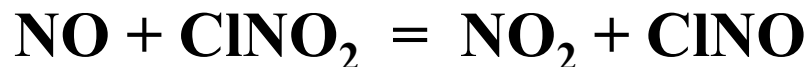


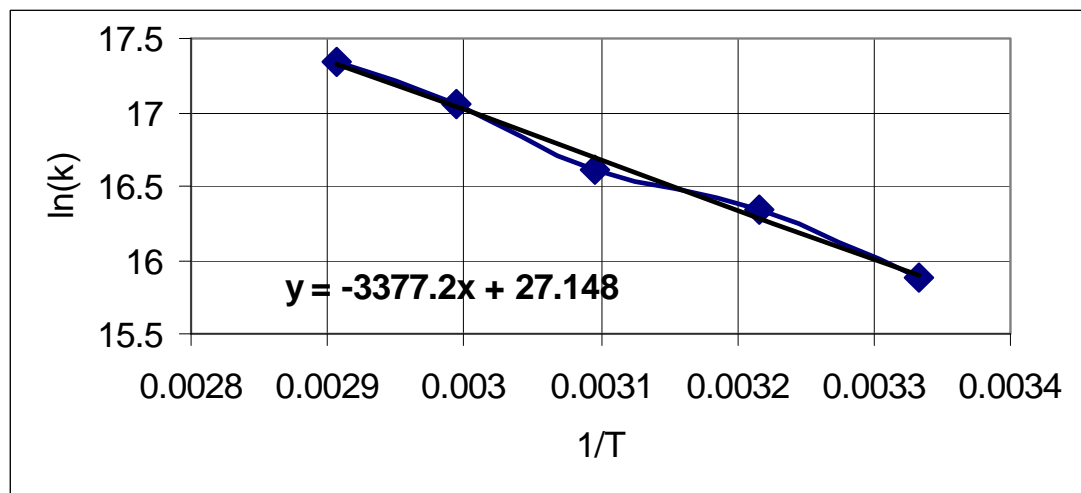
# Sample Problem – Arrhenius Relationship

The rate constant for the gas phase second order reaction



Was measured at several temperatures. What is the activation energy  
And the pre-exponential term?

Temp (K)	k x10e-7
300	0.79
311	1.25
323	1.64
334	2.56
344	3.4



**Slope = -3400 = -E<sub>act</sub>/R**

**E<sub>act</sub> = 28200 J/mol = 28.2 kJ/mol**

**Y intercept is ln(A) if Y is ln(k)**

**If Y is ln(rate) or some measure of  
Rate then intercept is ln(function of A)**

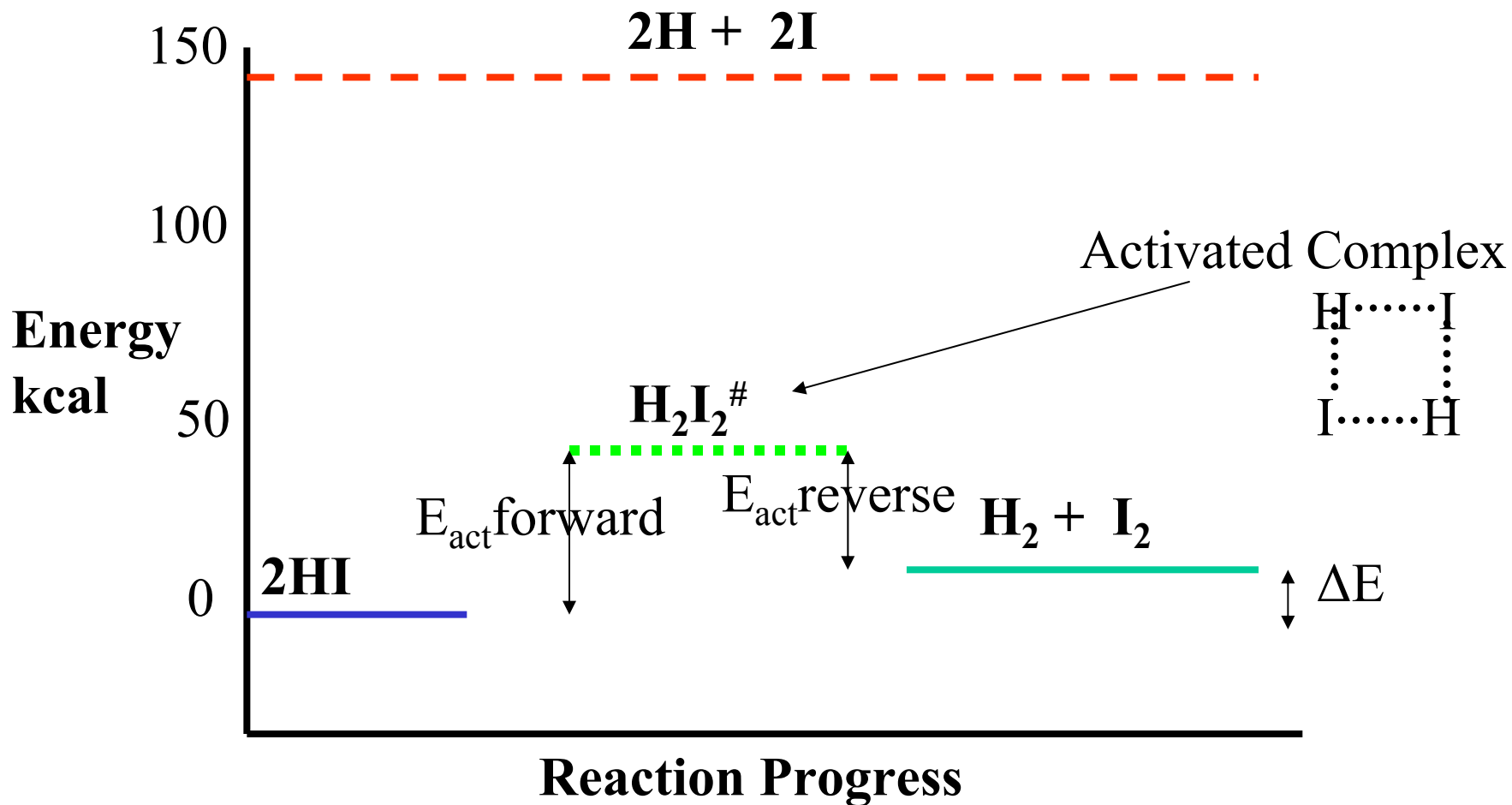
**Pre-exponential = e<sup>27.14</sup> = 6.5x10<sup>11</sup>**

Useful to determine k at some  
other temperature (not too far  
removed, don't extrapolate too far)

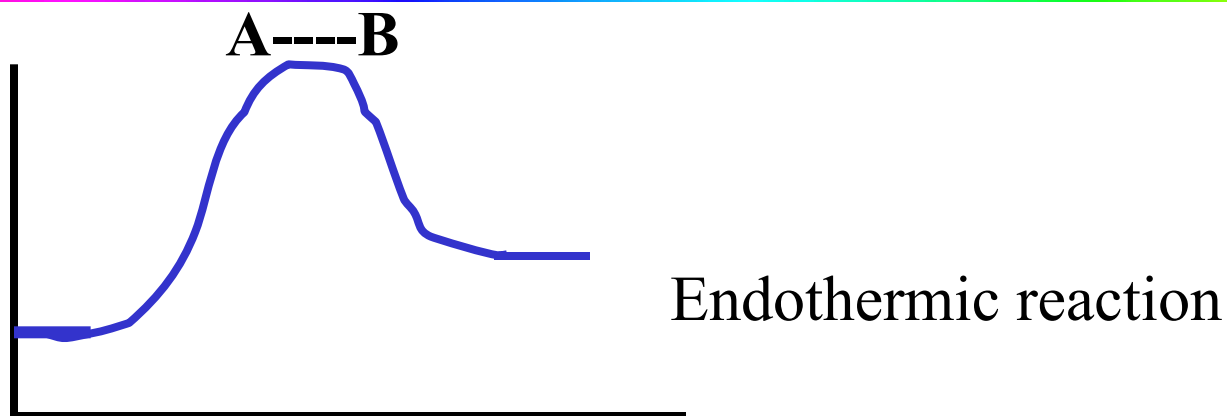
# Transition State – Activated Complex



$E_{\text{act}}$  forward = 44 kcal/mol



# Transition State

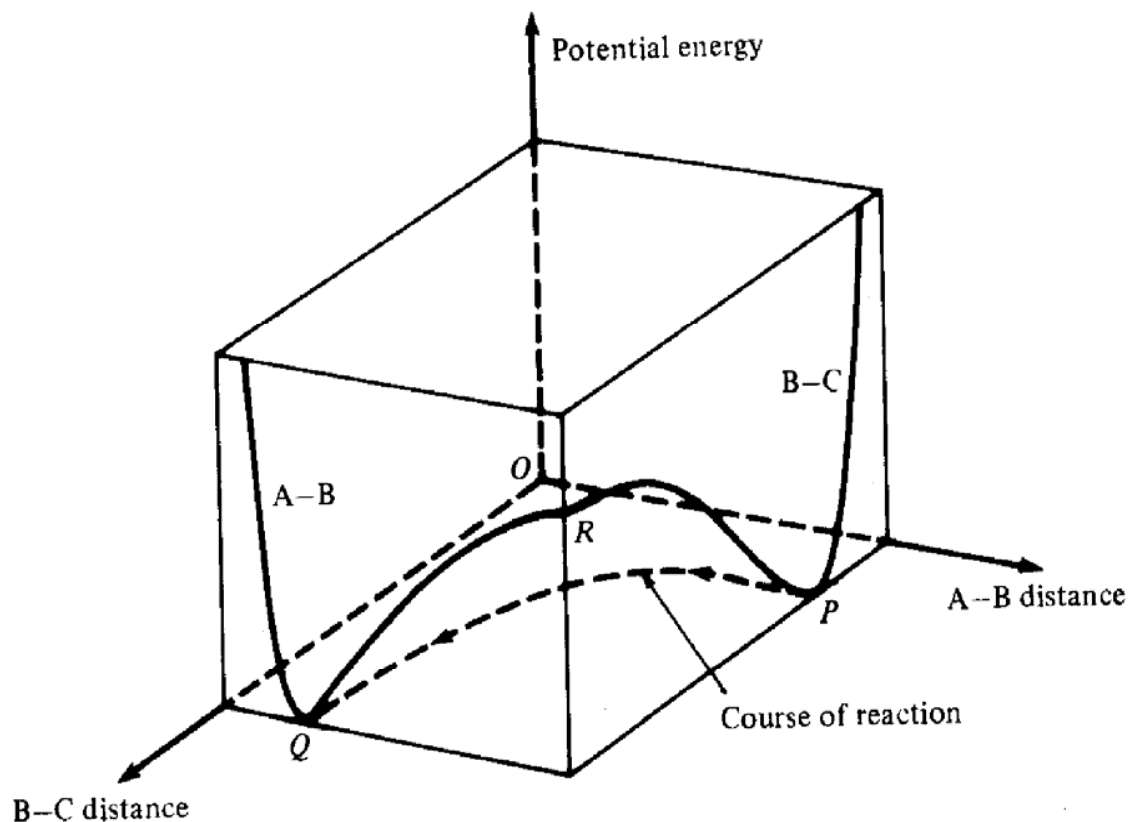


Above is a 1-dimension representation of reaction progress

A 2-Dimensional Representation of Reaction Progress would be better and more descriptive but more complex mathematically

What would be far better and more complex is a 3-D representation

# Potential Energy Surface – 3-D



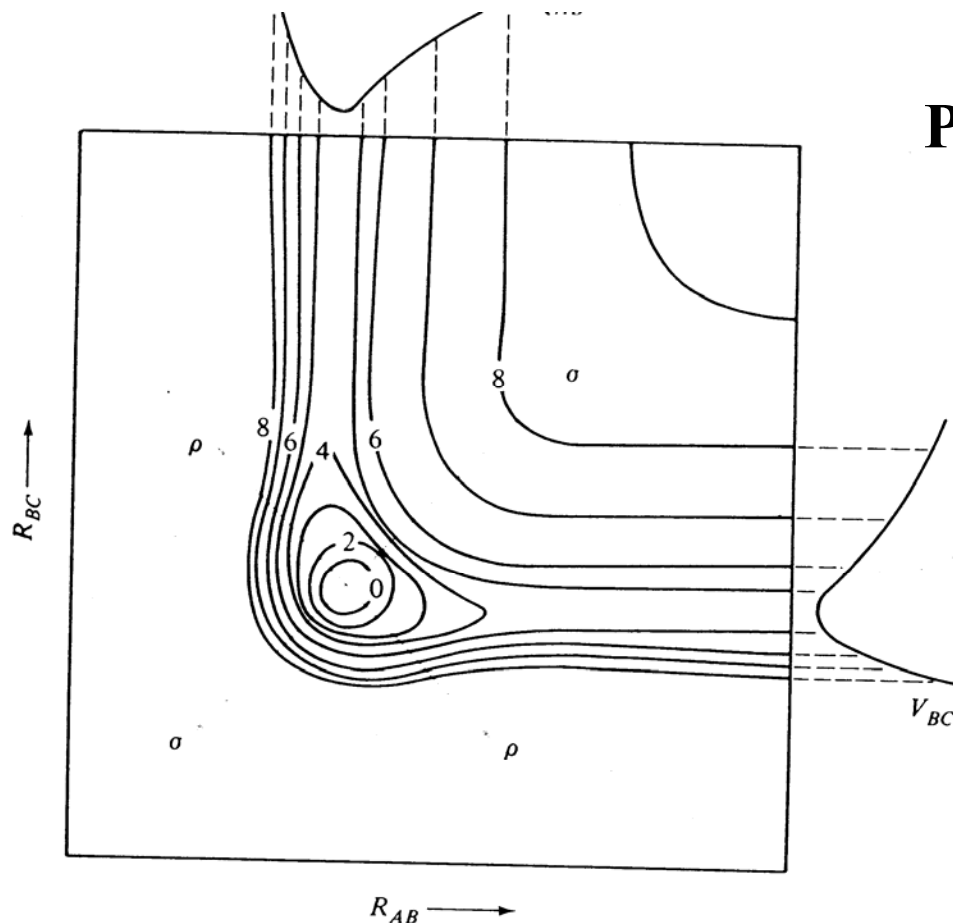
Variation of potential energy with the A-B and B-C distances, for the  $A \cdots B \cdots C$  system in which the A-B-C angle has been fixed.

# Transition State – Potential Energy Surface

3-dimensional energy surface representation of reaction progress



Potential Energy Surface

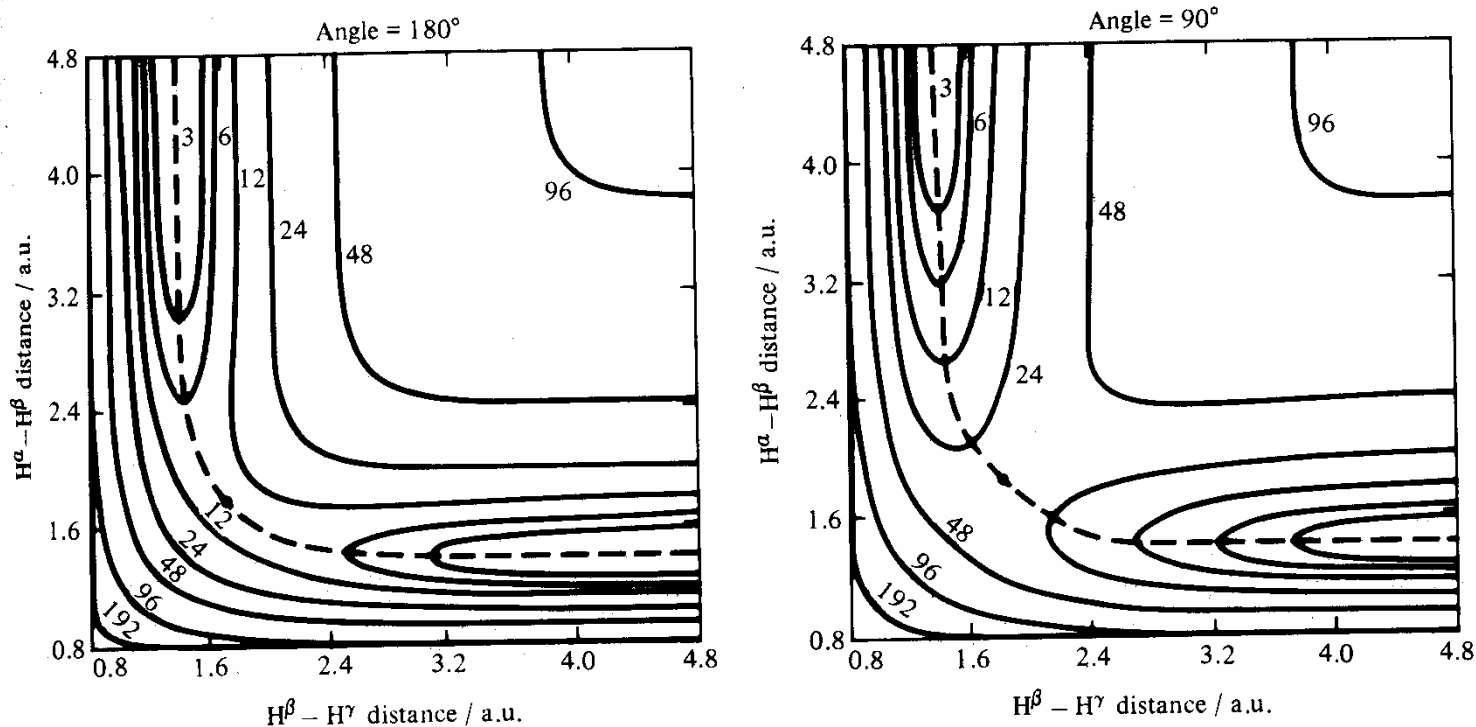


Reaction follows path  
along minimum energy

# Potential Energy Surface H---H---H

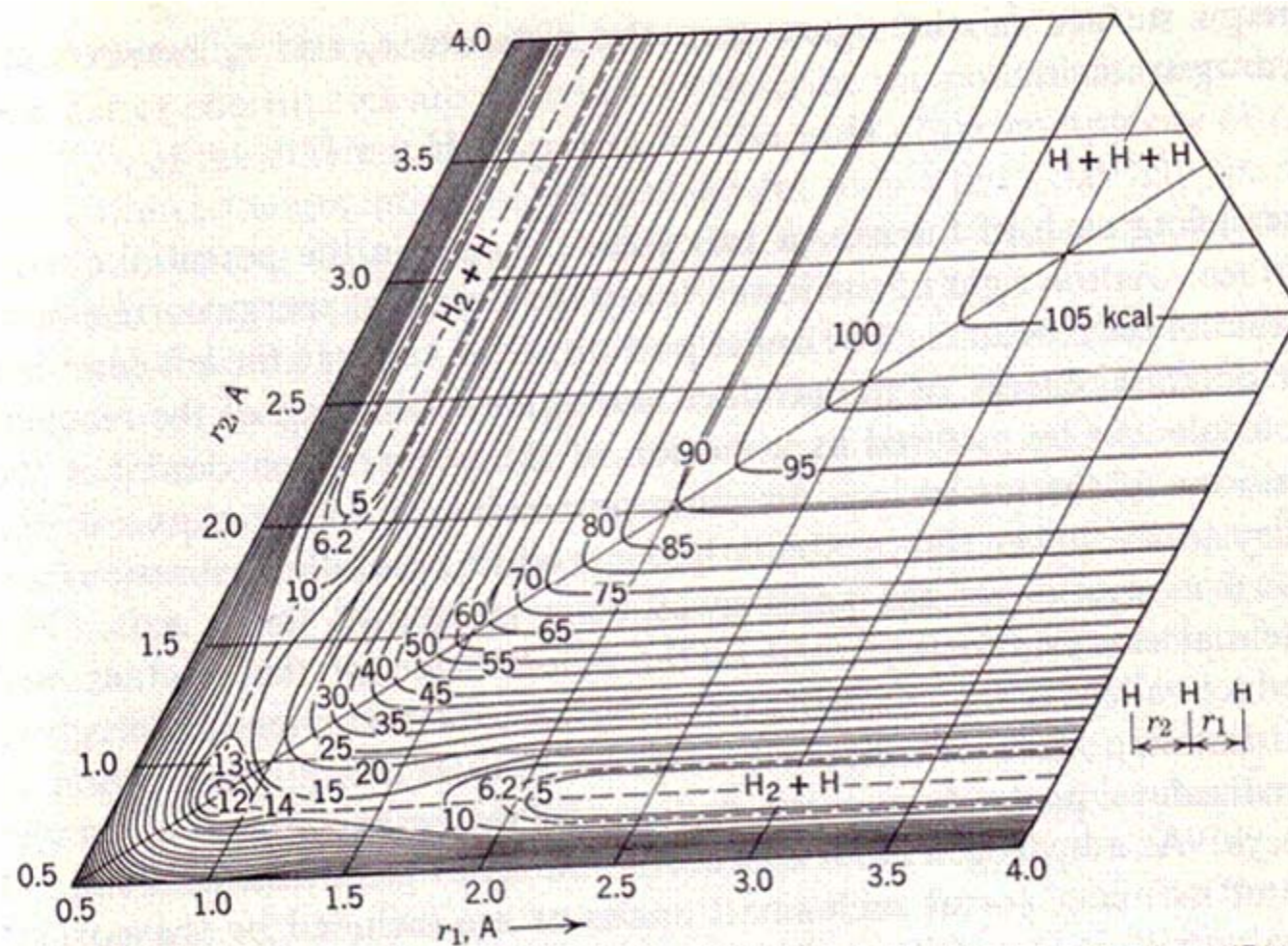


Angle of Transition State H---H---H



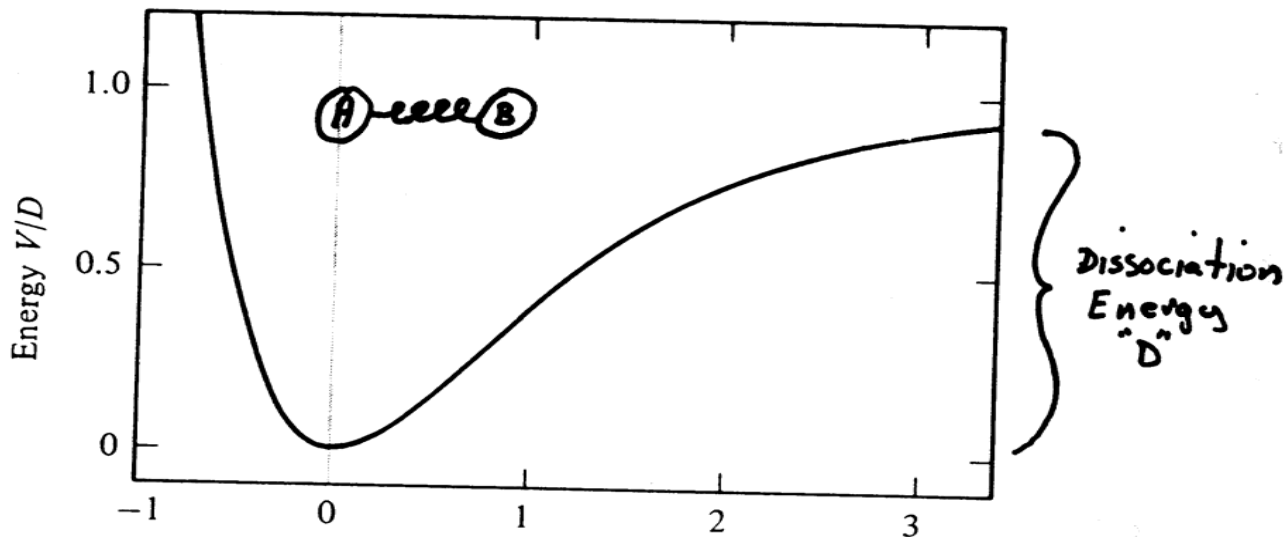
Potential-energy surfaces for the H + H<sub>2</sub> reaction, as given by Truhlar and Horowitz<sup>15</sup> on the basis of the ab initio calculations of Siegbahn and Liu. The numbers on the contours show the values of the energies in kcal mol<sup>-1</sup> (1 kcal = 4.184 kJ); the unit for the bond distances is the atomic unit, or bohr (1 bohr = 52.92 pm).

# Potential Energy Surface for $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$



Potential energy diagram for the reaction  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$ . From Eyring, Gershinowitz, and Sun.<sup>78c</sup>

# Vibration of Bond Between 2 Atoms



Morse potential for a diatomic molecule. The reduced energy ( $V/D$ ) is plotted as a function of reduced displacement from the equilibrium interatomic distance ( $\beta[R - R_0]$ ).

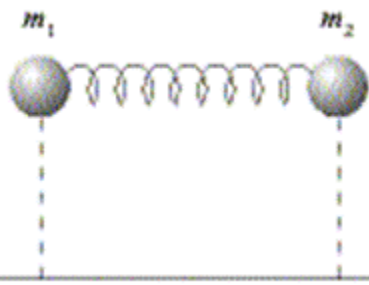
$$\beta = \omega \left( \frac{\mu}{D} \right)^{1/2}$$

$$\omega = \text{vib. frequency (from spectroscopy)} \quad \mu = \frac{m_A m_B}{m_A + m_B}$$

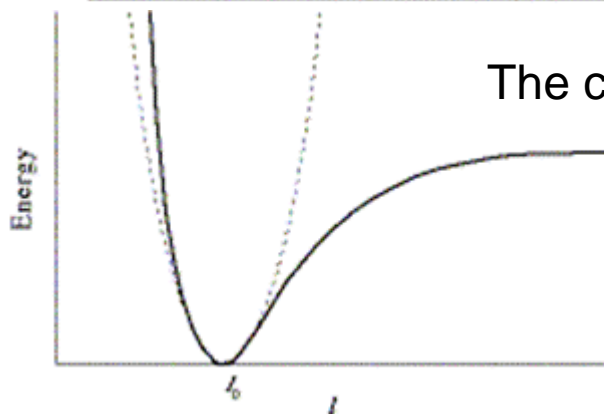
Rememb

$$E - \pi v - \pi c/\lambda$$

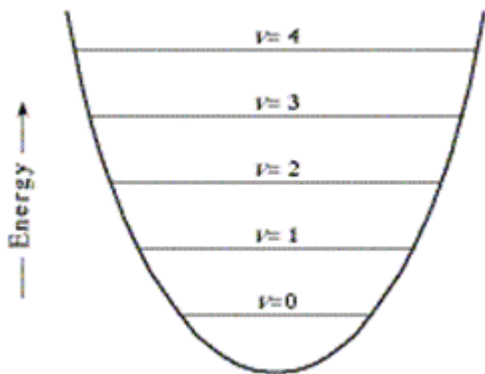
# A More Complex Harmonic Oscillator



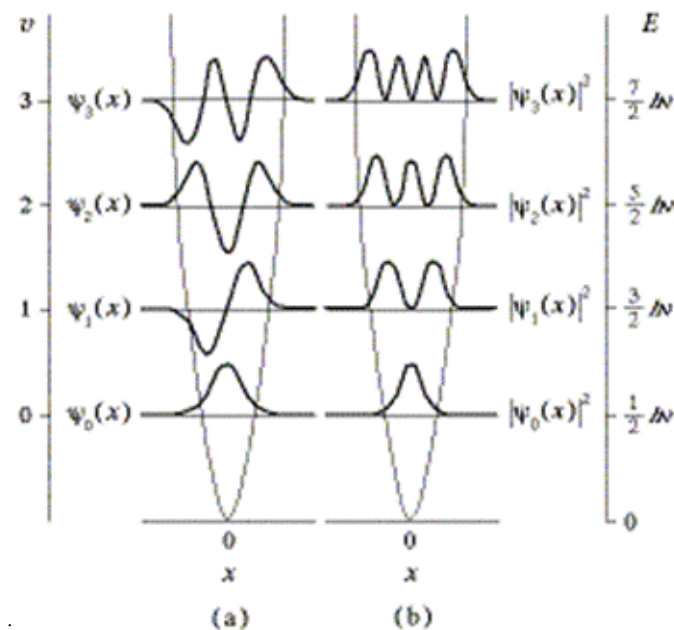
This is more like a vibrating diatomic molecule



The confining potential energy



Energy Levels  
Wavefunctions  
Probability Density



# Harmonic Oscillator – Morse Potential

$$V(R) = D_e \left( 1 - e^{-\beta(R-R_e)} \right)^2$$

where:

$D_e$  is the potential well depth.

$R$  is internuclear distance.

$R_e$  is the equilibrium internuclear distance.

$$\beta = \pi \nu_e \sqrt{\frac{2\mu}{D_e}}$$

$\nu_e$  is the vibrational constant and  $\mu$  is reduced mass.

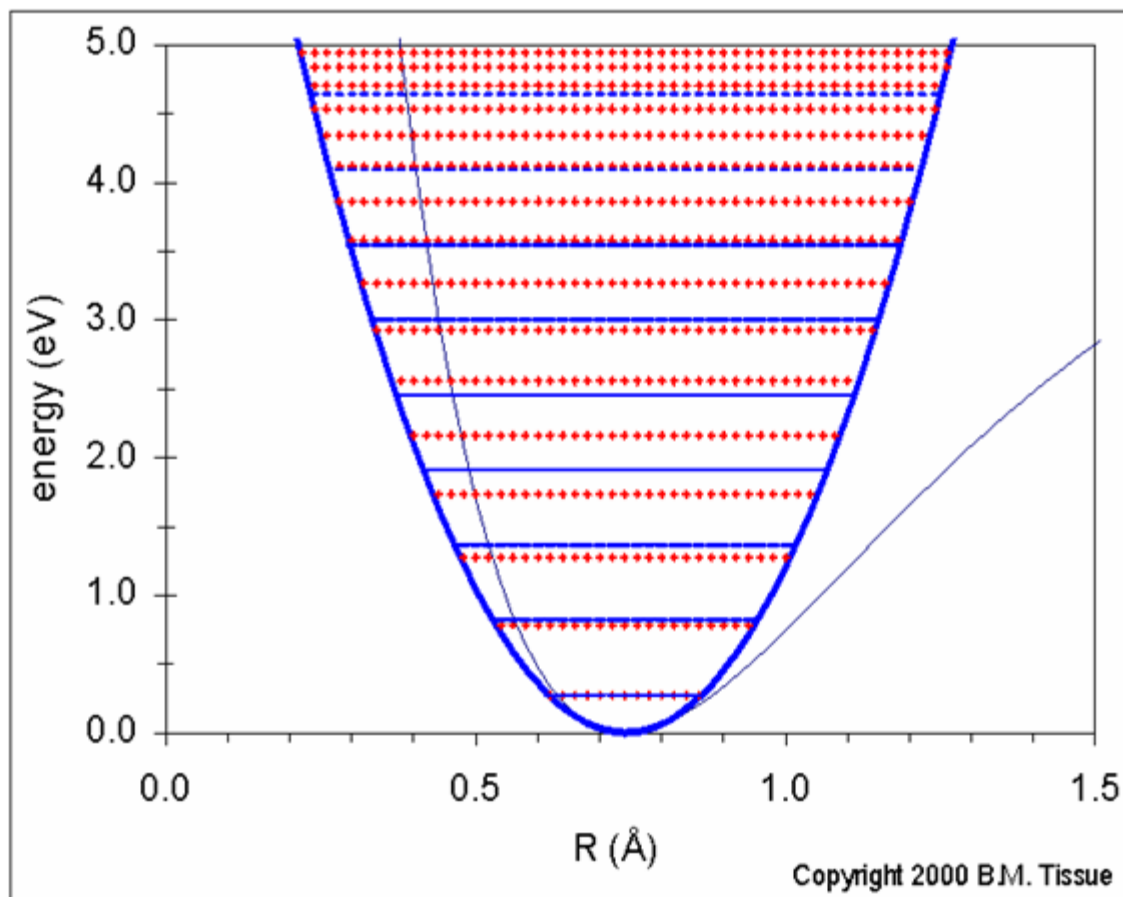
# Harmonic Oscillator – Morse Potential

## Morse Potential and Harmonic Oscillator for a Diatomic Molecule

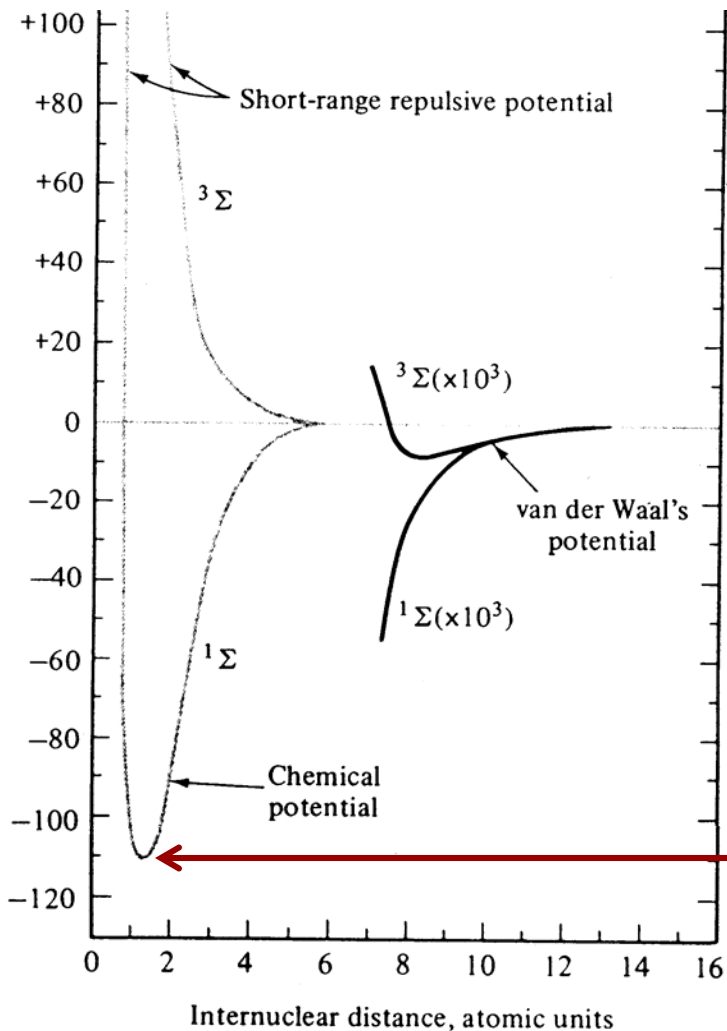
molecule:	<b>H-H</b>	
reduced mass =	0.50391	amu
Re =	0.7412	Å
$\nu_e$ =	4400.39	cm <sup>-1</sup>
De =	4.748	eV
$\nu_e X_e$ =	117.91	cm <sup>-1</sup>

Reduced mass calculator:

mass of atom 1:	1.00783
mass of atom 2:	1.00783
reduced mass:	0.50391

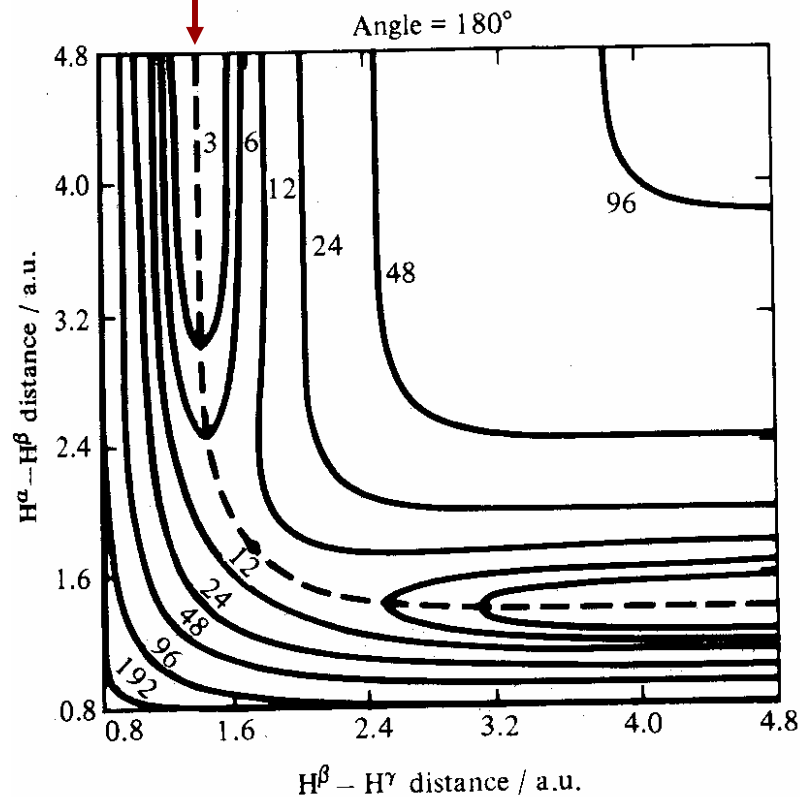


# Potential Energy for H---H Interactions



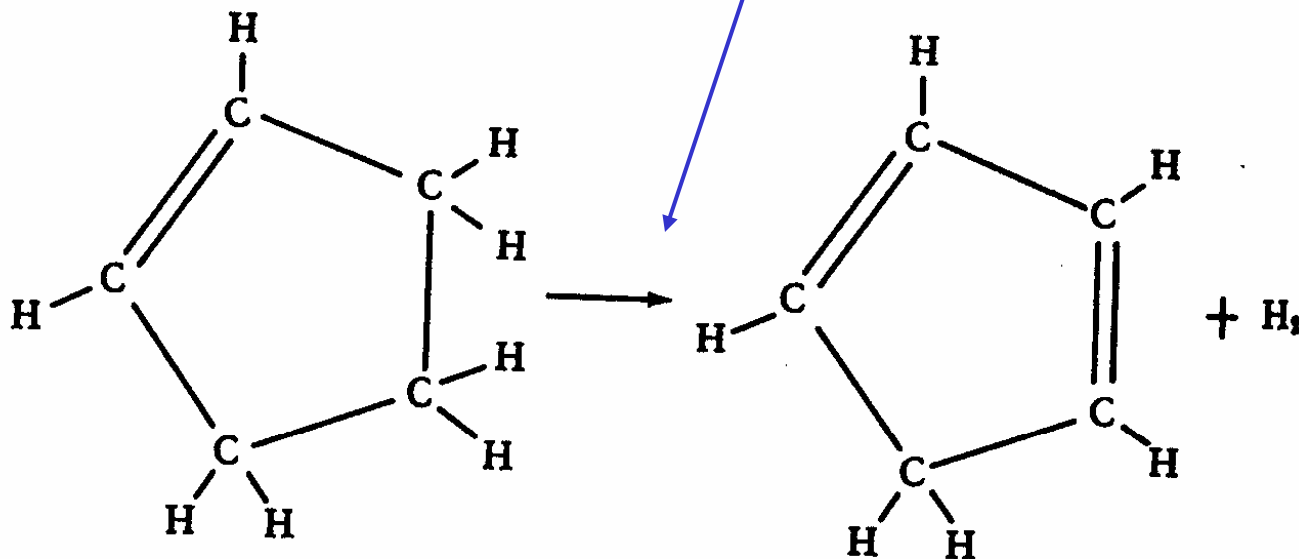
*Potential curves for H—H interaction*

Potential Energy Surface from slide 6 & 7.



# Transition State - example

What does transition state look like?



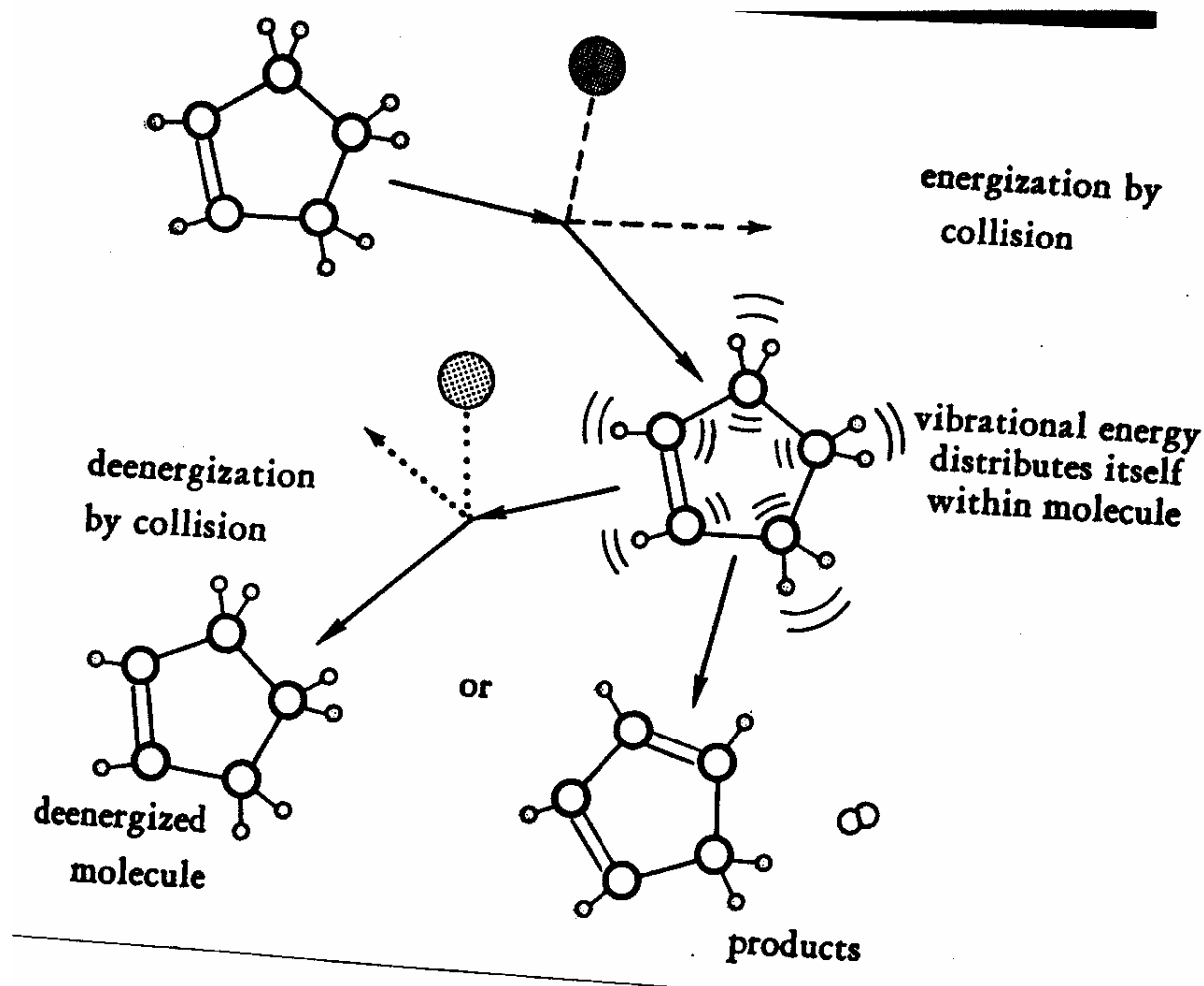
follows the rate law

$$-\frac{d[\text{cyclopentene}]}{dt} = k[\text{cyclopentene}],$$

First Order in  
cyclopentene

Rate can be experimentally measured by monitoring as fn(time) spectroscopy of the cyclopentene and/or diene and/or pressure increase as H<sub>2</sub> forms

# Transition State - example contd



# Quantum Mechanical Treatment of Transition State

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- If we knew all of the energy relationships of reactants, products, and the transition state we could predict kinetics
- We can not isolate and study the transition state, thus we can not experimentally determine its structure
- Quantum Mechanical Modeling can be used to make some predictions regarding the structure of the transition state
- *ab Initio* calculations of complex systems is difficult (impossible)
- Semi-empirical calculations of energy relationships give some idea as to the structure and energy relationships of the transition state
- Several methods with various simplifying assumptions developed (see section 3 in “Laidler” and also other books)

# Quantum Mechanical Treatment of Transition State

**$H\Psi = E\Psi$**       **H** is Hamiltonian operator for energy of system  
-includes all possible interactions between all particles in system

**London Treatment** (QM approximation) - semiempirical quantum mechanical calculation of energies of various species and all energy states of each species - generate potential energy surfaces for reaction

**Variation Principle Calculations** -  $E = \int \Phi^* H \Phi d\tau$     develop  $\Phi$ 's to minimize E which is the closest to the actual E of a system

- get closer and closer to the correct function  $\Phi$  - systematically
- $\Phi$  is a wave function and  $\Phi^*$  is its complex conjugate
- $d\tau = dx dy dz$     volume element
- use this to “calculate” value for Activation Energy (Theoretical)

# Quantum Mechanical Treatment of Transition State

Evans and Polayni (1938) -  $E_{\text{act}} = \alpha\Delta H + c$

$\Delta H$  = enthalpy of reaction (sometimes  $Q = -\Delta H$ )

$\alpha$  and  $c$  are empirical constants

Found for simple homolytic processes (in kcal)

$E_{\text{act}} \text{ forward} \sim 48.1 - 0.25Q$  for exothermic reaction  $Q^+$  or  $\Delta H^-$

$E_{\text{act}} \text{ reverse} \sim 48.1 - 0.25Q$  } for exothermic reaction

$E_{\text{act}} \text{ forward} \sim 48.1 - 0.75Q$

since  $Q = -\Delta H = E_{\text{act}} \text{ reverse} - E_{\text{act}} \text{ forward}$

## Connecting Thermodynamics and Kinetics

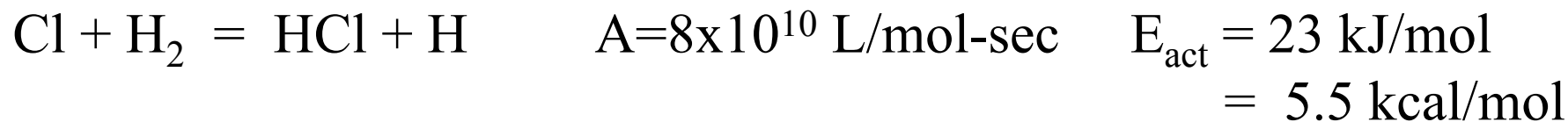
# Some Experimentally Measured Arrhenius Parameters

Sample Reactions	$A \text{ sec}^{-1}$	$E_a \text{ kJ/mol}$
<u>First order</u>		
$\text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_4 + \text{HI}$	$2.51 \times 10^{13}$	209
$\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3\cdot$	$2.5 \times 10^{17}$	384
$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$6.3 \times 10^{14}$	88
$\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}\cdot$	$7.9 \times 10^{11}$	250
$\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{H}$	$1 \times 10^{13}$	167

	<u>Second order</u>	$A \text{ l/mol sec}$	$E_a \text{ kJ/mol}$
Gas			
	$\text{O} + \text{N}_2 \rightarrow \text{NO} + \text{N}$	$1 \times 10^{11}$	315
	$\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$8 \times 10^{10}$	42
	$\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$	$8 \times 10^{10}$	23
	$\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	$2 \times 10^{10}$	~0
	$\text{SO} + \text{O}_2 \rightarrow \text{SO}_2 + \text{O}$	$3 \times 10^8$	27
	$\text{C}_6\text{H}_5 + \text{H}_2 \rightarrow \text{C}_6\text{H}_6 + \text{H}\cdot$	$1 \times 10^8$	25
Solution			
	$\text{C}_2\text{H}_5\text{ONa} + \text{CH}_3\text{I} \xrightarrow{\text{EtOH}} \text{NaI} + \text{C}_2\text{H}_5\text{OCH}_3$	$2.4 \times 10^{11}$	82
	$\text{C}_2\text{H}_5\text{Br} + \text{OH}^- \xrightarrow{\text{H}_2\text{O}} \text{C}_2\text{H}_5\text{OH} + \text{Br}^-$	$4.3 \times 10^{11}$	89.5

# Sample Problem

Using literature Arrhenius parameters, calculate the rate constant at 25 °C and 100 °C for the reaction of chlorine atoms with hydrogen gas forming hydrogen chloride gas and a free hydrogen atom.  
*(this is one of the steps in the gas phase chain reaction of H<sub>2</sub> with Cl<sub>2</sub>)*



At 25 °C

$$k = A e^{-E/RT}$$

$$k = 8 \times 10^{10} \times e^{-9.2878}$$

$$k = 7.4 \times 10^6 \text{ L/mol-sec}$$

at 75 °C

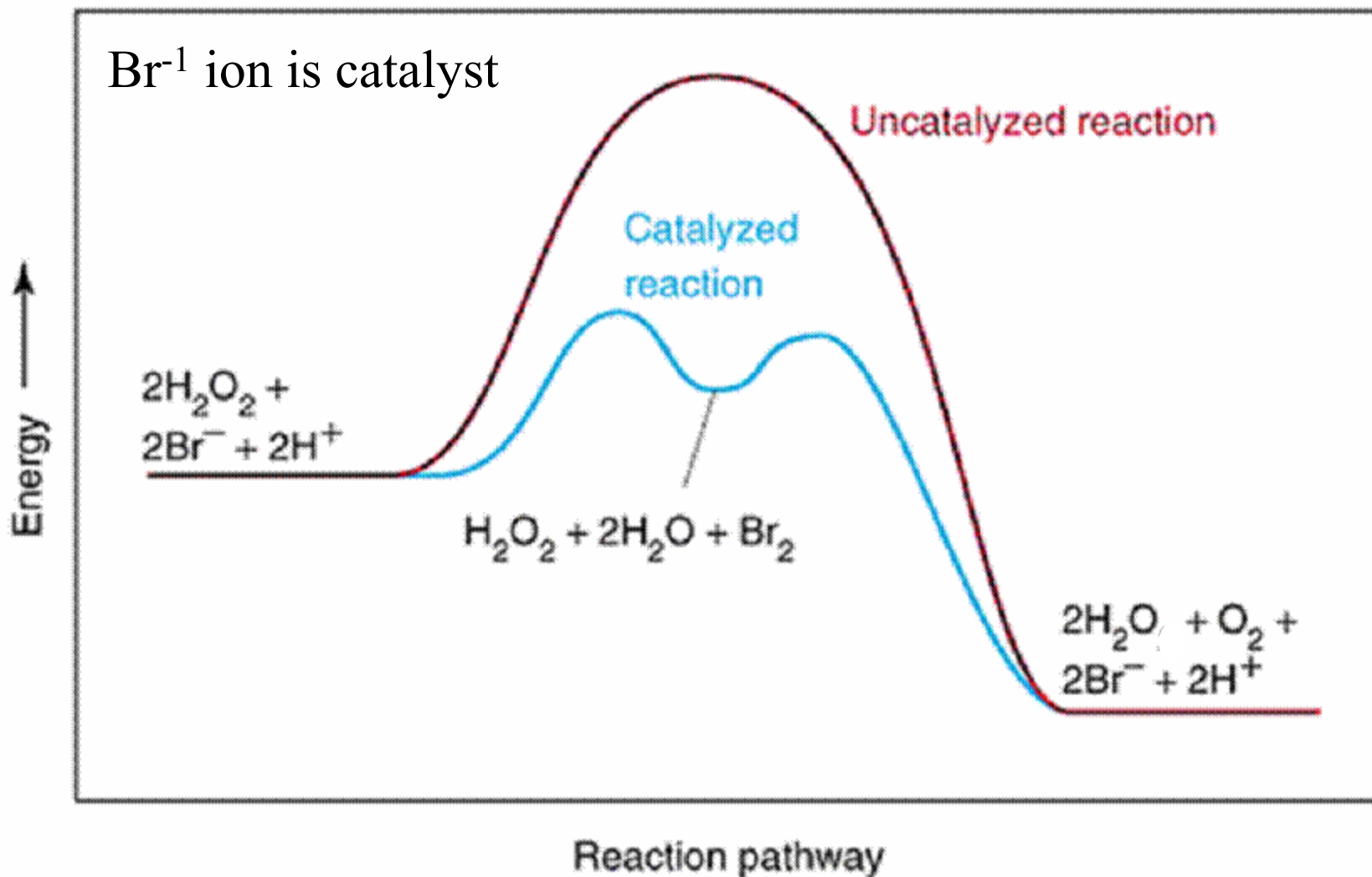
$$k = A e^{-E/RT}$$

$$k = 4.79 \times 10^7 \text{ L/mol-sec}$$

k increases a factor of about 6.5 with at temperature increase of 50 °C  
some reactions increase less others more, depends on size of E<sub>act</sub>

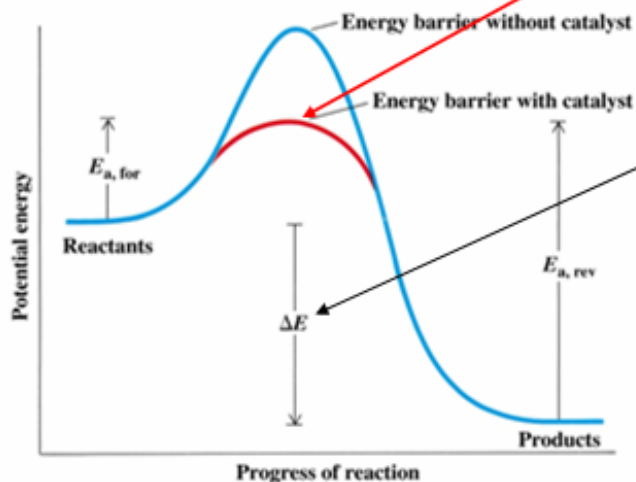
# Example Catalysis Mechanism and Activation Energy

overall reaction - hydrogen peroxide decomposes to water and oxygen gas



# Example - Activated Complex and Catalysis

Catalyst: Increase rate usually by reducing  $E_a$  by changing mechanism



$K_{eq}$ ,  $\Delta G_{rxn}$  do not change!!!

(Catalysts can also change A factor. See Prob. 14-18)

substitution

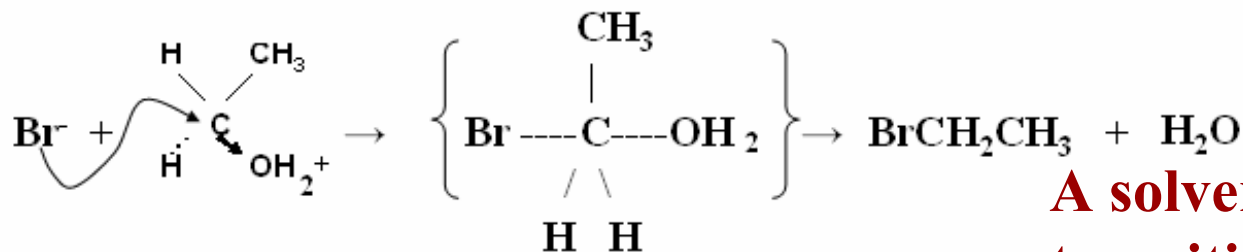
Second order

nucleophilic

Example of change in  $E_A$  by change in mechanism:

Conversion of alcohol to organic halide via  $S_N2$  reaction

Acid Catalyzed:  $H^+ + CH_3CH_2OH \rightleftharpoons CH_3CH_2-OH_2^+$  rapid equilibrium



Lowers activation energy of  $OH^-$  leaving group

**A solvent that makes the transition state more stable accelerates reaction rate**

# Problem Example – Arrhenius

For the gas phase reaction  $2\text{I}(\text{g}) + \text{H}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$  the rate constant was measured at 417.9 K to be  $1.12 \times 10^5 \text{ M}^{-2}\text{sec}^{-1}$  and at 737.9 K to be  $18.84 \times 10^5 \text{ M}^{-2}\text{sec}^{-1}$ . What is the activation energy? What is the rate constant at 633.2 K?

Note reaction goes about 16 times faster when temp increases from 144 C to 464 C (you can't just say when temp increases by 320°C since this is a ln function)

do at home and check your answer against mine below

$E_{\text{act}} = 22.5 \text{ kJ/mol}$      $k \text{ at } 633.2 = 1.0 \times 10^6 \text{ M}^{-2}\text{sec}^{-1}$

pre-exponential  $A = 7.4 \times 10^7 \text{ M}^{-2}\text{sec}^{-1}$

# Solvent Stabilized Transition State or Activated Complex

---

- Conduct experiments in various solvents at various temperatures.
- Determine effect of temperature and solvent on reaction rate.
- Arrhenius plots to determine differences in activation energy.
- If a solvent lowers activation energy it is stabilizing the transition state.  
(example – if transition state is more polar than reactants then polar solvents should increase rate and lower activation energy)

# Problem Example – Arrhenius

---

A common “rule”, especially in organic chemistry when temperature is not too high or too low (such as in water 0-100°C) -- “*increase the temperature by 10° and the rate should ~double*”. If that temp were from 25°C to 35°C what would be the activation energy for that reaction?

Solve at home and compare with my answer -     ~52.9 kJ/mole

the reason this statement is not far off is lots of reactions are conducted in the 0 to 100 C range and many chemical reactions have activation energies on the order of 30-75 kJ/mole