

Today

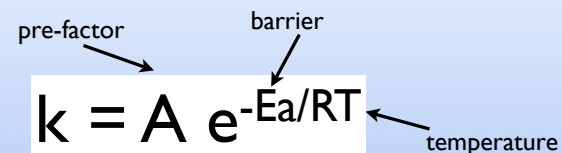
Review Transition State Theory
Arrhenius Theory

Kinetic Mechanisms

Why does a reaction follow a particular rate law?
What is actually happening in the reaction?

Arrhenius Law

The rate constant k is a function of temperature



Arrhenius Law

The higher the temperature the more molecules that have enough energy to make it over the barrier

Let's make a new Equation

$$k = A e^{-E_a/RT} \quad \ln k = \ln A - E_a/RT$$

let's look at two temperatures

$$\ln k_1 = \ln A - E_a/RT_1$$

$$\ln k_2 = \ln A - E_a/RT_2$$

Let's make a new Equation

$$k = A e^{-E_a/RT} \quad \ln k = \ln A - E_a/RT$$

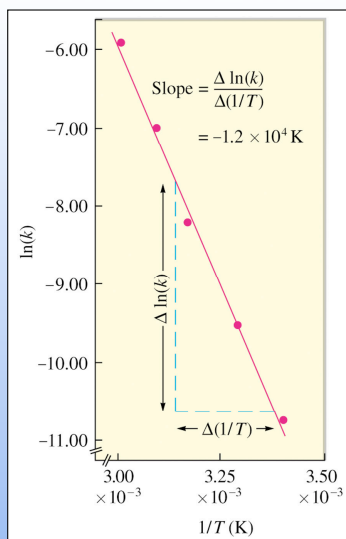
let's look at two temperatures

$$\ln k_1 = \ln A - E_a/RT_1$$

$$\ln k_2 = \ln A - E_a/RT_2$$

subtract to get a new equation that doesn't have A

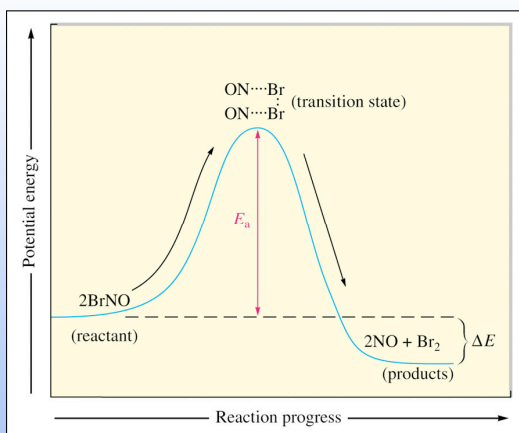
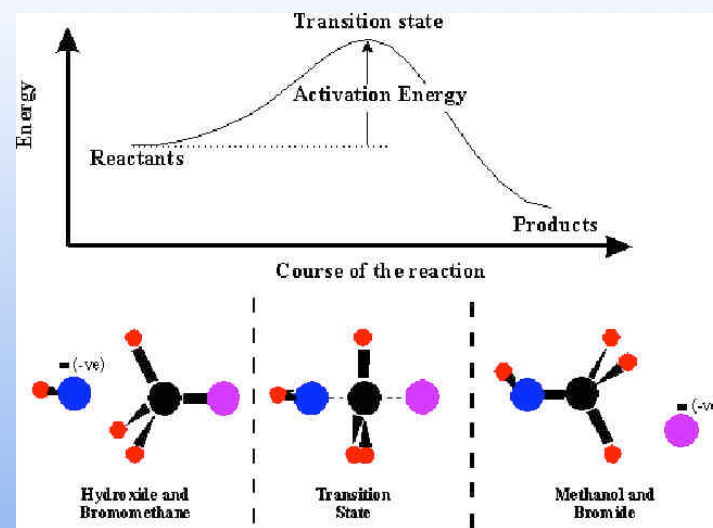
$$\ln(k_2/k_1) = \frac{-E_a}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$



The activation energy for this reaction is?

- A. $-1.2 \times 10^4 \text{ K}$
- B. $1 \times 10^5 \text{ J mol}^{-1}$
- C. $1.2 \times 10^4 \text{ J mol}^{-1}$
- D. $1 \times 10^5 \text{ K}$
- E. $-1 \times 10^2 \text{ kJ mol}^{-1}$

$\text{Slope} = -E_a/R$
 $E_a = -R \times \text{slope}$
 $E_a = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (-1.2 \times 10^4 \text{ K}) = 1 \times 10^5 \text{ J mol}^{-1}$



Why are reactions faster at higher temperatures?

More molecules have sufficient energy to get over the barrier. **BIG EFFECT**

More molecules have collisions (but this is a very small effect) that is ignored in Arrhenius view of transition state theory

Why is something first order?
second order?

Because of the number of molecules involved
in the "key" (slowest) step in the reaction

We need to think about what is actually happening

This is the mechanism of the reaction

Nonsense "real world" example

student + quiz + TA \longrightarrow happy student with
quiz turned in

student + TA + quiz \longrightarrow student with quiz + TA

student with quiz \longrightarrow student with completed quiz

student with completed quiz + TA \longrightarrow happy student with
quiz turned in

What controls the rate of this reaction?

Nonsense "real world" example

student + quiz + TA \longrightarrow happy student with
quiz turned in

student + TA + quiz \longrightarrow student with quiz + TA

student with quiz \longrightarrow student with completed quiz

student with completed quiz + TA \longrightarrow happy student with
quiz turned in

imagine step one was very slow (we passed out
preprinted bubble sheets in alphabetical order checking ID
before handing you the quiz)

Rate dominated by "handing" out the quiz

Nonsense "real world" example

student + quiz + TA \longrightarrow happy student with
quiz turned in

student + TA + quiz \longrightarrow student with quiz + TA

student with quiz \longrightarrow student with completed quiz

student with completed quiz + TA \longrightarrow happy student with
quiz turned in

What we want. All steps to be fast except step 2
Then the rate is dominated by step 2
However step 1 still matters

Nonsense "real world" example

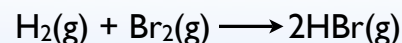
student + quiz + TA \longrightarrow happy student with quiz turned in

student + TA + quiz \longrightarrow student with quiz + TA

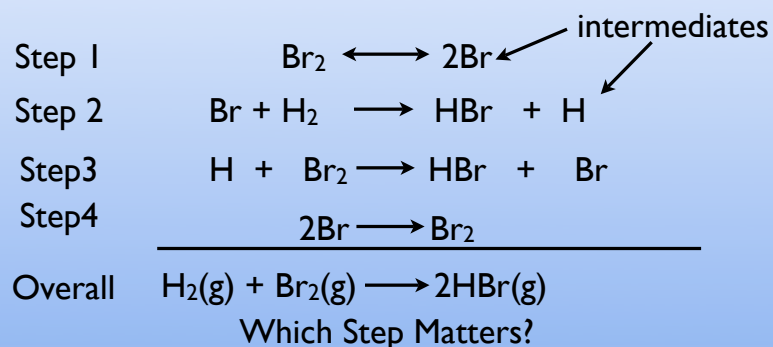
student with quiz \longrightarrow student with completed quiz

student with completed quiz + TA \longrightarrow happy student with quiz turned in

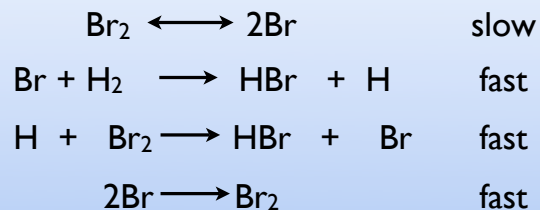
dominated by step 3. You need to have your quiz notarized before turning it in.
All three steps matter



What actually happens?
Does a H_2 and a Br_2 molecule collide and react?
Does something else happen?

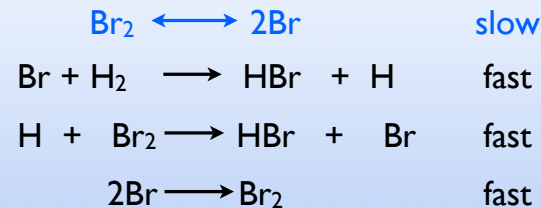


The rate is dominated by the slowest step
this is called the "rate limiting step"



As soon as some Br is formed it reacts very rapidly through the other step.
The rate is dominated by "waiting" for step 1

With this mechanism what is the predicted rate law?

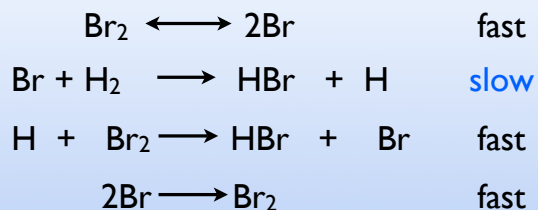


What molecules are reactants in the slow step?

only one molecule of Br_2

Therefore rate = $k[\text{Br}_2]$

What if this was the mechanism?

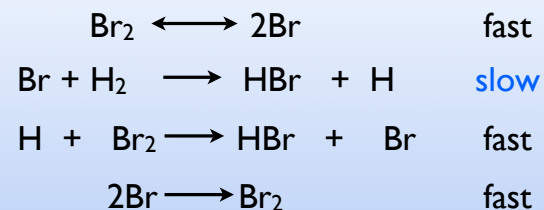


$$\text{rate} = k[\text{Br}][\text{H}_2]$$

Can't have Br in the rate law it is an intermediate

where did the Br come from?

What if this was the mechanism?

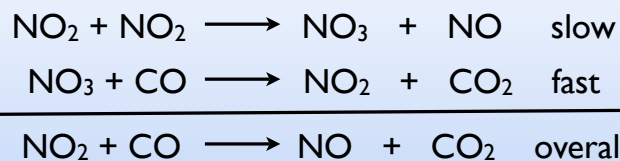


$$\text{rate} = k[\text{Br}][\text{H}_2]$$

You need 1/2 mole of Br₂ to get one mole Br
therefore

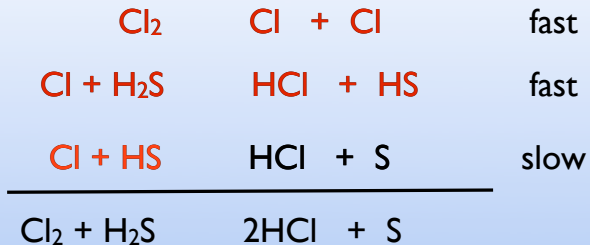
$$\text{rate} = k[\text{Br}_2]^{1/2}[\text{H}_2]$$

What is the rate law expected for the given mechanism?



- A. rate = $k[\text{NO}_2][\text{CO}]$
B. rate = $k[\text{NO}_3][\text{CO}]$
C. rate = $k[\text{NO}_2]^2[\text{CO}]$ ← two molecules of NO₂ in rate limiting step
D. rate = $k[\text{NO}_2]^2$
E. rate = $k[\text{NO}_2]^2[\text{NO}_3][\text{CO}]$

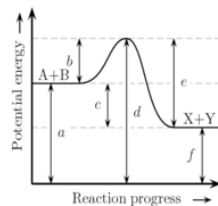
Mechanisms that involve products



$$\text{rate} = k \frac{[\text{Cl}][\text{H}_2\text{S}]}{[\text{HCl}][\text{HS}]} \times \frac{[\text{Cl}_2]}{[\text{Cl}]^2} = \frac{[\text{Cl}_2][\text{H}_2\text{S}]}{[\text{HCl}]}$$

001

Consider the following potential energy diagram.



Which arrow represents the activation energy?

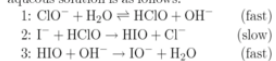
1. *a*
2. *e*
3. *b*,
4. *f*
5. *d*
6. *c*

Explanation:

Principle

001

The mechanism proposed for the oxidation of the iodide ion by the hypochlorite ion in aqueous solution is as follows:



What is the rate law for the formation of HIO implied by this mechanism?

1 rate = $k \frac{[\text{ClO}^-][\text{I}^-]}{[\text{H}_2\text{O}]}$

2 rate = $k \frac{[\text{OH}^-][\text{ClO}^-]}{[\text{I}^-]}$

3 rate = $k \frac{[\text{ClO}^-]}{[\text{OH}^-]}$

4 rate = $k \frac{[\text{OH}^-][\text{I}^-]}{[\text{ClO}^-]}$

5 rate = $k \frac{[\text{ClO}^-][\text{I}^-]}{[\text{OH}^-]}$

Principle

Bout