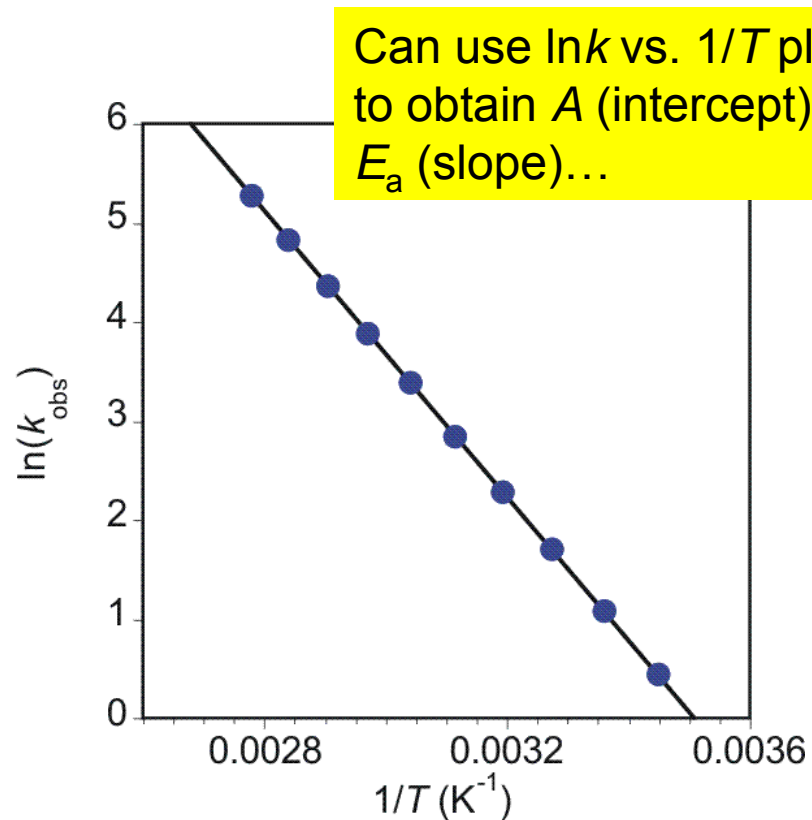
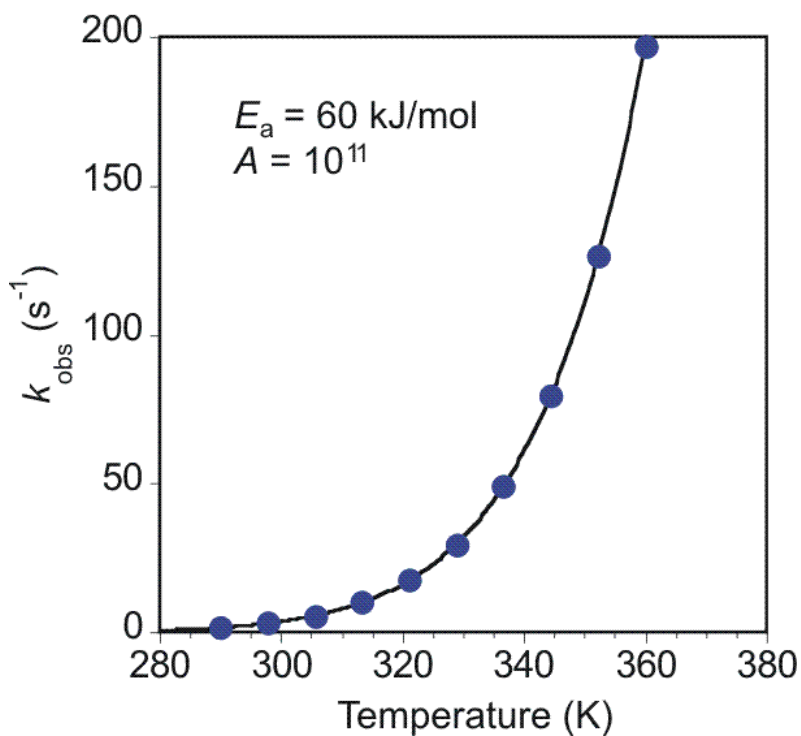


# Arrhenius Relationship and Plots

$$k_{\text{obs}} = Ae^{-E_a/RT}$$

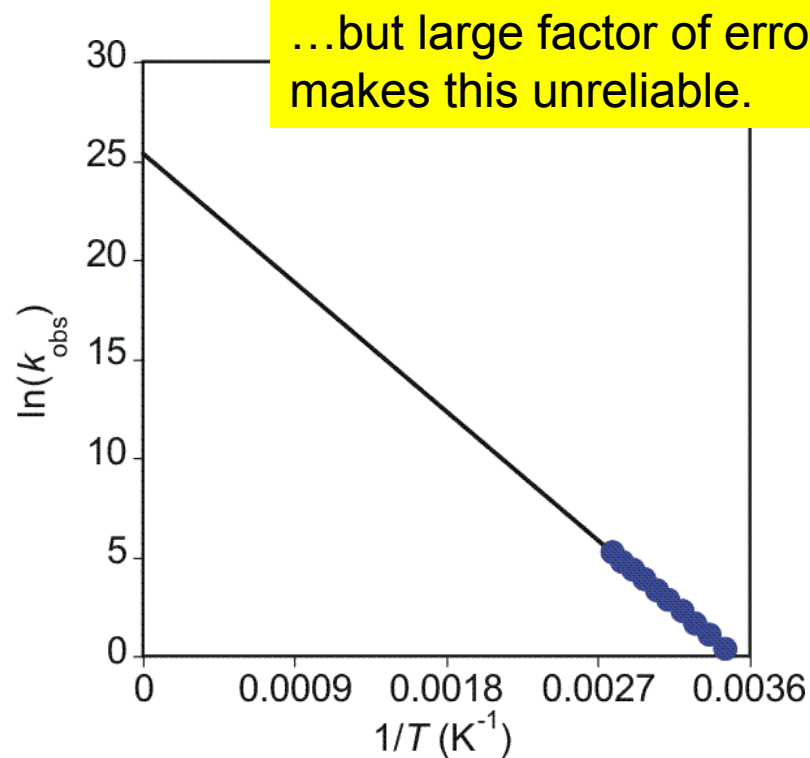
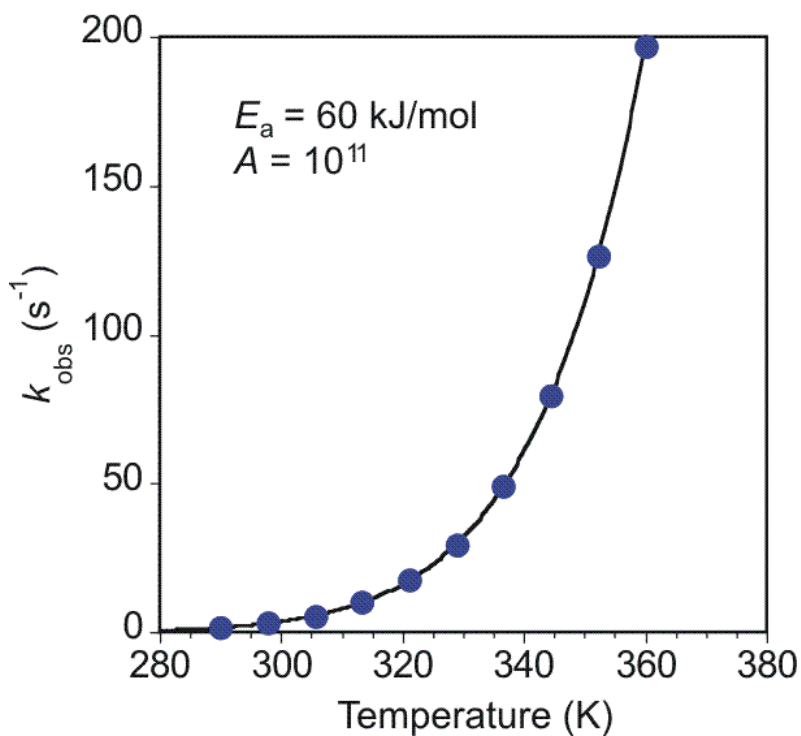
$$\ln(k_{\text{obs}}) = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$



# Arrhenius Relationship and Plots

$$k_{\text{obs}} = Ae^{-E_a/RT}$$

$$\ln(k_{\text{obs}}) = \ln A - \left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right)$$



# Theoretical Kinetics

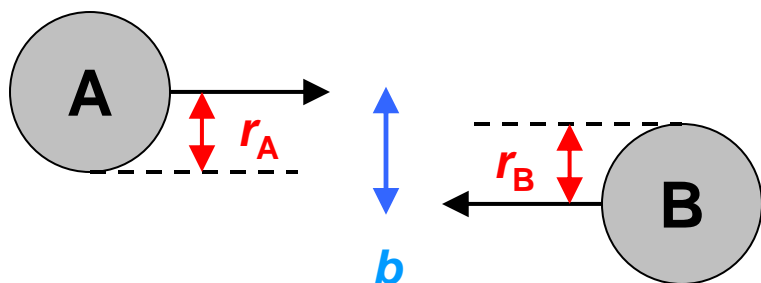
*Problem:* Variable components of Arrhenius equation ( $E_a$ ,  $A$ ) are not based in chemical theory; Nevertheless, equation works fantastically.

*Challenge:* How do we reproduce form of Arrhenius equation using theory instead of just observation?

In other words, how do we express  $E_a$  and  $A$  in terms of real physical parameters?

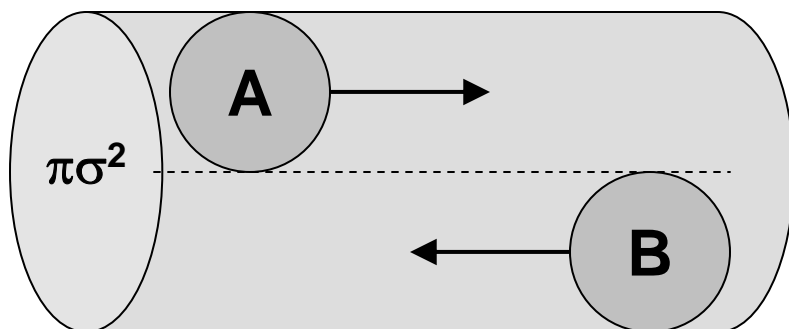
# Collision Theory of Reactions

*Theoretical Basis:* Rate parameters are defined by collision frequency and energy.



Collision occurs if  $b \leq r_A + r_B$ .

Another way of saying it:

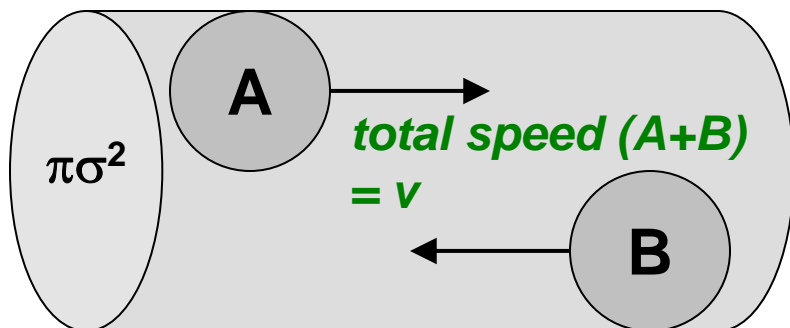


Maximum radius of a cylinder that will (barely) produce collision:

$$(r_A + r_B) = \sigma$$

$$\text{Area} = \pi(r_A + r_B)^2 = \pi\sigma^2$$

# Collision Theory of Reactions



Volume swept in time  $\Delta t$ :  
 $\pi\sigma^2 v \Delta t$

Probability of collision = 1  
Frequency of collision ( $Z$ )  
= *rate* of reaction

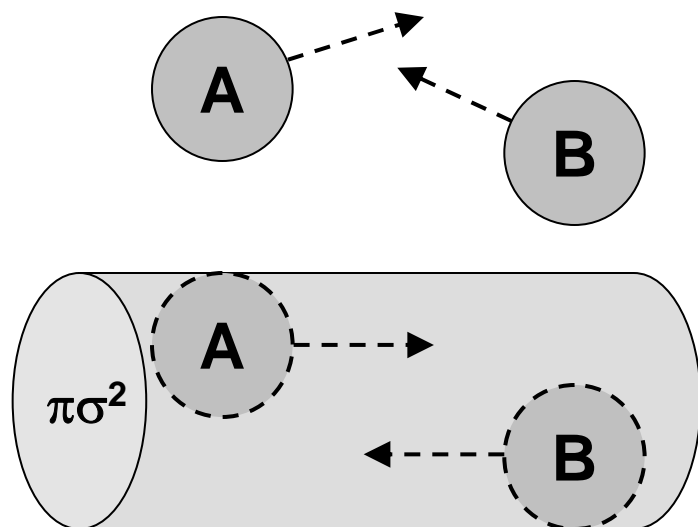
= # of collision volumes/time

$$Z = \pi\sigma^2 v \Delta t / \Delta t = \pi\sigma^2 v$$

In the real world, cylinder that contains A won't always contain B; depends on reagent concentration.

$$Z = \pi\sigma^2 v [A][B]$$

# Collision Theory of Reactions



In the real world, A and B won't always be pointed right at each other.

Solve this by mapping trajectory onto cylinders using "relative" velocity:

$$v_{\text{rel}} = \sqrt{\frac{8\pi k_B T}{\mu}}, \quad \mu = \frac{m_A m_B}{m_A + m_B} \quad (\text{from kinetic theory of gases})$$

$$Z = \pi\sigma^2 \sqrt{\frac{8\pi k_B T}{\mu}} [A][B], \quad k_{\text{coll}} = \pi\sigma^2 \sqrt{\frac{8\pi k_B T}{\mu}} \quad (k_B = \text{Boltzmann constant})$$

# Collision Theory of Reactions

$$Z = \pi\sigma^2 \sqrt{\frac{8\pi k_B T}{\mu}} [A][B] \quad \text{How well does this work?}$$



calculated  $Z = 10^{34}$  molecules/m<sup>3</sup> sec;  
actual *rate* =  $10^{20}$  molecules/m<sup>3</sup> sec

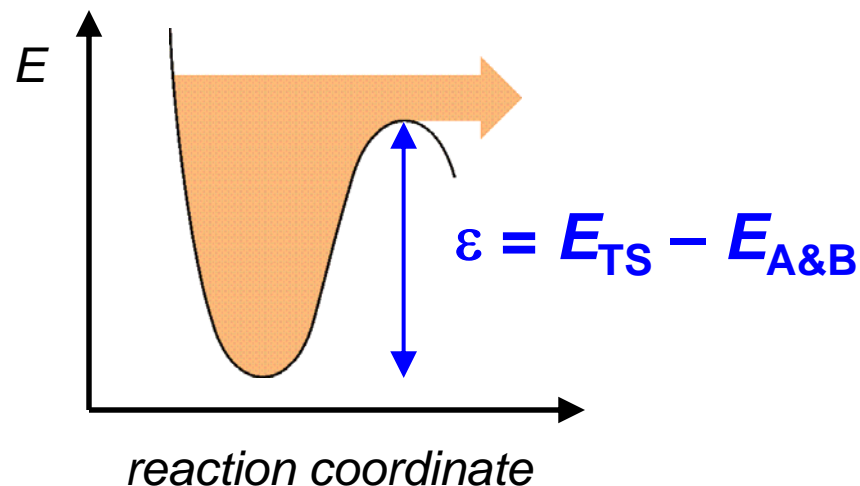
Only one collision in  $10^{14}$  succeeds.

*Theory:* Is because only reactions that have minimum energy “ $\epsilon$ ” succeeds.

# Collision Theory of Reactions

$$\frac{n_{\text{success}}}{n_{\text{total}}} = e^{-\varepsilon/kT}$$

(Maxwell-Boltzmann relationship)



$$Z = \pi\sigma^2 \sqrt{\frac{8\pi k_B T}{\mu}} [A][B] e^{-\varepsilon/kT} \quad \text{in terms of molecules,}$$

$$\text{rate} = \pi\sigma^2 \sqrt{\frac{8\pi RT}{\mu}} [A][B] e^{-\varepsilon/RT} \quad \text{in terms of moles.}$$



# Collision Theory of Reactions

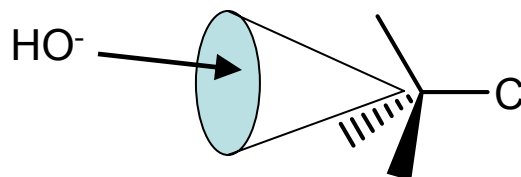
$$k_{\text{coll}} = \underbrace{\pi\sigma^2 \sqrt{\frac{8\pi RT}{\mu}}}_A e^{-\varepsilon/RT}$$

$E_a$

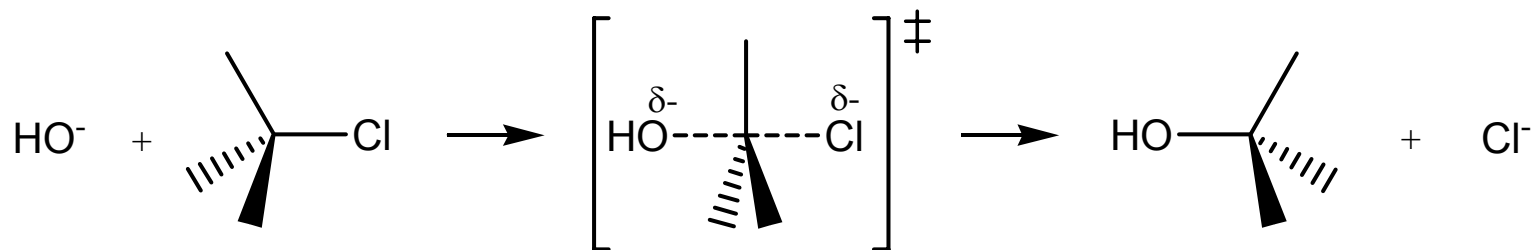
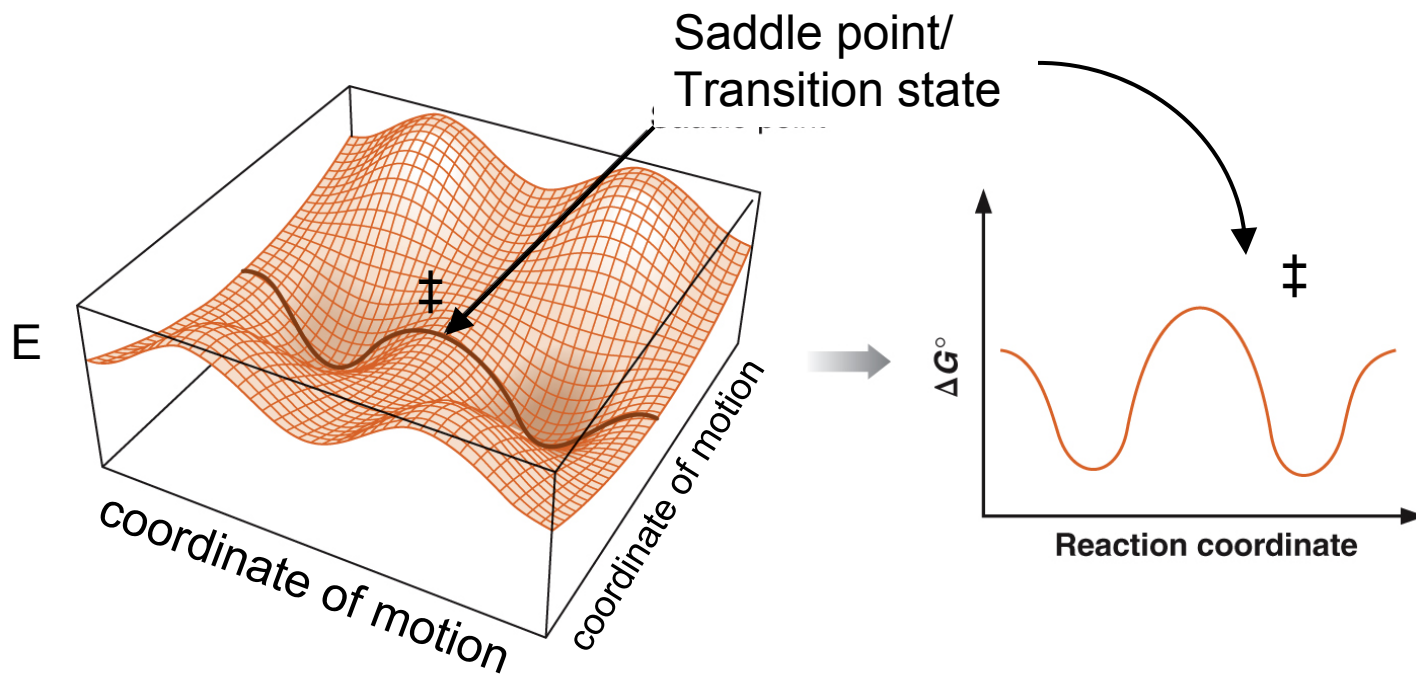
This has Arrhenius form!

In practice, this  $A$  is much larger than measured  $A$ .  
*Theory:* Is because ignores orientational bias of reactions.

Think  $S_N2$  reaction:

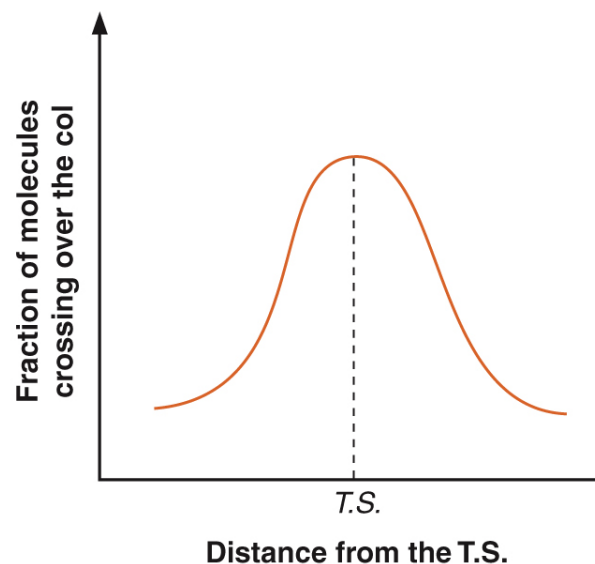
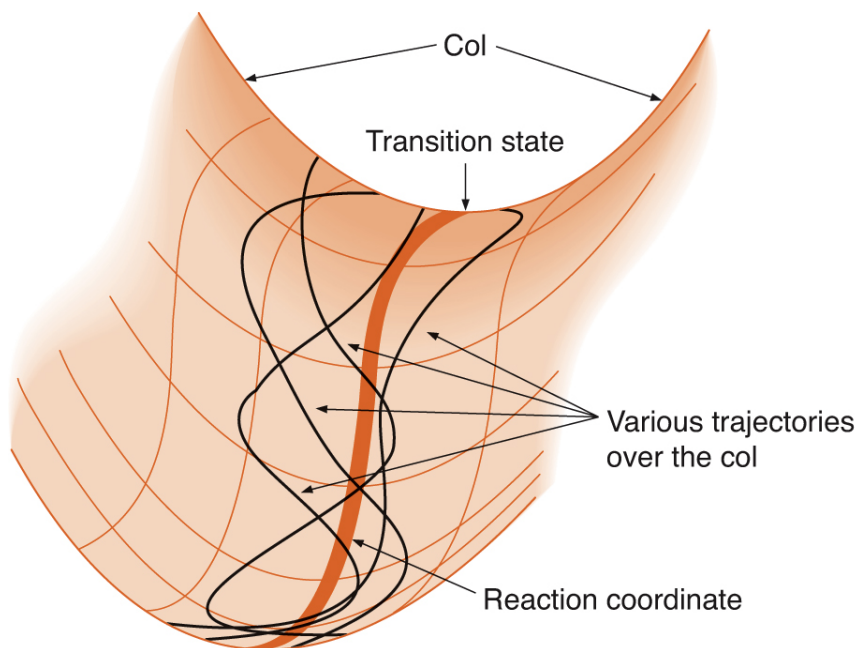


# Transition State Theory of Reactions



*Central premise:* Pretend TS has the characteristics of a molecule.

# Transition State Theory of Reactions



In reality, molecules take many paths near saddle point towards product.

We will use one transition state to represent distribution of reaction trajectories.