Physical Chemistry (Chem 132A)

Lecture 21
Monday, November 27

Midterm 2
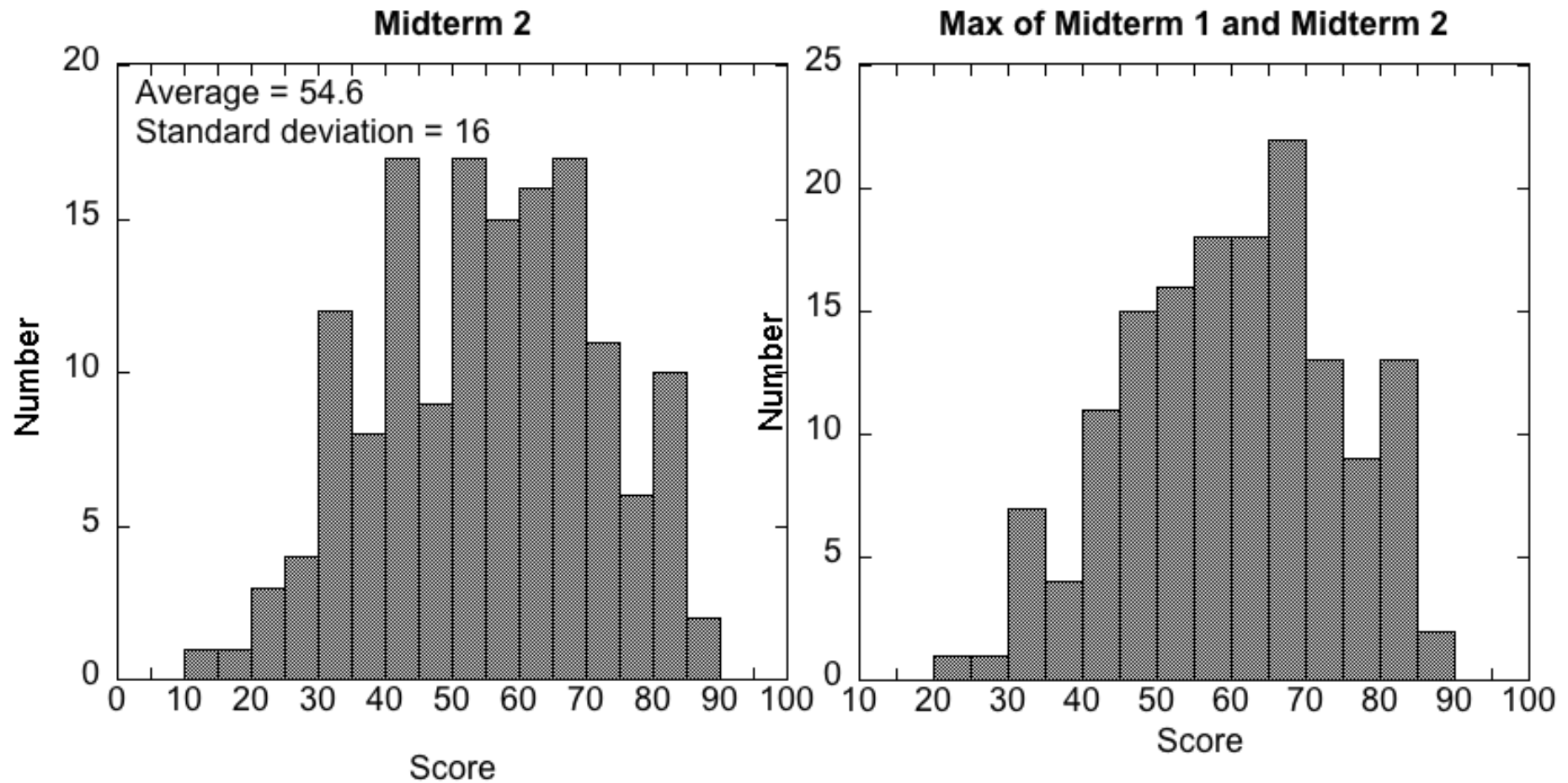
Schedule:

Week	Dates	Topics	Readings
0	Before Sept 28	The Properties of Gases	Chapter 1 A, B, C
1	October 1-7	The First Law of Thermodynamics	Chapter 2
2	October 8-14	The First and Second Laws	Chapter 2, 3
3	Oct 15-Oct 21	Third Law; Physical Transformations	Chapter 3, 4
4	October 22-28	Physical Transformations; Mixtures	Chapter 4, 5
Midterm 1 (Chapters 1-4, 5A), Wednesday, October 25			
5	Oct. 29-Nov. 4	Mixtures; Chemical Equilibrium	Chapter 5, 6
6	Nov. 5-11	Chemical Equilibrium	Chapter 6
7	Nov. 12-18	Molecular Motion	Chapter 19
8	Nov. 19-25	Molecular Motion	Chapter 19
Midterm 2 (Chapters 1-6, 19), November 22			
9	Nov. 26-Dec. 2	Chemical Kinetics	Chapter 20
10	Dec. 3-Dec. 9	Chemical Kinetics, Collision Theory	Chapter 20, 21A
Final Exam (Chapters 1-6, 19, 20, 21A), Friday, Dec. 15, 8:00Am-10:00Am			

New Homework (WebAssign) available tonight. Due Sat. Dec 2

We will probably cover through Chapter 21C
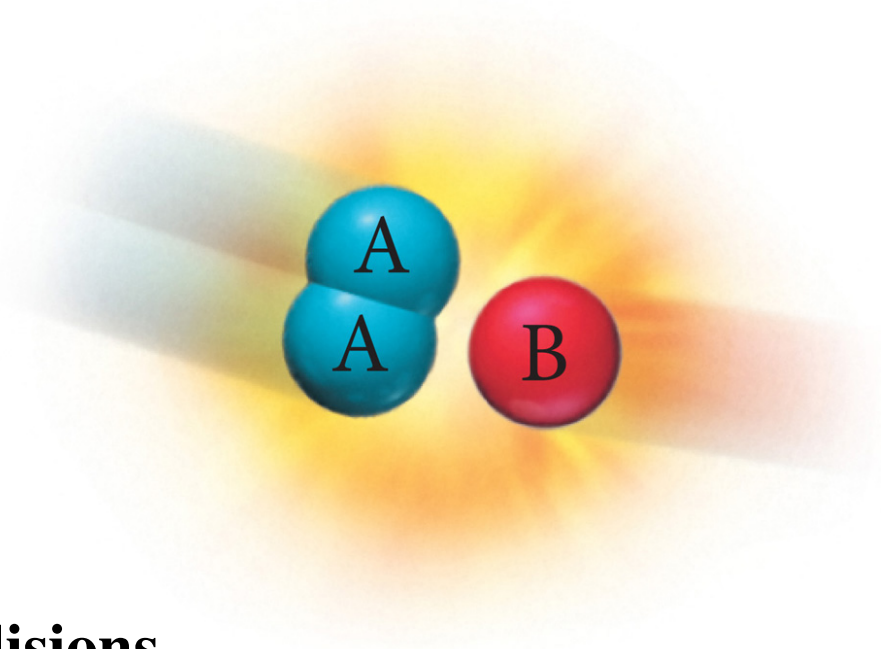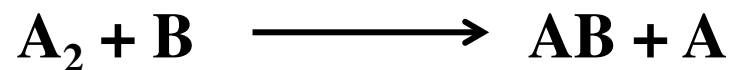
$$A_2 + B \longrightarrow AB + A$$

Collisions
> **Concentrations**
> **Speed**

Is every collision effective???
> **orientation**
> **speed---energy requirement**

REACTION RATES

What do we mean by "rate" of a reaction

$$H_2 + I_2 \longrightarrow 2HI$$
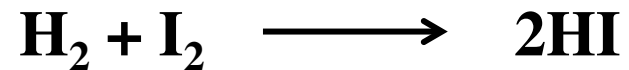
Chemical reaction rate: definition

Can we provide a definition for the reaction rates?

Reaction rate is the number (mol) of chemical reactions occurring in the system per reaction volume (L) per time (s)

Reaction rate is usually measured in mol L^{-1} s^{-1}

$$A \longrightarrow B$$

Reaction rate is the number of mol/L of A that are converted into B every second (**A POSITIVE NUMBER**)

$$\text{rate} = -\frac{d[A]}{dt}$$

d[A] = change in concentration of A over time period dt

$$\text{rate} = +\frac{d[B]}{dt}$$

d[B] = change in concentration of B over time period dt

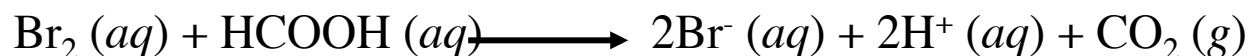Because [A] decreases with time, d[A] is negative.
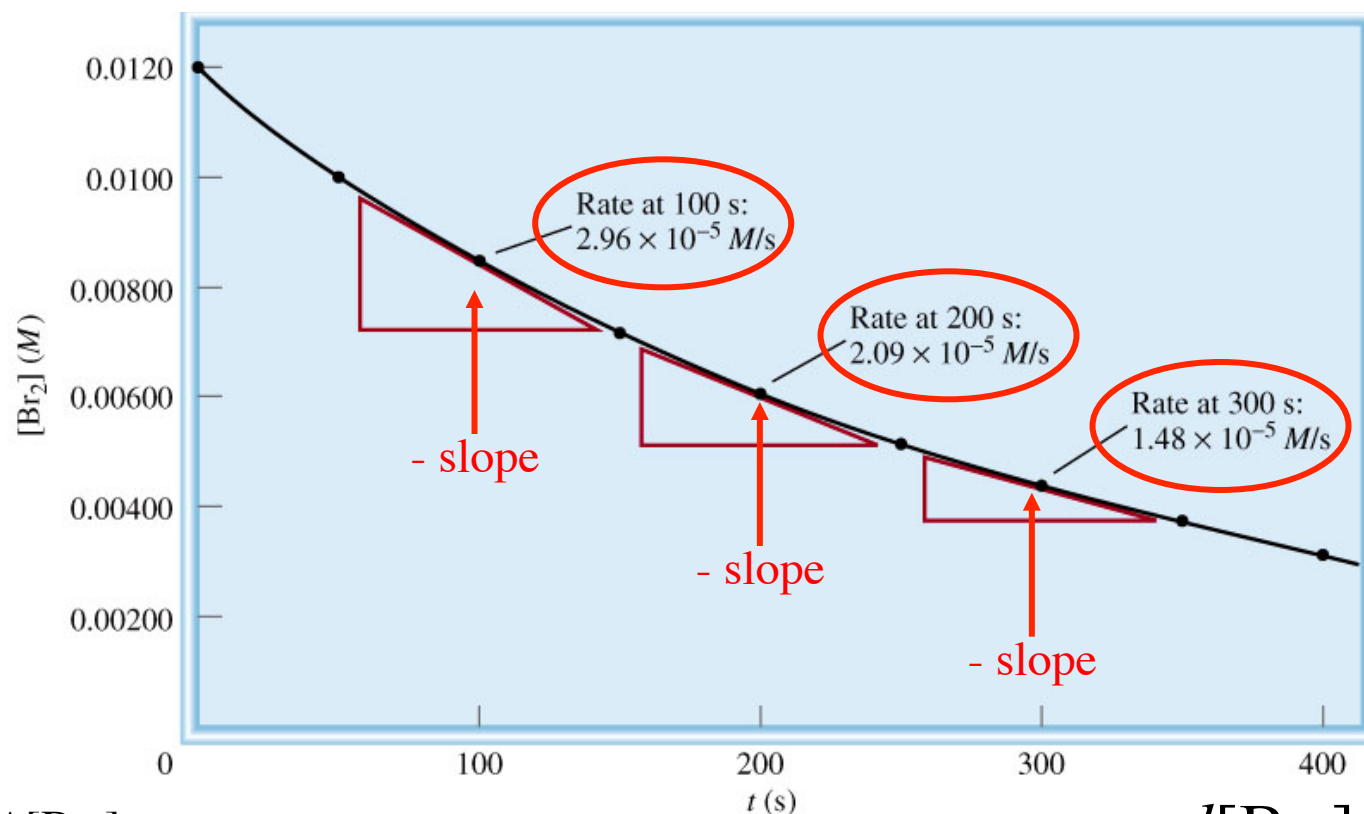
STOICHIOMETRY AND RATES

IN GENERAL

$$a\,\text{A} + b\,\text{B} \longrightarrow c\,\text{C} + d\,\text{D}$$

$$\text{rate} = -\frac{1}{a}\frac{d[\text{A}]}{dt} = -\frac{1}{b}\frac{d[\text{B}]}{dt} = +\frac{1}{c}\frac{d[\text{C}]}{dt} = +\frac{1}{d}\frac{d[\text{D}]}{dt}$$

RATES CHANGE WITH TIME—WHY??

$$Br_2\ (aq) + HCOOH\ (aq) \longrightarrow 2Br^-\ (aq) + 2H^+\ (aq) + CO_2\ (g)$$

Time (s)	$[Br_2]$ (M)
0.0	0.0120
50.0	0.0101
100.0	0.00846
150.0	0.00710
200.0	0.00596
250.0	0.00500
300.0	0.00420
350.0	0.00353
400.0	0.00296

Rate at 100 s:
2.96×10^{-5} M/s

Rate at 200 s:
2.09×10^{-5} M/s

Rate at 300 s:
1.48×10^{-5} M/s

- slope
- slope
- slope

$[Br_2]$ (M)

t (s)

$$average\ rate = -\ \frac{\Delta[Br_2]}{\Delta t}$$

$$= -\ \frac{[Br_2]_{final} - [Br_2]_{initial}}{t_{final} - t_{initial}}$$

$$instantaneous\ rate = -\ \frac{d[Br_2]}{dt}$$

$$\Delta t \longrightarrow 0$$

RATE LAWS (tells how the rate depends on concentrations)

Discuss "elementary steps" first

$$A + B \longrightarrow C \qquad ???$$

$$RATE \sim [A][B] = k[A][B]$$

WHAT ABOUT

$$2D + E \longrightarrow F \ ??? \quad \text{Unlikely to be an elementary step}$$

HOW ABOUT

$$H_2O_{2(aq)} + 3I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow I_3^-{}_{(aq)} + 2H_2O_{(l)} \ \ ????$$

$$aA + bB \longrightarrow cC + dD$$
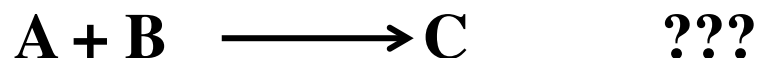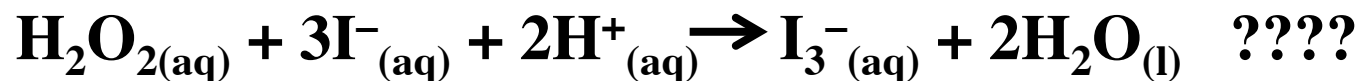
Unless you KNOW that the reaction as written is an ELEMENTARY STEP you don't know how to write down the rate law simply from the stoichiometric coefficients.

THE RATE LAW MUST BE DETERMINED EXPERIMENTALLY---BY MEASURING HOW THE RATE CHANGES AS THE CONCENTRATIONS ARE CHANGED.

HOW IS THE RATE LAW DETERMINED?

A $\longrightarrow$ PRODUCTS (not an elementary step)

SIMPLE CASES:

Rate = k [A]^0 zeroth order rate law

Rate = k[A]^1 first order rate law

Rate = k[A]^2 second order rate law

aA + bB $\longrightarrow$ cC + dD

In general:
Rate = k[A]^m[B]^n

Consider the reaction between nitrogen dioxide and carbon monoxide:

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

The initial rate of the reaction is measured at several Different concentrations of the reactants with the results shown at right. From the data, determine:

$Rate_0 = k[NO_2]_0^a$

$\log(Rate_0) = \log k + a \log[NO_2]$

Plot $\log(Rate_0)$ vs $\log[NO_2]$ to get a

(a) the rate law for the reaction
(b) the rate constant (k) for the reaction

Experiment Number	[NO₂] (M)	[CO] (M)	Initial Rate (M/s)
1	0.10	0.10	0.0021
2	0.20	0.10	0.0082
3	0.20	0.20	0.0083
4	0.40	0.10	0.033

$$Rate = k[NO_2]^2[CO]^0 = k[NO_2]^2$$

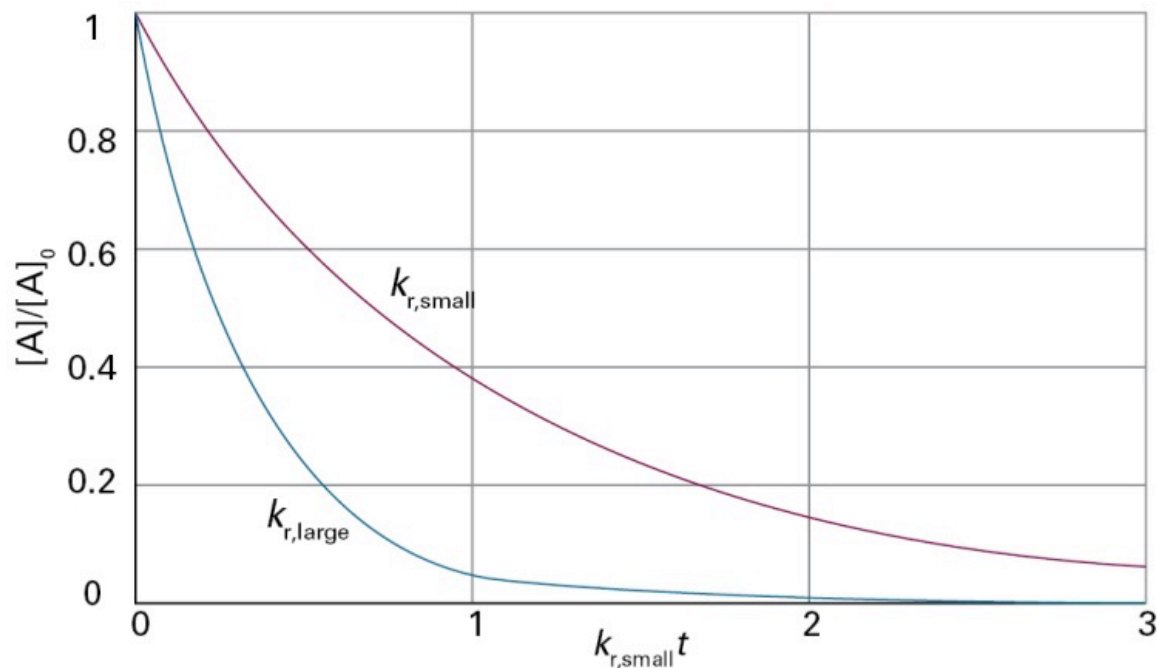# INTEGRATED RATE LAWS

Example: First order reaction

$$\frac{d[A]}{dt} = -k_r[A]$$

$$\frac{d[A]}{[A]} = -k_r dt$$

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k_r \int_0^t dt$$

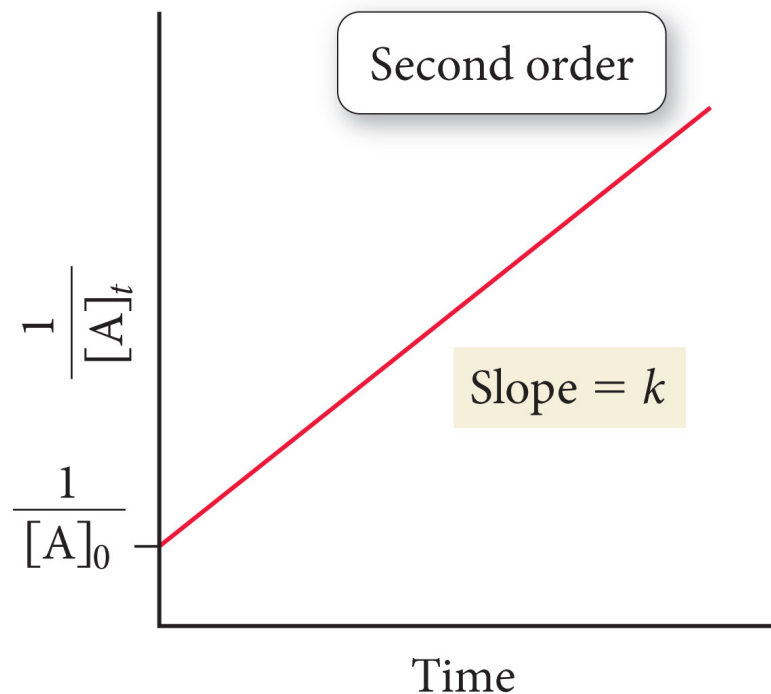$$\ln \frac{[A]}{[A]_0} = -k_r t$$

$$[A] = [A]_0 e^{-k_r t}$$
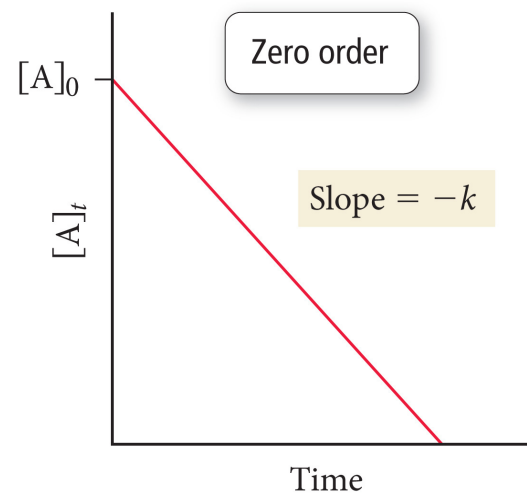
INTEGRATED RATE LAWS

SECOND ORDER

RATE = k[A]²

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

Second order

$\frac{1}{[A]_t}$

Slope = k

$\frac{1}{[A]_0}$

Time

ZEROTH ORDER

RATE = k[A]⁰ = k

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

Zero order

$[A]_0$

$[A]_t$

Slope = $-k$

Time

HALF LIFE

Time required for reactant concentration to fall by a factor of 2.

$$\ln \frac{[A]_t}{[A]_0} = -kt$$

FOR SECOND ORDER REACTION??

$$t_{1/2} = \frac{1}{k}\frac{1}{[A]_0}$$

Not as useful because it depends on the starting concentration.

More complicated Integrated Rate Laws

Table 20B.3 Integrated rate laws

Order	Reaction	Rate law*	$t_{1/2}$
0	$A \rightarrow P$	$v = k_r$ $k_r t = x$ for $0 \le x \le [A]_0$	$[A]_0 / 2k_r$
1	$A \rightarrow P$	$v = k_r [A]$ $k_r t = \ln \dfrac{[A]_0}{[A]_0 - x}$	$(\ln 2)/k_r$
2	$A \rightarrow P$	$v = k_r [A]^2$ $k_r t = \dfrac{x}{[A]_0 ([A]_0 - x)}$	$1/k_r [A]_0$
	$A + B \rightarrow P$	$v = k_r [A][B]$ $k_r t = \dfrac{1}{[B]_0 - [A]_0} \ln \dfrac{[A]_0 ([B]_0 - x)}{([A]_0 - x)[B]_0}$	
	$A + 2\,B \rightarrow P$	$v = k_r [A][B]$ $k_r t = \dfrac{1}{[B]_0 - 2[A]_0} \ln \dfrac{[A]_0 ([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
	$A \rightarrow P$ with autocatalysis	$v = k_r [A][P]$ $k_r t = \dfrac{1}{[A]_0 + [P]_0} \ln \dfrac{[A]_0 ([P]_0 + x)}{([A]_0 - x)[P]_0}$	
3	$A + 2\,B \rightarrow P$	$v = k_r [A][B]^2$ $k_r t = \dfrac{2x}{(2[A]_0 - [B]_0)([B]_0 - 2x)[B]_0}$ $+ \dfrac{1}{(2[A]_0 - [B]_0)^2} \ln \dfrac{[A]_0 ([B]_0 - 2x)}{([A]_0 - x)[B]_0}$	
$n \ge 2$	$A \rightarrow P$	$v = k_r [A]^n$ $k_r t = \dfrac{1}{n-1} \left\{ \dfrac{1}{([A]_0 - x)^{n-1}} - \dfrac{1}{[A]_0^{n-1}} \right\}$	$\dfrac{2^{n-1} - 1}{(n-1)k_r [A]_0^{n-1}}$

* $x = [P]$ and $v = dx/dt$

THINGS THAT EFFECT THE RATE

Collisions

    Concentrations

    Speed

Is every collision effective???

    orientation

    speed---energy requirement

TEMPERATURE DEPENDENCE

EFFECT OF TEMPERATURE ON RATES

Svante Arrhenius

Arrhenius Equation:

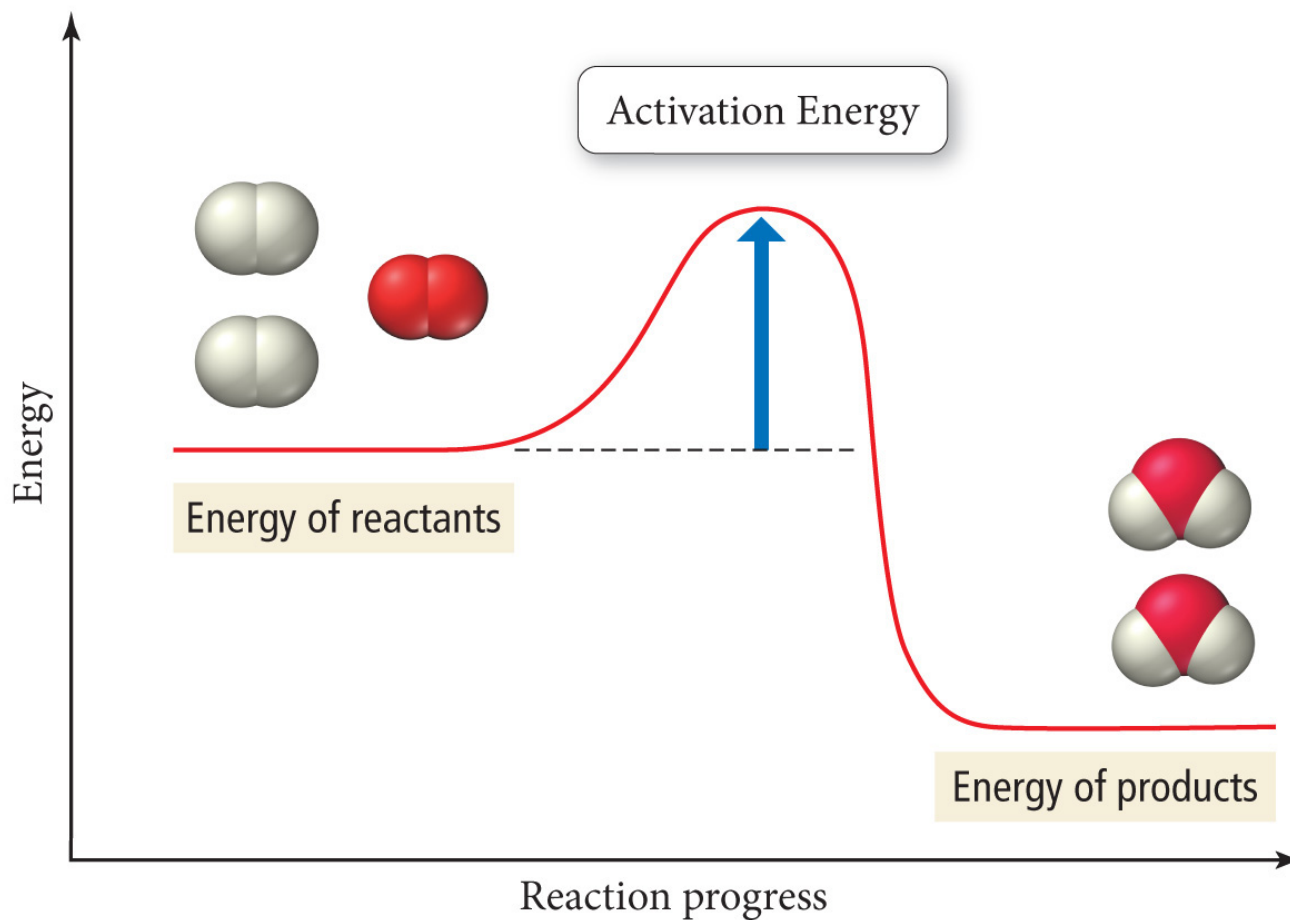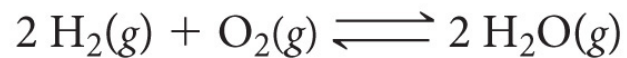$$k = A e^{\frac{-E_a}{RT}}$$

A = "Arrhenius pre-exponential factor"

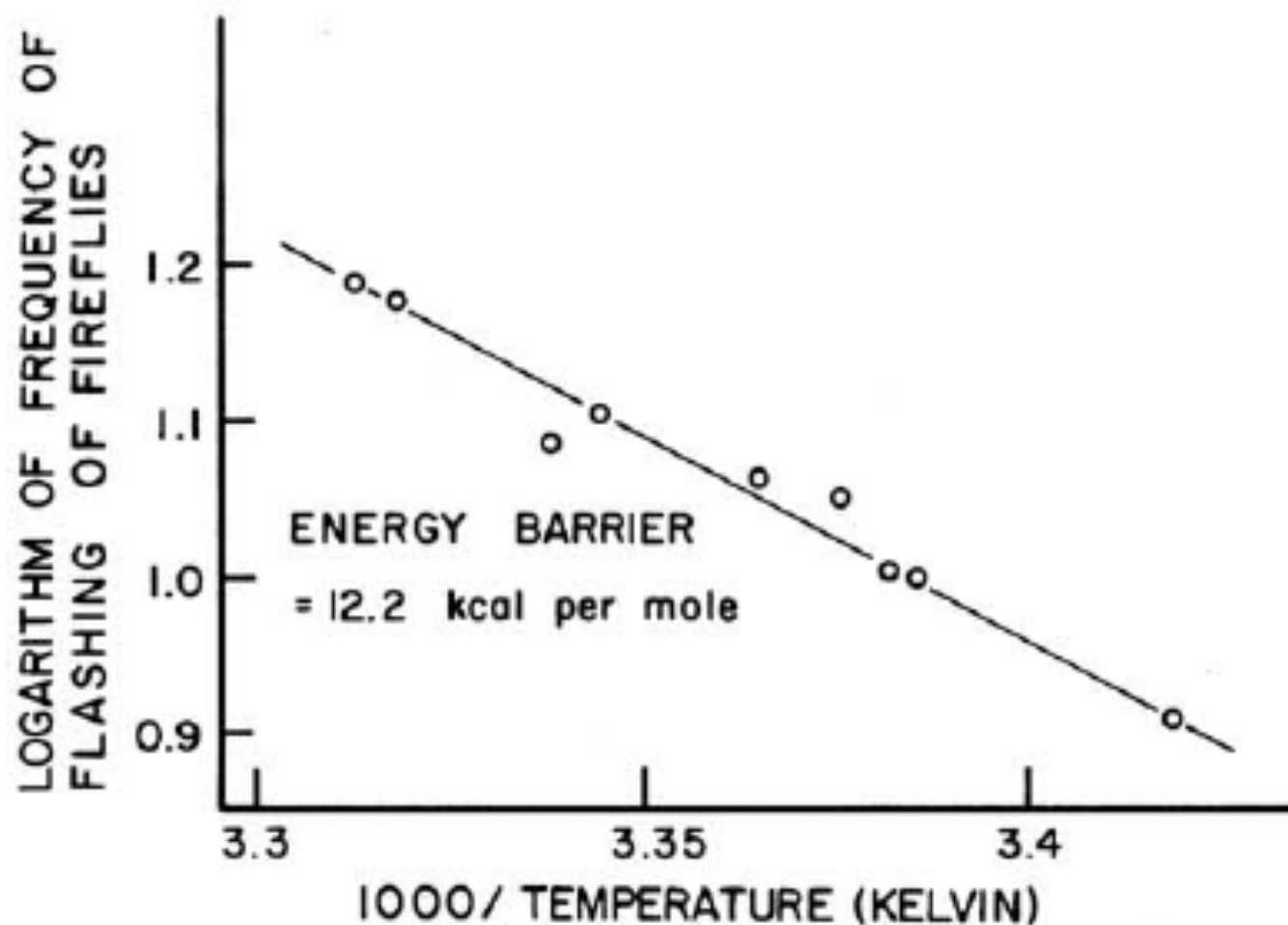**R = the gas constant = 8.314 J/mol•K**

T=temperature (in Kelvin!!)

Activation Energy

$$2\ H_2(g)\ +\ O_2(g)\ \rightleftharpoons\ 2\ H_2O(g)$$

Activation Energy

Energy of reactants

Energy of products

Energy

Reaction progress

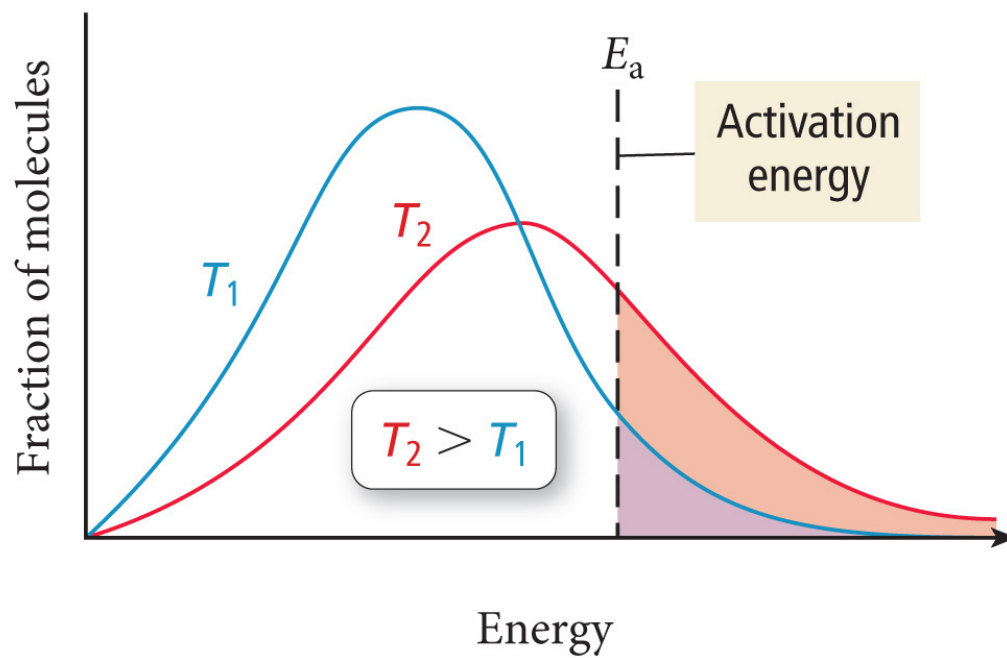**Journal of Chemical Education, Vol 49, Number 5, pg 343, 1972**
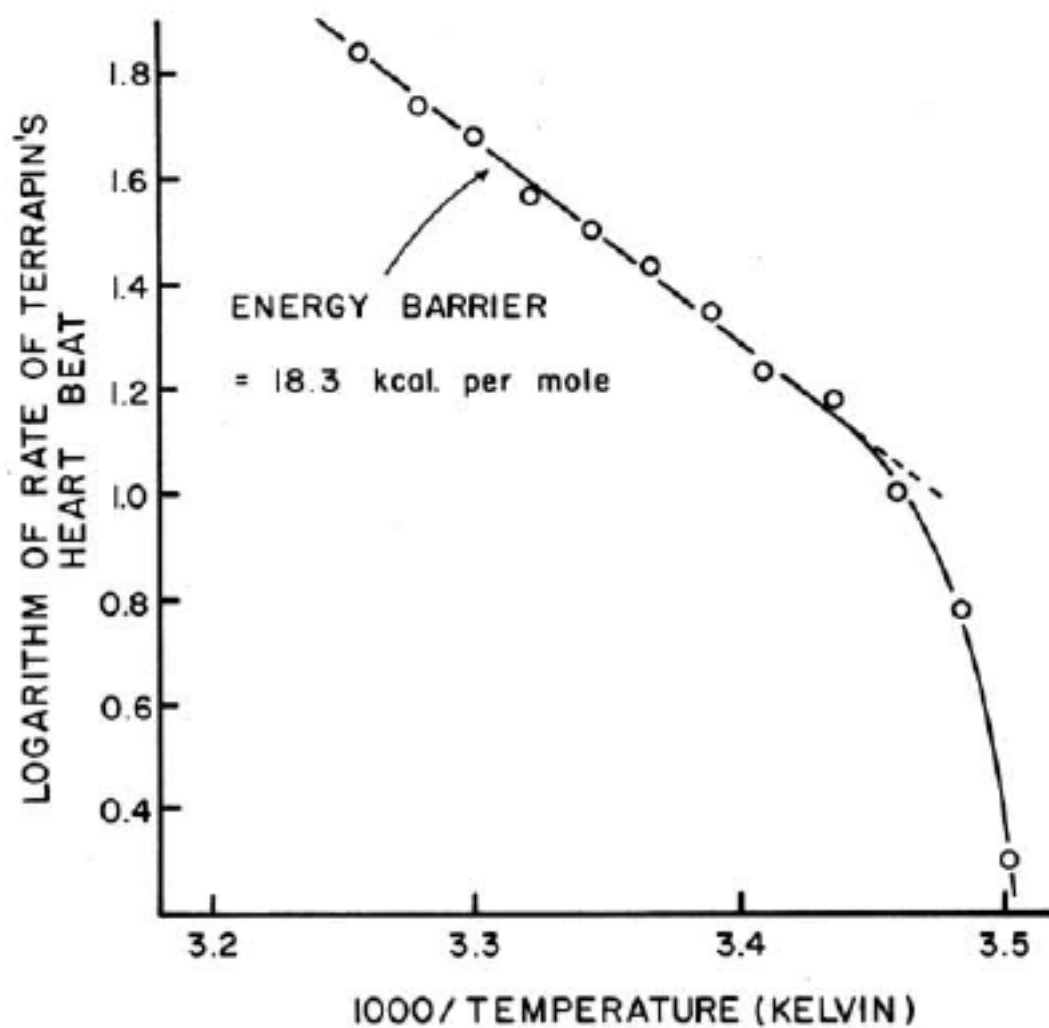
Journal of Chemical Education, Vol 49, Number 5, pg 343, 1972

HOW TEMPERATURE IMPACTS RATE

Thermal Energy Distribution

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

THE ARRHENIUS PRE-FACTOR

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

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

Orientation factor   Collision frequency

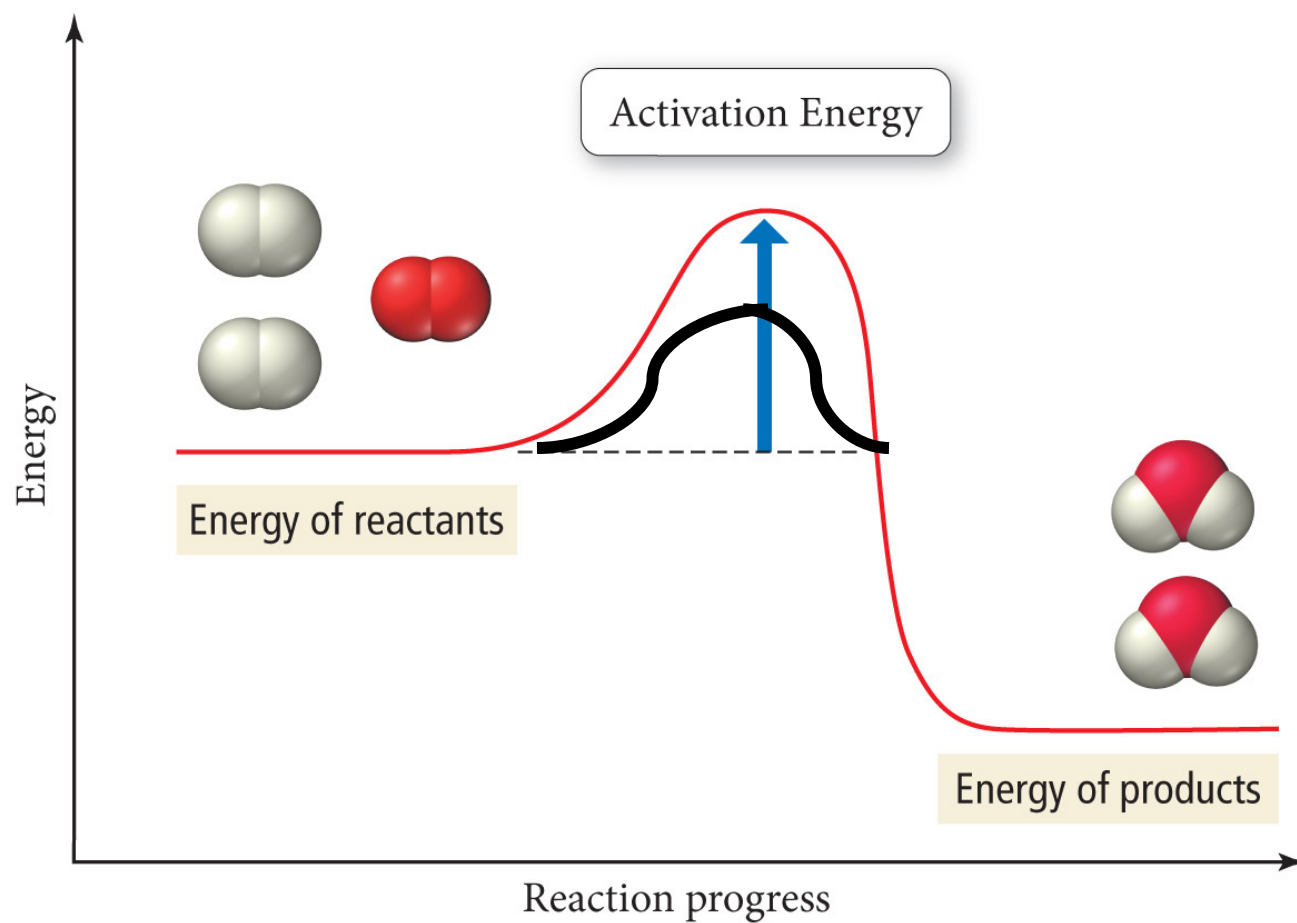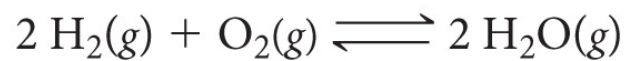# CAN WE INCREASE THE RATE??
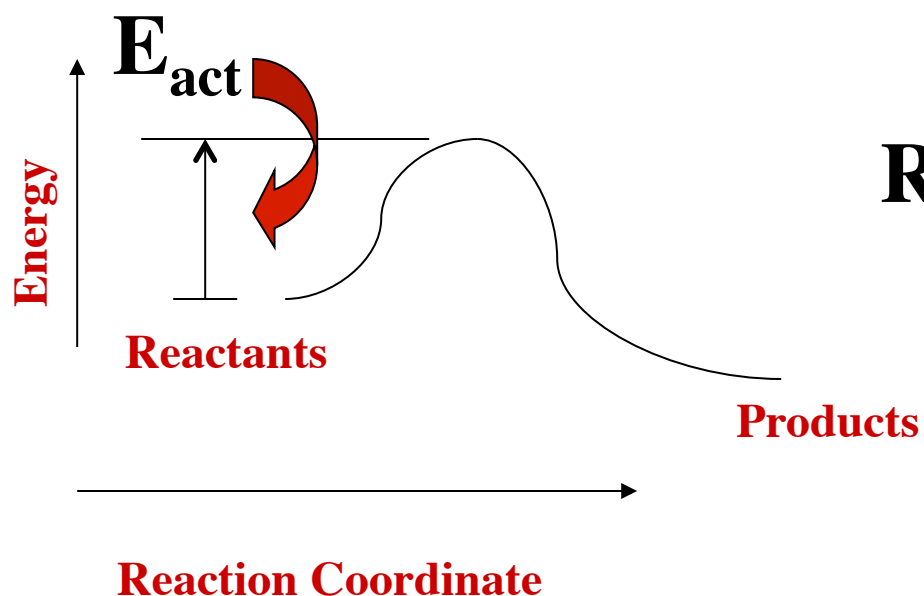
Temperature

A Catalyst
e.g. Automobile exhaust catalyst
   how does this work??

Activation Energy

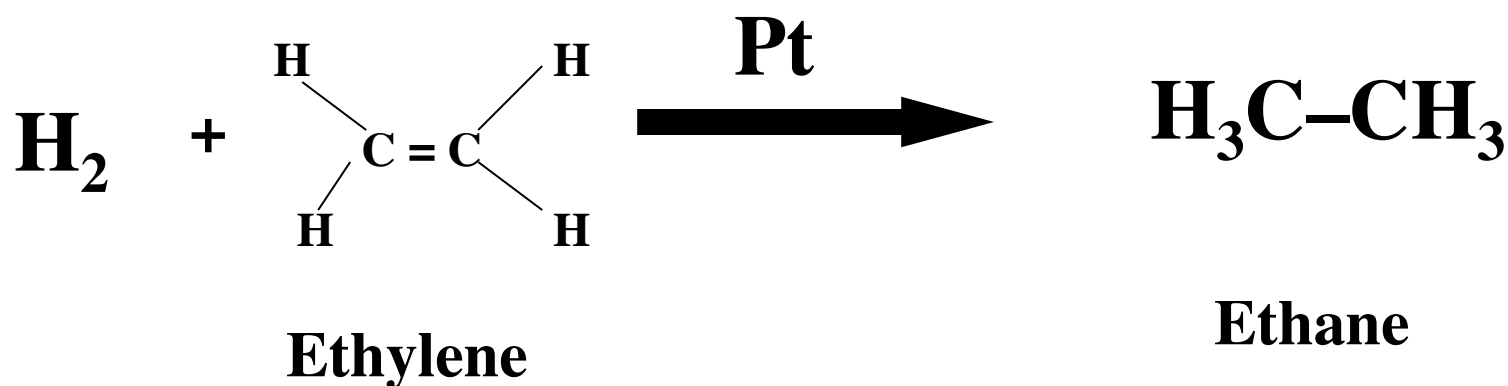$$2\,H_2(g) + O_2(g) \rightleftharpoons 2\,H_2O(g)$$

Catalysis

B + C ⟶ D

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

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

An Example: Hydrogenation of Ethylene

$$H_2 \; + \; \underset{\text{Ethylene}}{\overset{\displaystyle \underset{H}{\overset{H}{}}}{\underset{}{C = C}}} \quad \xrightarrow{\text{Pt}} \quad \underset{\text{Ethane}}{H_3C\text{–}CH_3}$$

**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 meter^2/ gram**

SEE YOU WEDNESDAY