$\text{Rate} = \frac{\text{change in concentration of money}}{\text{change in time}}$$

Remember, change (Δ) is always [final – initial]

Positive because I am the product which gains the money

$$\text{Rate} = \frac{+ [3\text{-}0 \text{ dollars}]}{[5\text{-}0 \text{ secs}]}$$

Rate = 0.6 dollars/sec

What is the rate with respect to you?

Negative because you are the reactant and you are losing money

$$\text{Rate of reaction} = \frac{- [0\text{-}3 \text{ dollars}]}{[5\text{-}0 \text{ secs}]}$$

Rate of reaction = 0.6 dollars/sec

Therefore, you can determine the rate of reaction either by using the reactants or the products. It will give you the same rate of reaction*

Let's consider the rates for chemical reactions:

$$NO(g) + \tfrac{1}{2} O_2(g) \rightarrow NO_2(g)$$

Rate of the disappearance of NO:

$$\text{Rate} = \frac{-\Delta[NO]}{\Delta t}$$

Rate of the disappearance of O_2:

$$\text{Rate} = \frac{-\Delta[O_2]}{\Delta t}$$

Rate of the appearance of NO_2:

$$\text{Rate} = \frac{+\Delta[NO_2]}{\Delta t}$$

If you know the rate of one species in a reaction you can determine the rate of any other species by the mole to mole ratio.

Consider the previous reaction:

$$NO(g) + \tfrac{1}{2} O_2(g) \rightarrow NO_2(g)$$

The nitrogen dioxide increases at a rate of 0.0396 mol/L •s. What is the rate of oxygen decreasing?

$$\frac{0.0396 \text{ mol } NO_2}{L \cdot sec} \times \frac{\frac{1}{2} \text{ mol } O_2}{1 \text{ mol } NO_2} = 0.0198 \text{ mol } O_2/L \cdot s$$

$$NO(g) + \tfrac{1}{2} O_2(g) \rightarrow NO_2(g)$$

To determine the rate of reaction, you take the rate that you are given and divide by the stoichiometry in the balance reaction.

The rate of disappearance of O_2 is 0.0198 mol/L •s. What is the rate of reaction?

$$\frac{0.0198 \text{ mol } O_2}{\frac{1}{2} \ L \cdot s} = 0.0396 \text{ mol/L} \cdot s$$

Rate of the reaction

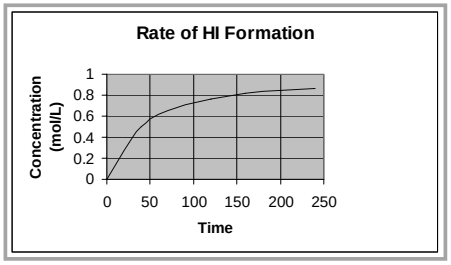
Test Your Skill:

For the reaction:

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

The NOCl concentration increases at a rate of 0.030 mol/L•s under a particular set of conditions. Calculate the rate of disappearance of chlorine at this time and the rate of reaction.

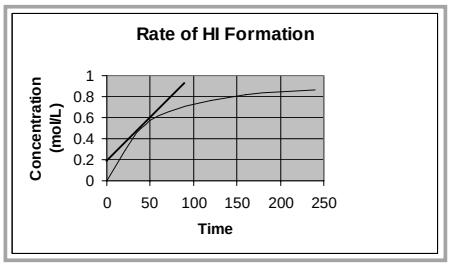
$H_2(g) + I_2(g) \rightarrow 2HI(g)$



Using the previous graph, answer these questions:

(a) Write an expression for the rate of reaction in terms a changing concentration
(b) Calculate the average rate of reaction between 20 and 60 s
(c) Calculate the instantaneous rate of reaction after 40 s
(d) Calculate the initial rate of reaction
(e) Calculate the instantaneous rate of consumption of hydrogen 60 s after the start of the reaction

$H_2(g) + I_2(g) \rightarrow 2HI(g)$



Reaction Conditions and Rates

Several factors affect the speed of a reaction are:

Concentration of reactants

Temperature

Catalyst

Effect of Concentration on Reaction Rates

The best way to describe how concentration of reactants affect rates is to use a rate law

Consider the reaction:

Rate constant $A + B \rightarrow C$

$$\text{Rate} = k[A]^x[B]^y$$

x and y are NOT necessarily the from the stiochiometry in the reaction

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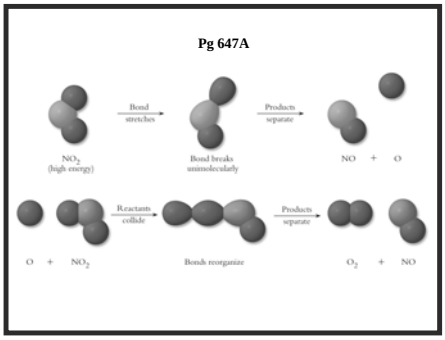

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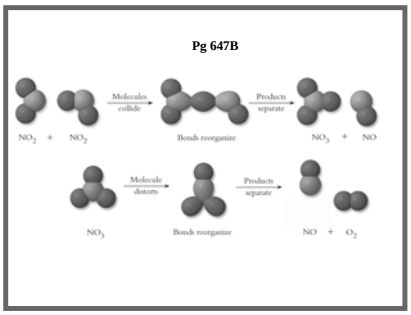


Mechanism I

Step I-1 $NO_2 \rightarrow NO + O$ (rate determining)

Step I-2 $O + NO_2 \rightarrow O_2 + NO$ (fast)

Overall reaction: $2NO_2 \rightarrow 2NO + O_2$

Mechanism II

Step II-1 $2NO_2 \rightarrow NO_3 + NO$ (rate determining)

Step II-2 $NO_3 \rightarrow O_2 + NO$ (fast)

Overall reaction: $2NO_2 \rightarrow 2NO + O_2$

A rate law equation may be written directly from the balanced reaction if one of the following are noted:

- rate-determining step
- one step reaction
- slow step

If one of the above are mentioned, the rate law is written using just the reactants of that reaction.

Mechanism I

Step I-1 $NO_2 \rightarrow NO + O$ (rate determining)

Step I-2 $O + NO_2 \rightarrow O_2 + NO$ (fast)

Overall reaction: $2NO_2 \rightarrow 2NO + O_2$

Rate = $k[NO_2]$

Mechanism II

Step II-1 $2NO_2 \rightarrow NO_3 + NO$ (rate determining)

Step II-2 $NO_3 \rightarrow O_2 + NO$ (fast)

Overall reaction: $2NO_2 \rightarrow 2NO + O_2$

Rate = $k[NO_2]^2$

If a slow step is not noted, experimental data must be used to calculate the rate law.

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl$$

Exp	[NO]	[Cl_2]	Initial Rate of Rxn
1	0.01	0.01	2.5
2	0.01	0.02	5.1
3	0.02	0.01	5.2
4	0.02	0.02	10.3

The Sum of the Exponents in a Rate Law Gives the Overall Order of the Reaction.

We will be mostly dealing with overall orders of:

Zero Order
First Order
Second Order

Most of this material will be on the board

How temperature and Catalysts Affect Reaction Rates

Consider Arrhenius' Equation

$$k = A\, e^{-Ea/RT}$$

Temperature

Frequency of collisions

Activation energy

Gas constant 8.314 J/mol • K

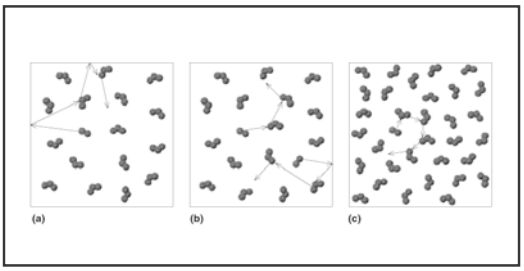
The A term in the Arrenhius Equation

In order for molecules to react, they must collide.

Collision Theory

1. **The reaction molecules must collide with one another.**
2. **The reaction molecules must collide with sufficient energy.**
3. **The molecules must collide in an orientation that can lead to rearrangement of the atoms.**

Effect of Concentration on the frequency of collisions



Therefore, increase the number of collisions, increase the rate

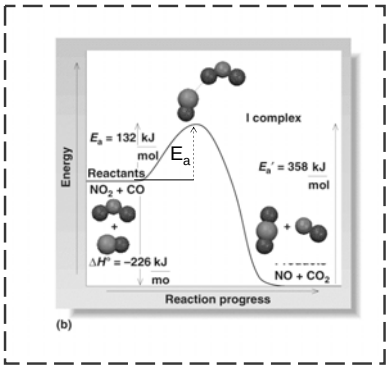
Effect of Temperature

$$k = A\, e^{-Ea/RT}$$

The larger the temperature, the smaller the negative term. The smaller negative term, the larger the value once you have applied e^x.

Therefore, increase temperature, increase reaction rate.

Activation Energy, Ea



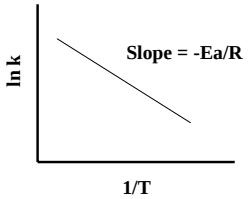
$$k = A\, e^{-Ea/RT}$$

Take the ln of both sides.

$$\ln k = \ln A - \frac{Ea}{R}(1/T)$$

y b m x

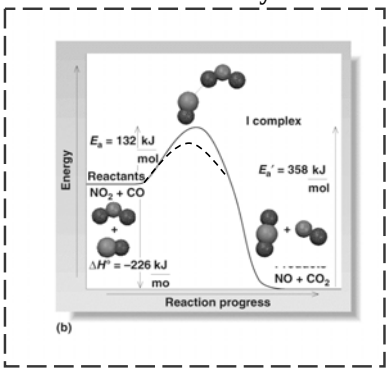
If we were going to graph this, what would we graph?



If we have two different k values at different temperatures, you can combine the two reactions to give:

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

Effect of a Catalyst



Homogeneous catalyst: a catalyst is present in the same phase as the reacting substances

Heterogeneous catalyst: a catalyst is present in a different phase as the reaction substances