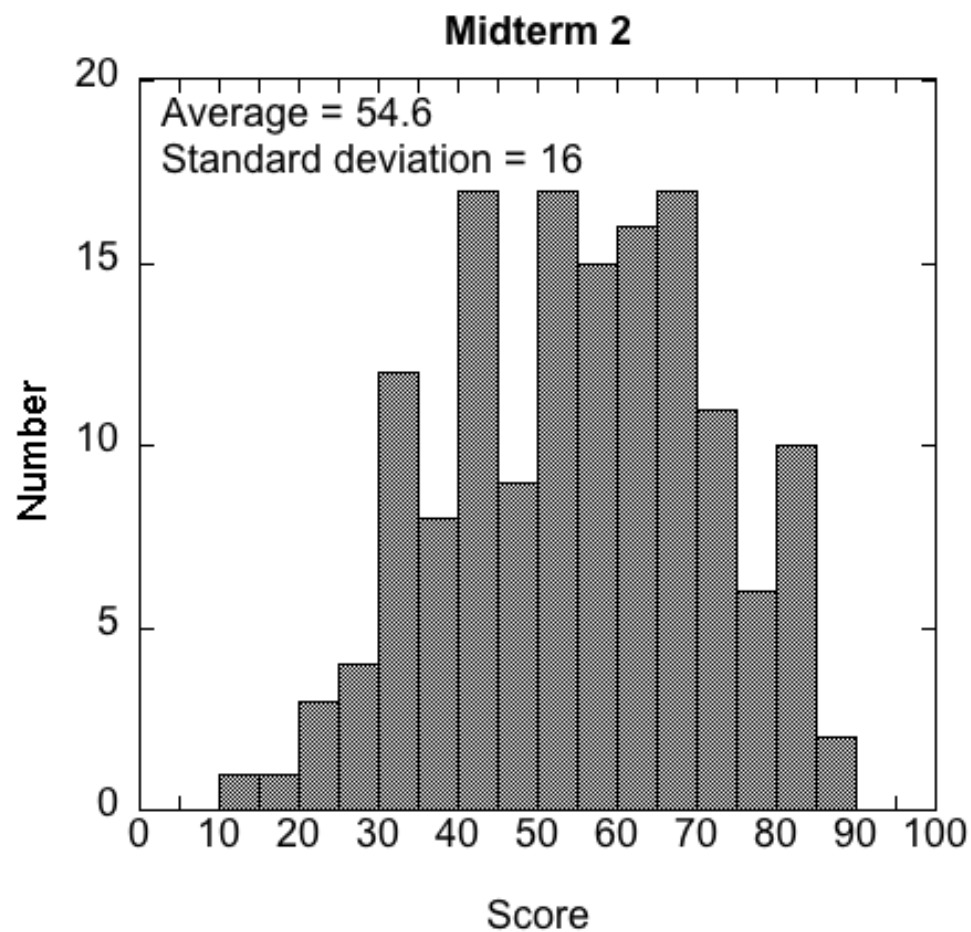


Physical Chemistry (Chem 132A)



Lecture 22

Monday, November 29



MIDTERM 2



1. Check your exam for clerical errors
 - did we transfer scores to the front page correctly
 - did we add your scores on the front page correctly
 - was your total score recorded correctly in the eee gradebook
2. Review the Midterm 2 answers that are posted on the course Canvas website.
3. If there is a clerical error send me an email.
Include your student id and attach exam pdf.

**NEW HOMEWORK ASSIGNMENT
AVAILABLE ON WEBASSIGN
DUE SATURDAY: 11:59PM**

EFFECT OF TEMPERATURE ON RATES



Svante Arrhenius

Arrhenius Equation:

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

A = “Arrhenius pre-exponential factor”

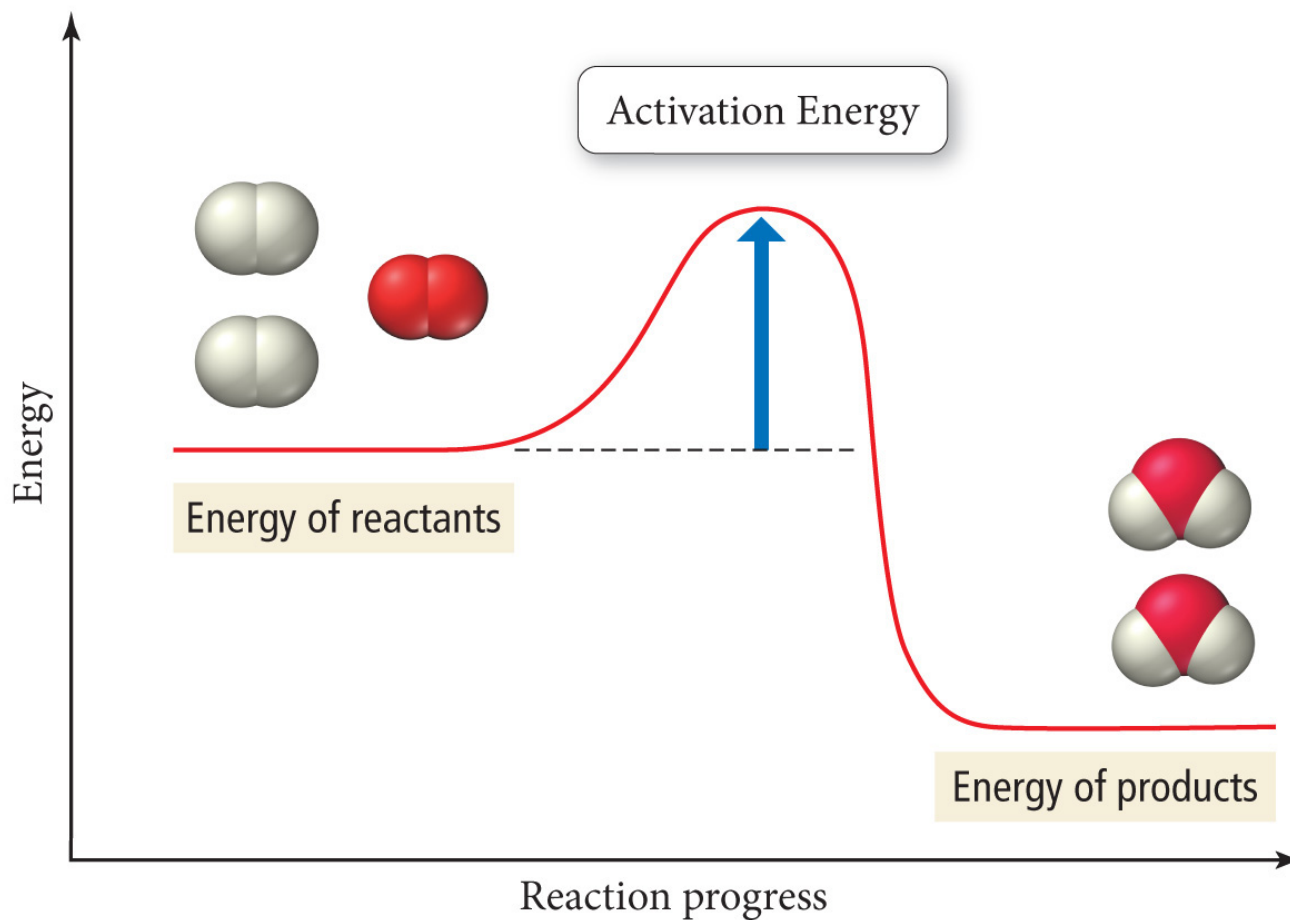
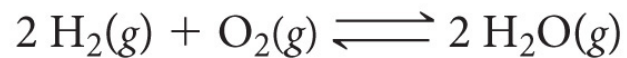
R = the gas constant = 8.314 J/mol•K

T=temperature (in Kelvin!!)

ENERGY BARRIER TO REACTION



Activation Energy



THE ARRHENIUS PRE-FACTOR



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

$$= pze^{\frac{-E_a}{RT}}$$

Orientation factor

Collision frequency

CAN WE INCREASE THE RATE??



Temperature

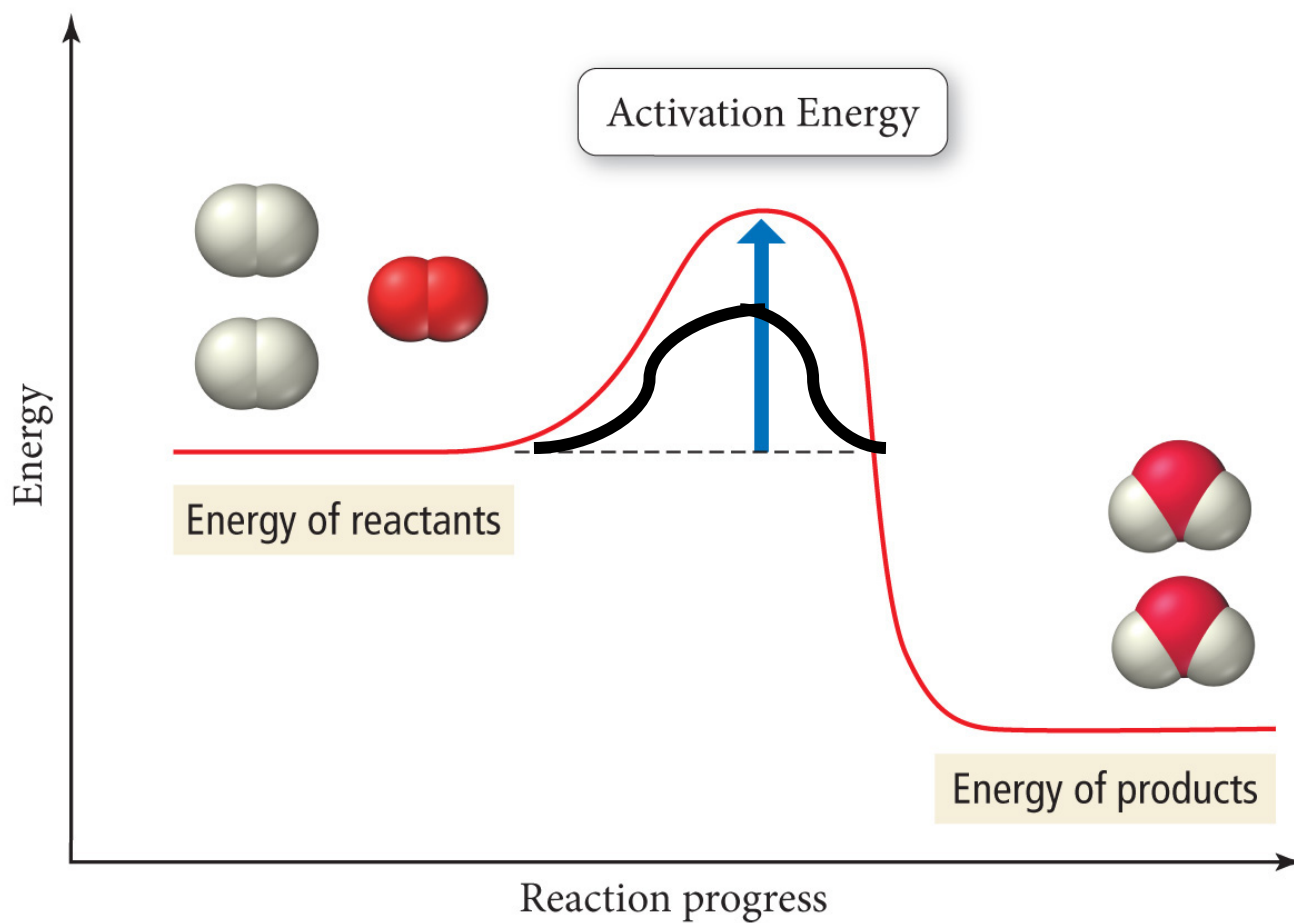
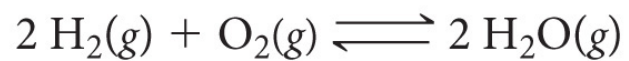
A Catalyst

e.g. Automobile exhaust catalyst

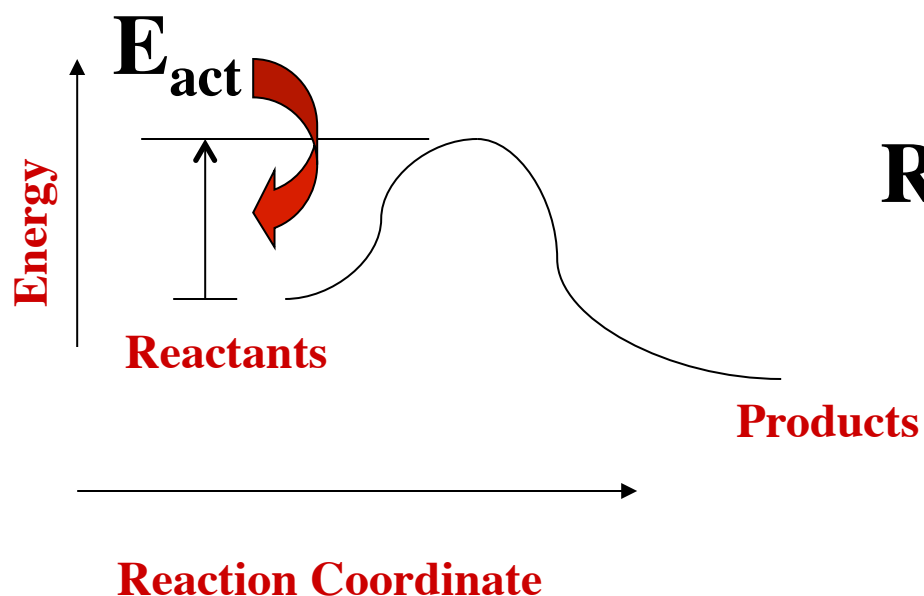
how does this work??



Activation Energy



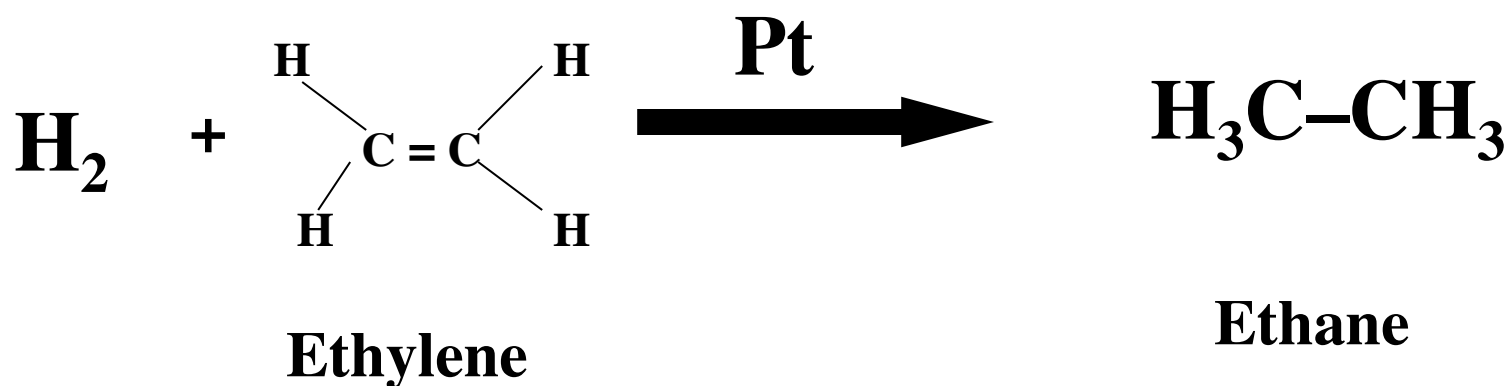
Catalysis



$$\text{Rate} = A \exp(-E_{\text{act}}/kT)$$

A catalyst can increase the rate by
increasing A , or by decreasing E_{act}

An Example: Hydrogenation of Ethylene



To minimize the amount of expensive metal (Pt) a catalyst is often
Made by dispersing the metal on a high surface area support
(e.g. alumina, silica). Surface areas can be as high as 1000 meter²/ gram

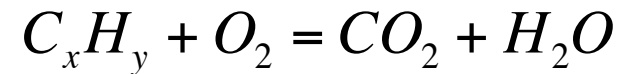
Automobile Exhaust Catalytic Converter



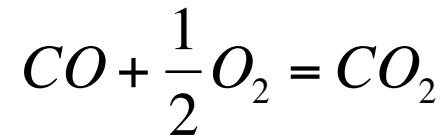
Compounds we would like to remove from car exhaust

1. Unburned hydrocarbons (C_xH_y)

Oxidation

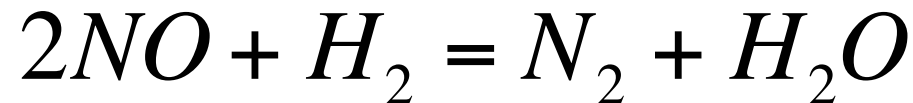


2. CO



Reduction

3. NO_x



“Three Way Catalyst”



Oxidizes hydrocarbons and CO at the same time that it reduces NO_x

Commercial catalyst is Pt/Rh supported on a “honeycomb” oxide structure

A example of the success of fundamental science in US industry

Air Fuel Ratio has to be controlled

too rich oxidation doesn't work well

too lean reduction doesn't work well

Oxygen Sensors

Multivalent Oxide supports such as CeO_x to act as oxygen storage

Have to avoid catalyst POISONS

LEAD

SULFUR

New catalysts that do not use precious metals are under development



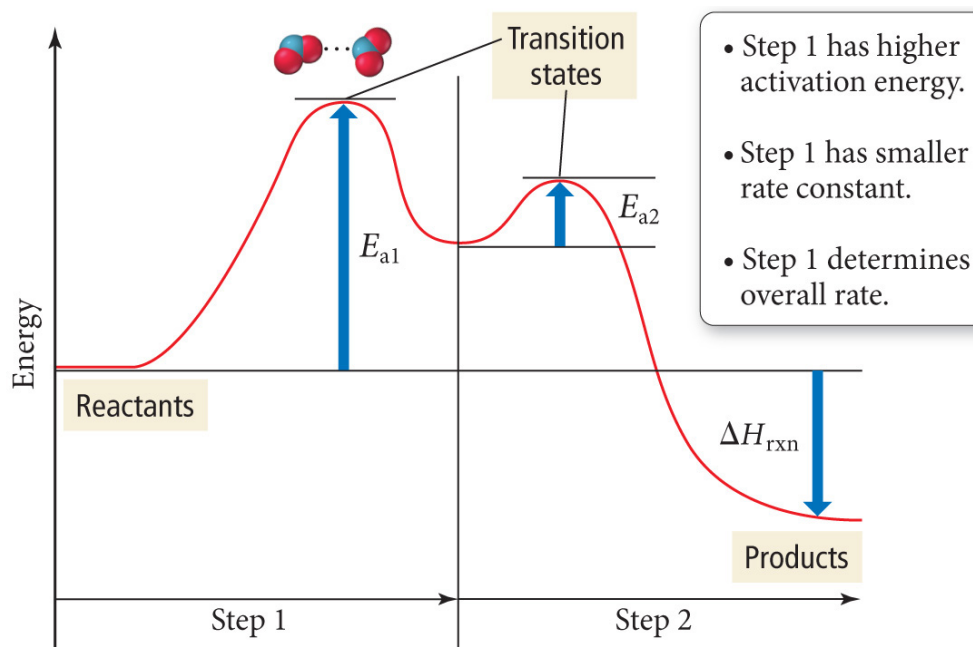
Relationship between reaction mechanisms and rate laws when overall reaction is not an elementary step??

TWO STEP REACTION WITH SLOW FIRST STEP



The slow first step controls the rate of the reaction

$$\text{Rate} = k[\text{NO}_2]^2$$



REACTION INTERMEDIATES

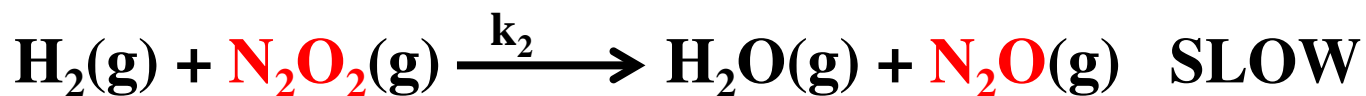
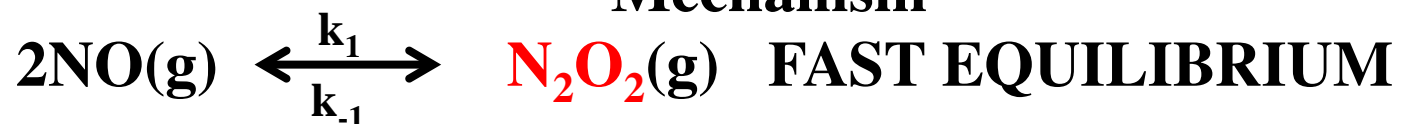


Intermediate---formed and used up in course of reaction.
In last example NO_3 is an intermediate.

What if the first elementary step is not SLOW?



Mechanism

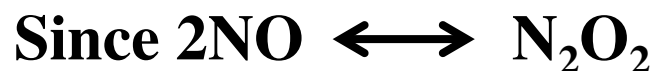


USE THE EQUILIBRIUM CONDITION



$$\text{Rate} = k_2[\text{H}_2][\text{N}_2\text{O}_2] \quad \text{**Based on the SLOW STEP**}$$

We don't want the N_2O_2 in the rate law since it isn't a reactant or product.



Is at equilibrium----forward rate = reverse rate

$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]_{\text{EQ}}$$

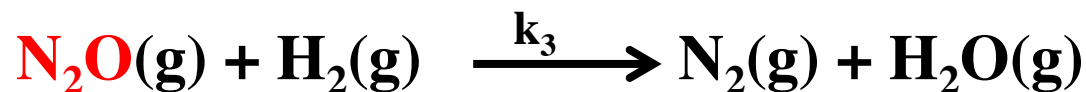
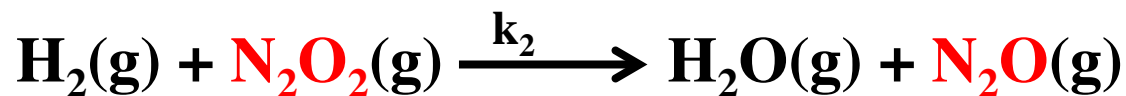
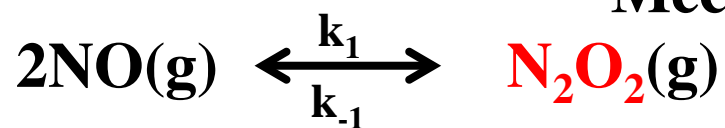
$$[\text{N}_2\text{O}_2]_{\text{EQ}} = (k_1/k_{-1})[\text{NO}]^2$$

$$\text{Rate} = k_2[\text{H}_2](k_1/k_{-1})[\text{NO}]^2 = k[\text{H}_2][\text{NO}]^2$$

WHAT IF WE DON'T KNOW THAT STEP 2 IS SLOW? STEADY STATE APPROXIMATION



Mechanism



We might write: $\text{Rate} = \frac{d[\text{N}_2]}{dt} = k_3[\text{N}_2\text{O}][\text{H}_2]$

Intermediate



Steady State Approximation