

Chapter 13 RATES OF REACTION

These Notes are to **SUPPLEMENT** the Text, They do NOT Replace reading the Text Material.
Additional material that is in the Text will be on your tests!

To get the most information, READ THE CHAPTER prior to the Lecture, bring in these lecture notes and make comments on these notes. These notes alone are NOT enough to pass any test!

Chemical Reactions require various times to run. These reaction times are dependent on the properties of the reactants, products and the reaction conditions. Hydrogen will burn in Oxygen to form water at a very fast reaction rate. Concrete may require a long time to cure.

Chemical Kinetics is the study of reaction rates.

The rate of a reaction is dependent on:

1. The concentration of the reactants. The more concentrated the reactants the better the likelihood of a successful collision.

EXAMPLE: Crumpled up steel wool does not burn very well in air. Spreading the steel wool out [increasing the surface area] and putting it in pure oxygen, steel wool burns with a very hot white flame.

2. The concentration of a catalyst. A catalyst is a substance that increases the rate of a reaction without being consumed in the reaction. The catalyst usually does not appear in the balanced equation, but may be given above the reaction arrow.

A catalyst speeds up the reaction by reducing the “activation energy” needed for the reaction.

A catalyst may provide an alternative mechanism for the reaction.

EXAMPLE: Hydrogen Peroxide will decompose to oxygen and water: $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2$ very slowly under normal conditions. Put in a catalyst such as Manganese Dioxide or put the peroxide on a cut, and that will act as a catalyst increasing the rate of the reaction and the production of oxygen.

3. The temperature of the reaction. An increase in temperature usually will increase the rate of a reaction. A rule of thumb is increase the temperature by 10°C and the reaction rate doubles.

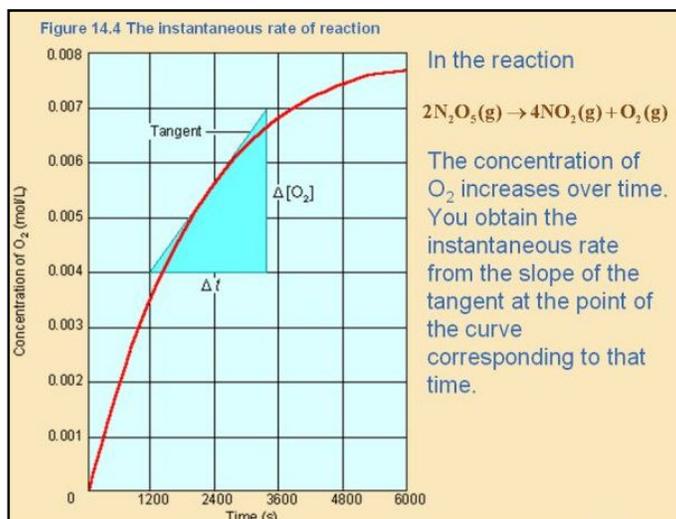
4. The surface area of a solid reactant. Increasing the surface area of a solid reactant will increase the rate of a reaction. Most reactions occur at the surface of a solid.

A solid log will burn slowly. Cut the log up into slivers and it burns very fast. The smaller pieces are now more exposed to oxygen to undergo the burning chemical reaction.

Reaction Rate is the increase in molar concentration of product of a reaction per unit time or the decrease in molar concentration of the reactant per unit time.

Reaction Rate Units are moles per liter per second – mol / (L s)

The Gas Phase Reaction: $2 \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$ proceeds according to the following rate graph:



Note: for “Tangent” lines, if the line goes pretty much up and down, the reaction rate is very fast, if the “Tangent” line goes horizontal, the reaction rate is slow!!

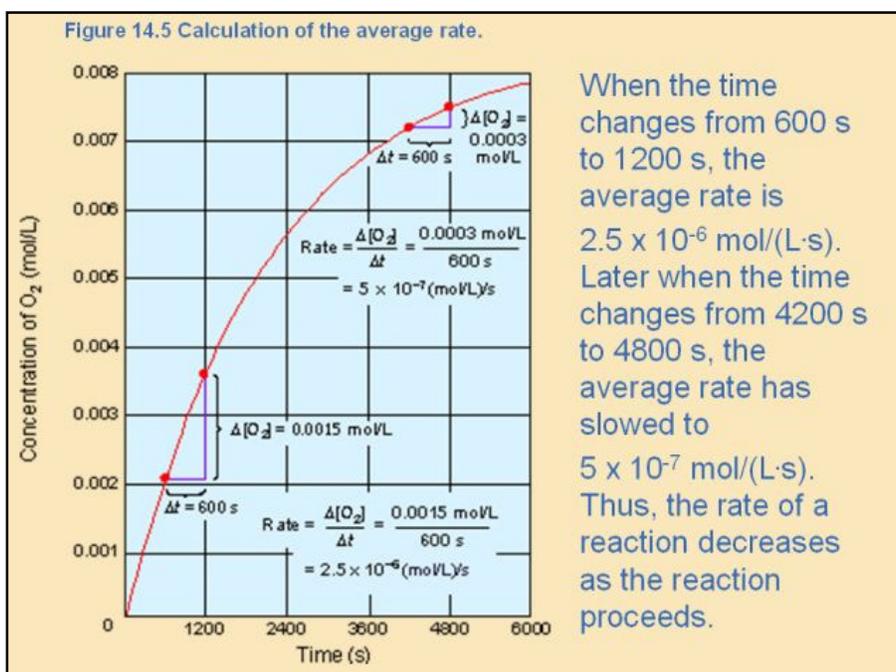
The **concentration of Oxygen** – O_2 is expressed as $[\text{O}_2]$. The **change in concentration of Oxygen** is $\Delta [\text{O}_2]$.

The **rate of formation** of oxygen is the change in concentration over time or: $\Delta [\text{O}_2] / \Delta t$

This equation gives the average rate over the time interval. That is, the rate at a particular instant of time. The **instantaneous rate** is $\Delta [\text{O}_2] / \Delta t$ or a tangent to the rate line at a particular point for a short period of time.

Note the rate of formation of O_2 decreases as time increases. Most reaction rates will decrease over time!

Example: A car travels 84 miles in 2.0 hours. It’s average speed is $84 \text{ miles} / 2.0 \text{ hrs} = 42 \text{ mph}$. but at any instant, it’s speed could be 60 mph or 0 mph.



600 seconds \rightarrow 1200 Seconds

Concentration goes from 0.002 \rightarrow 0.0035

Lower Left Value: $\Delta t = 600 \text{ s}$, $\Delta [\text{O}_2] = 0.0015 \text{ mol/L}$

$$\text{Rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{0.0015 \text{ mol/L}}{600 \text{ s}} = 2.5 \times 10^{-6} \text{ mol/Ls}$$

Upper Right Value: $\Delta t = 600 \text{ s}$, $\Delta [\text{O}_2] = 0.0003 \text{ mol/L}$

$$\text{Rate} = \frac{\Delta [\text{O}_2]}{\Delta t} = \frac{0.0003 \text{ mol/L}}{600 \text{ s}} = 5 \times 10^{-7} \text{ mol/Ls}$$

Because the amounts of reactants and products are **related by stoichiometry**, any compound in the reaction can be used to express the rate of the reaction.

Instead of working with the rate of formation of oxygen, we can show the rate of decomposition of N_2O_5 :

$$\text{Rate of decomposition of } \text{N}_2\text{O}_5 = -\Delta [\text{N}_2\text{O}_5] / \Delta t \quad [\text{minus because it's disappearing}]$$

Note for 2 moles of N_2O_5 there is 1 mole of O_2 formed, so:

$$\frac{\Delta [\text{O}_2]}{\Delta t} = \frac{-\frac{1}{2} \Delta [\text{N}_2\text{O}_5]}{\Delta t}$$

Example 13.1 For the following reaction: $2 \text{NO}_2 (\text{g}) + \text{F}_2 (\text{g}) \rightarrow 2 \text{NO}_2\text{F} (\text{g})$

How is the rate of formation of NO_2F related to the rate of reaction of fluorine?

$$\text{Rate of formation of } \text{NO}_2\text{F} = \Delta [\text{NO}_2\text{F}] / \Delta t$$

$$\text{Rate of reaction of } \text{F}_2 = - \Delta [\text{F}_2] / \Delta t$$

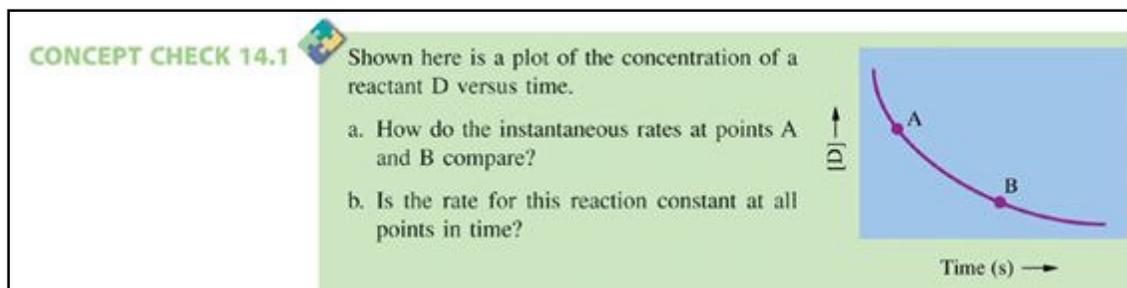
$$\frac{1}{2} \Delta [\text{NO}_2\text{F}] / \Delta t = \Delta [\text{F}_2] / \Delta t$$

Example 13.2 Calculate the average rate of decomposition of N_2O_5 . $2 \text{N}_2\text{O}_5 (\text{g}) \rightarrow 4 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$

From the following data:	Time	$[\text{N}_2\text{O}_5]$
	600 s	$1.24 \times 10^{-2} \text{ M}$
	1200 s	$0.93 \times 10^{-2} \text{ M}$

The Average Rate of decomposition of $\text{N}_2\text{O}_5 = - \Delta [\text{N}_2\text{O}_5] / \Delta t$

$$= - [0.93 - 1.24] \times 10^{-2} \text{ M} / [1200 - 600] \text{ s} = 5.2 \times 10^{-6} \text{ M/s}$$

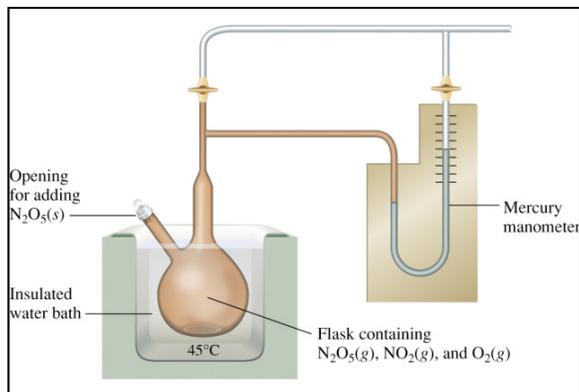


How do the instantaneous rates of reaction at A and B compare? Class discussion about this answer!

How to obtain the rate of reaction:

1. Withdraw a sample and analyze it during the reaction [sometimes very difficult]
2. Monitor some physical property of one of the compounds during the reaction. This includes UV/Vis spectra [good method], GC, NMR, ORD [Optical Rotary Dispersion], Index of Refraction, Pressure changes.

Gas-Phase partial pressure: $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ A manometer follows the pressure increase.



Color change / absorption of light $\text{ClO}^- (\text{aq}) + \text{I}^- (\text{aq}) \rightarrow \text{IO}^- (\text{aq} - \text{blue at } 400 \text{ nm}) + \text{Cl}^- (\text{aq})$

Do Example of dropping a \$100 bill once a second as a rate determining step and how fast the students will pick it up.

Dependence of Reaction Rate on Concentration: $2 \text{NO}_2 + \text{F}_2 \rightarrow 2 \text{NO}_2\text{F}$

Rate Law is an equation that relates the rate of a reaction to the concentration of reactants [and catalyst] raised to various powers. **Rate = k [NO₂] [F₂]**

Rate Constant is a proportionality constant in the relationship between rate and concentration:

$$k = \text{Rate} / [\text{NO}_2] [\text{F}_2] = \text{mol} / (\text{Ls}) / (\text{mol/L})^2 = \text{L} / (\text{mol s})$$

$$\text{C } [\text{C} = \text{a Catalyst }]$$

- or for a general equation: **a A + b B → d D + e E**

$$\text{Rate} = k [\text{A}]^m [\text{B}]^n [\text{C}]^p$$

Where m, n, p are not always integers and must be experimentally determined and are not usually related to a, b, d, or e.

Reaction Order with respect to a given reactant is the exponent of the concentration of that species in the rate law as determined experimentally. Fraction, zero order and negative values are possible.

1. Cyclopropane C_3H_6 when heated opens up: C_3H_6 [cyclic] \rightarrow $\text{CH}_2 = \text{CH}-\text{CH}_3$
 Experimental Rate = k [C_3H_6] The reaction is **First Order** in Cyclopropane

2. Nitric Oxide and Hydrogen give: $2 \text{NO} + \text{H}_2 \rightarrow \text{N}_2 + 2 \text{H}_2\text{O}$
 Experimental Rate = k [NO]² [H_2] The reaction is **Second Order** in NO, **First Order** in H_2

3. Acetone and Iodine gives: $\text{CH}_3\text{-CO-CH}_3 + \text{I}_2 \rightarrow \text{H}^+ \rightarrow \text{CH}_3\text{-CO-CH}_2\text{I} + \text{HI}$
 Experimental Rate = k [$\text{CH}_3\text{-CO-CH}_3$] [H^+ Cat]
 The reaction is **First Order** in Acetone and H^+ and **Zero Order** in I_2

Example 13.3 Bromide is oxidized to Bromate by $5 \text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3 \text{Br}_2 + 3 \text{H}_2\text{O}$
 What is the order of the reaction? See p 532.

Determining the Rate Law: The Rate Law is determined experimentally [it must be determined experimentally] for any reaction.

For $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$	Experiment	Initial [N_2O_5]	Rate of disappearance of N_2O_5
	1	$1.0 \times 10^{-2} \text{ mol / L}$	$4.8 \times 10^{-6} \text{ mol / Ls}$
	2	$2.0 \times 10^{-2} \text{ mol / L}$	$9.6 \times 10^{-6} \text{ mol / Ls}$

Rate = k [N_2O_5]^m

If you double the concentration, the reaction rate multiplier is: $\frac{9.6 \times 10^{-6} \text{ mol / Ls}}{4.8 \times 10^{-6} \text{ mol / Ls}} = 2.0$

Therefore for this reaction, the reaction rate multiplier = 2, look up the value for m:

Table 13.1

Effect on Rate Doubling:	m	-1	0	1	2
	Rate Multiplier:	½	1	2	4

m = 1, thus the rate equation is: Rate = k [N₂O₅]¹ [the one is now the exponent]

or substituting in the values for experiment #1:

$$k = \text{Rate} / [\text{N}_2\text{O}_5] = 4.8 \times 10^{-6} \text{ mol/L s} / 1.0 \times 10^{-2} \text{ mol/L} = 4.8 \times 10^{-4} / \text{s}$$

If doubling the concentration of a reactant doubles the rate, the order is First Order

If doubling the concentration quadruples the rate, the order is Second Order

If doubling the concentration 8 folds the rate, the order is Third Order

Example 13.4 **H₂O₂ + 3 I⁻ + 2 H⁺ → I₃⁻ + 2 H₂O**

Find the Reaction Orders and then the Rate Constant

	[H ₂ O ₂]	[I ⁻]	[H ⁺]	Initial Rate [mol/Ls]
Exp 1	0.010 mol/L	0.010 m/L	0.00050 m/L	1.15 x 10 ⁻⁶
Exp 2	0.020 mol/L	0.010 m/L	0.00050 m/L	2.30 x 10 ⁻⁶
Exp 3	0.010 mol/L	0.020 m/L	0.00050 m/L	2.30 x 10 ⁻⁶
Exp 4	0.010 mol/L	0.010 m/L	0.00100 m/L	1.15 x 10 ⁻⁶

Assume Rate = k [H₂O₂]^m [I⁻]ⁿ [H⁺]^p

Exp 1 to Exp 2, [H₂O₂] is **doubled**, the reaction rate = 2.30 x 10⁻⁶ / 1.15 x 10⁻⁶ = Doubles. Therefore **m = 1**

Exp 1 to Exp 4, [H⁺] is **doubled**, the reaction is not changed. Therefore **p = 0**

Exp 1 to Exp 3, [I⁻] is **doubled**, the reaction rate = 2.30 x 10⁻⁶ / 1.15 x 10⁻⁶ = Doubles. Therefore **n = 1**

Rate = k [H₂O₂] [I⁻]

k = Rate / [H₂O₂] [I⁻] = 1.15 x 10⁻⁶ mol/Ls / [0.010 mol/L] * [0.010 mol/L] = 1.2 x 10⁻² L / mol s

Changes of Concentration with Time [BSOTC] NOTE CALCULUS REQUIRED!!

Integrated Rate Law: the mathematical relationship between concentration and time

First-Order Rate Law

Second-Order Rate Law

Zero Order Reactions

Half-Life of a Reaction

The **half-life of a reaction**, $t_{1/2}$, is the time it takes for the reactant concentration to decrease to one-half the initial value.

For a First Order Reaction, It can be shown that: $0.693 = k t_{1/2}$ or $t_{1/2} = 0.693 / k$

Or, simply that the half life is **NOT dependant on the amount of starting material!**

Example 13.6 Sulfuryl Chloride, SO_2Cl_2 decomposes to $\rightarrow \text{SO}_2 + \text{Cl}_2$

At 320°C , the rate constant is $2.20 \times 10^{-5} / \text{s}$. What is it's half life? How long in hours will it take for 50% of the starting material to decompose? How long for 75% to decompose?

$$t_{1/2} = 0.693 / k = 0.693 / 2.20 \times 10^{-5} / \text{s} = 3.25 \times 10^4 \text{ s}$$

$$\text{For 50\% to decompose it is } 3.25 \times 10^4 \text{ s} / [60 \text{ s} / \text{min} * 60 \text{ min} / \text{hr}] = 8.75 \text{ hr}$$

$$\text{For 75\% to decompose, that is } \frac{1}{2} \text{ plus } \frac{1}{2} \text{ the remaining. It is } 8.75 + 8.75 \text{ hrs} = 17.5 \text{ hrs}$$

For a second order reaction, where the Rate = $k [A]_0^2$, then $t_{1/2} = 1 / k [A]_0$

The **half life depends on the initial concentration**, and each additional half-life becomes larger.

Decomposition of NO_2 at 330°C , it takes 430 s for the 1st concentration to decrease from 0.0030 mol/L to 0.0014 mol/L. It then takes 860 s [twice as long] to decrease by one half again.

For zero order reactions: $t_{1/2} = [A]_0 / 2 k$ So each additional half life gets shorter.

Graphing of Kinetic Data

[BSOTC] NOTE CALCULUS REQUIRED!!

The goal is to get an equation where the plot is a straight line so the equation of a straight line: $y = mx + b$ can be used.

Temperature and Rate; Collision and Transition-State Theories.

As an approximation, the rate of a reaction doubles for each 10°C rise in temp.

Collision Theory: assumes that for a reaction to occur, reactant molecules must collide with an energy greater than some minimum valued and with the proper orientation.

Activation Energy, E_a is the minimum energy of collision required for two molecules to react.

In the **collision theory**, the **rate constant** for a reaction = $k = Z f p$

Z = collision frequency, f = fraction having activation energy, p = fraction with proper orientation.

Transition-State Theory: a reaction results from the collision of two molecules in terms of an **activated complex**.

Activated Complex is an unstable grouping of atoms that can break up to form products.



Assume you have two billiard balls on a table and each is coated with a slightly sticky stuff and they are stuck together. Take a third ball coated with a very sticky good and hit the two that are stuck together. If the third ball has enough energy, it will break the two stuck together apart. At the instant that all three balls are together, we have an unstable transition state.

ΔH – Change in Enthalpy See Ch 6.3

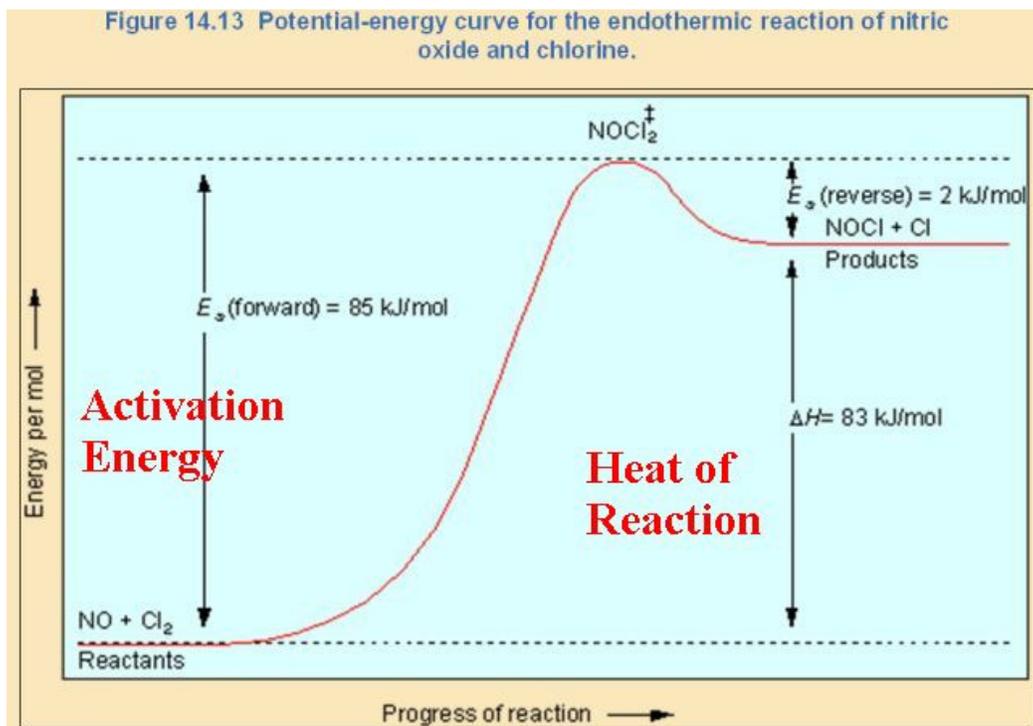
Potential-Energy Diagrams for Reactions

These graphs show the change in energy of a system relative to time.

Endothermic Reaction of $\text{NO} + \text{Cl}_2 \rightarrow \text{NOCl} + \text{Cl}$

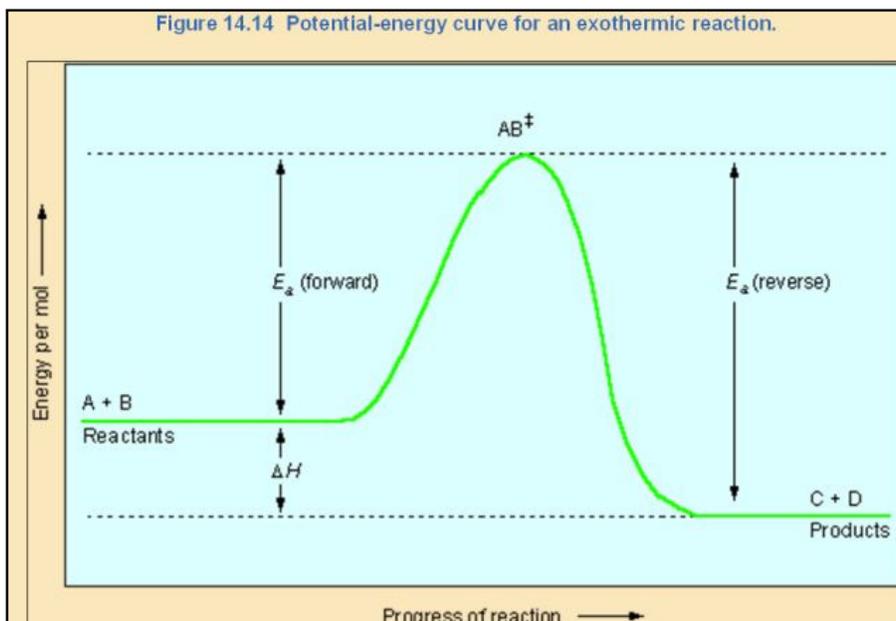
Note there is a forward activation energy necessary to form the activated complex

The ΔH of the reaction is the net change in energy between reactants and products.

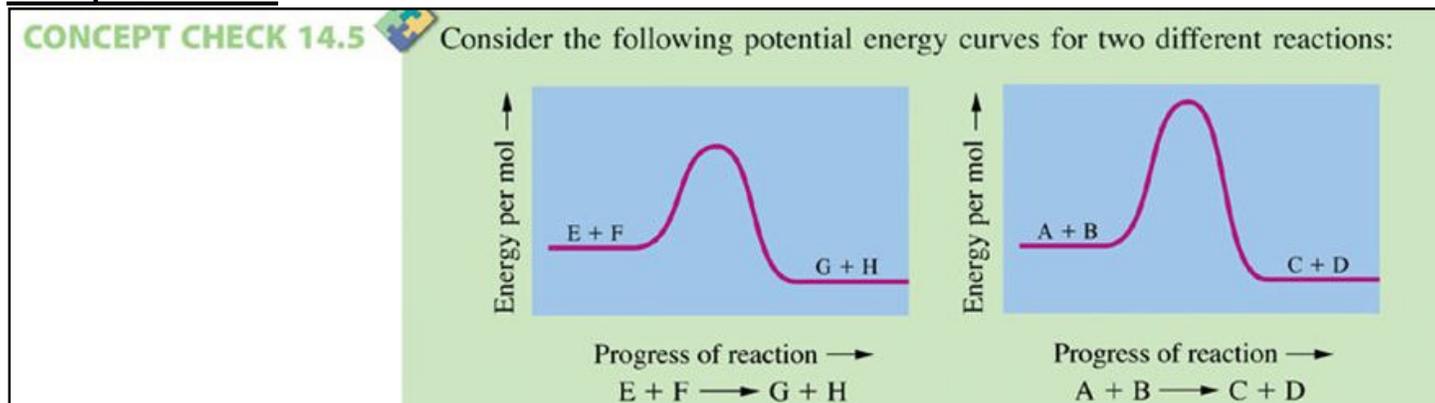


The ΔH of 83 kJ/mole is the heat of the reaction, the amount of energy that remains with the products.

For an exothermic reaction, the products are at a lower energy level than the reactants. Therefore they are more stable.



Concept Check 13.5



- Which Reaction has the higher activation energy for the forward reaction?
- Which has the higher activation energy for the reverse reaction?
- Are these exothermic or endothermic?

Arrhenius Equation

The Arrhenius Equation is a mathematical equation, $k = A e^{-E_a/R}$

It expresses the dependence of the rate constant on temperature.

e is natural log E_a is the Activation Energy

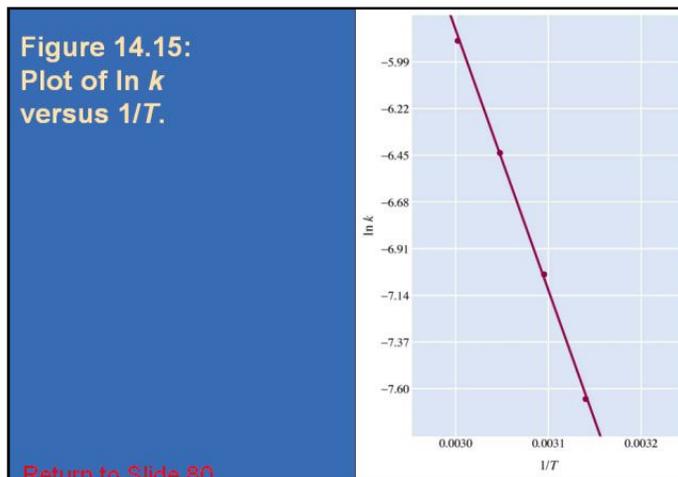
R is the gas constant 8.31 J/K mole,

T is the temperature in °K and

A is a constant called the "Frequency Factor".

The Frequency Factor is related to the number of collisions with the proper orientation (pZ).

Taking the natural log of each side of the above equation gives: $\ln k = \ln A - E_a/RT$ or the equation of a straight line: $y - mx + b$ [people like to work with straight lines – quiz question – WHY?]



Plot of $\ln k$ vs $1/\text{Temp}$

Example 13.7 The rate constant for the formation of HI from the elements: $\text{H}_2 + \text{I}_2 \rightarrow 2 \text{HI}$

Is $2.7 \times 10^{-4} \text{ L/mol s}$ at 600°K and

$3.5 \times 10^{-3} \text{ L/mol s}$ at 650°K .

Find the activation energy E_a and then the rate constant at 700°K ?

Rearranged Arrhenius Equation: $\ln k_2 / k_1 = [1/T_1 - 1/T_2] * E_a / R$

$$\ln [3.5 \times 10^{-3} / 2.7 \times 10^{-4}] = [1 / 600^\circ\text{K} - 1 / 650^\circ\text{K}] * E_a / 8.31 \text{ J/(mol K)}$$

$$\ln [1.30 \times 10^1] = 2.56 = [1.28 \times 10^{-4} \text{ }^\circ\text{K}] * E_a / 8.31 \text{ J/mol}$$

Rearrange and solve for E_a :

$$E_a = 2.56 * 8.31 \text{ J/mol} / 1.28 \times 10^{-4} = 1.66 \times 10^5 \text{ J/mol}$$

Substitute in for E_a above and 700°K and get $k_2 = 3.2 \times 10^{-2} \text{ L/(mol s)}$

Exercise 13.7 Acetaldehyde, $\text{CH}_3\text{-CHO}$, decomposes when heated to:



At 759°K , the rate constant is $1.05 \times 10^{-3} / (\text{M}^{1/2} \text{ s})$

At 836°K , the rate constant is $2.14 \times 10^{-2} / (\text{M}^{1/2} \text{ s})$.

What is the activation energy for this decomposition? What is the rate constant at 865°K .

$$\ln [2.14 \times 10^{-2} / 1.05 \times 10^{-3}] = [1 / 759^\circ\text{K} - 1 / 836^\circ\text{K}] * E_a / 8.31 \text{ J/(mol K)}$$

$$3.0146 = [1.21 \times 10^{-4} / \text{ }^\circ\text{K}] * E_a / 8.31 \text{ J/mol}$$

Rearrange and solve for E_a :

$$E_a = 3.0146 * 8.31 \text{ J/mol} / 1.21 \times 10^{-4} = 2.06 \times 10^5 \text{ J/mol}$$

Plug in the values now for 865°K

$$\ln [k_2 / 2.14 \times 10^{-2} / (\text{M}^{1/2} \text{ s})] = [1 / 836^\circ\text{K} - 1 / 865^\circ\text{K}] * 2.06 \times 10^5 \text{ J/mol} / 8.31 \text{ J/(mol K)}$$

$$k_2 / 2.14 \times 10^{-2} / (\text{M}^{1/2} \text{ s}) = e^{0.99623} = 2.708$$

$$k_2 = 2.708 * 2.14 \times 10^{-2} / (\text{M}^{1/2} \text{ s}) = 5.80 \times 10^{-2} (\text{M}^{1/2} \text{ s})$$

Reaction Mechanisms



At temperatures below 500 °K, it is believed to occur via the following steps:



An **Elementary Reaction** is a single molecular event resulting in a reaction

Reaction Mechanism is a set of elementary reactions whose overall effect is given by the net chemical equation

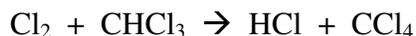
A **Reaction Intermediate** is a species produced during a reaction that does not appear in the net equation because it reacts in a subsequent step in the mechanism.

Example 13.8 Carbon Tetrachloride is obtained from chlorinating methane. The elementary reactions are:



What is the net equation?

Add them all up and cross out what's on both sides:



TEST QUESTION: What are the Reaction Intermediates?

Molecularity

Molecularity is the number of molecules on the reactant side of an elementary reaction.

A **Unimolecular reaction** is an elementary reaction that involves one reactant molecule



A **Bimolecular reaction** is an elementary reaction that involves two reactant molecules

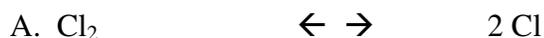


A **Termolecular reaction** is an elementary reaction that involves three reactant molecules.



Note: Chemical reactions occur in steps that we may not be aware of, and so we cannot predict the reaction rate or rate equation just on the overall reaction!

Example 13.9 What is the molecularity of each step? What are the Reaction Intermediates?



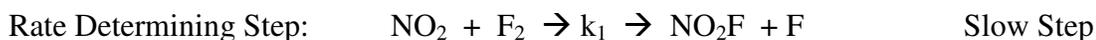
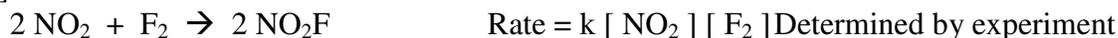
Step A Forward is Unimolecular

Step A Reverse, Step B and Step C are Bimolecular

Class Quiz – What are the reaction intermediates?

Rate Law and the Mechanism:

The mechanism of a reaction usually cannot be observed, but some of the steps can be indirectly observed [How?]



The **Rate Determining Step** is the slowest step in the reaction mechanism.

Mechanisms with an Initial Fast Step

See pages 594 ff

The Reaction $2 \text{N}_2\text{O}_5 \rightarrow 4 \text{NO}_2 + \text{O}_2$ as the overall reaction is known to go by the mechanism:



In short, the reaction rate is pretty much equal to the slow reaction rate k_2 . As the NO_2 is used up in the slow reaction, it is rapidly generated back again in the fast first reaction.

This is analogous to the story of the Chemistry Instructor dropping \$100 bills at the rate of 1/second. The students can pick it up faster, but the total rate time is still depending upon the rate of the slowest – the dropping of the bills!

Concept Check 13.5 A chemist is trying to increase the reaction rate of the following reaction:



A. One researcher found that a special material significantly lowers the activation energy of the reaction. What effect does this have on the reaction? Answer: Lowering the Activation Energy should increase the rate [see diagrams above and the Arrhenius Equation where $\ln k = \ln A - E_a / RT$]

B. The rate law was experimentally determined to be: $\text{Rate} = k [\text{X}] [\text{Y}]$ Is this possible?

Answer: Yes as the rate law is not related to the reaction stoichiometry.

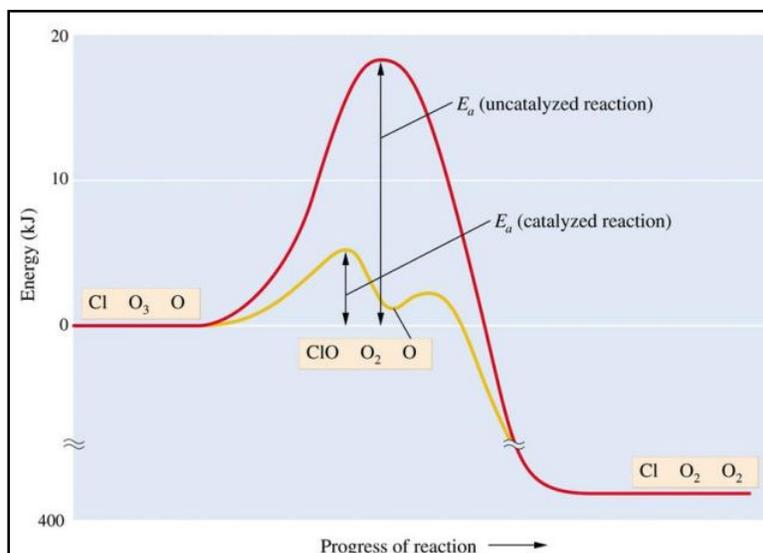
C. The mechanism is determined to be:

$$2 \text{Y} \rightarrow \text{I} \quad \text{Slow}$$
$$\text{X} + \text{I} \rightarrow \text{Z} \quad \text{Fast}$$

Is the rate law consistent with this mechanism? Answer: No – since the rate law shows the slow step is related only to the concentration of Y. So $\text{Rate} = k [\text{Y}]^2$.

Catalysis

A catalyst is a substance that speeds up a reaction without being consumed. It lowers the Activation Energy:



Homogeneous Catalyst is used in the same phase as the reaction species:

STUDENTS FIND AN EXAMPLE For the test

Heterogeneous Catalyst is used in a different phase from the reaction species, usually a solid catalyst in contact with a gas or liquid solution of reactants.

STUDENTS FIND AN EXAMPLE For the test

Enzyme Catalyst

STUDENTS FIND AN EXAMPLE For the test

Practice Questions:

Review Questions: 13.1, 13.3, 13.4, 13.7, 13.9, 13.11, 13.12, 13.15, 13.18, 13.20

Concept Questions: 13.25, 13.26, 13.28, 13.30

Practice Problems:

Reaction Rates: 13.33, 13.37, 13.39
Rate Laws 13.41, 13.43, 13.45, 13.47
Integrated Rate Laws 13.51, 13.53, 13.57
Rate & Temperature 13.69, 13.71
Reaction Mechanism 13.77, 13.78, 13.87
Cumulative Skills 13.123