

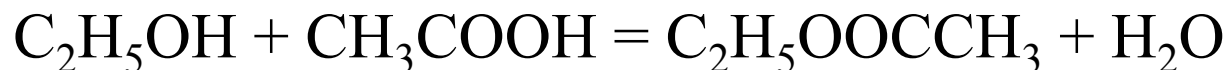
Temperature Dependence of Rate

How is the rate of chemical reaction affected by temperature?

Historic Perspective-

1850 – L. Wilhelme – Inversion of Sucrose – Effect of conc. on rate

1862 – M. Berthelot - rate proportional to product of concentration of two reactants and independent of concentration of products



1878 - J. J. Hood - empirical observation of rate as function of temp

$$\log k = B - A'/T \quad A' \text{ \& B empirical constants} \quad T \text{ in } ^\circ\text{K}$$

1884 - J. H. van't Hoff - effect of temp on equilibrium constant

$$d(\ln K)/dT = \Delta H^\circ/RT^2 \quad \text{or} \quad \ln(K) = -\Delta H^\circ/RT + \text{const}$$

1889 - S. Arrhenius - quantitative explanation of temperature effect on reaction rate $k = A e^{-E/RT}$ (*A and E have meaning - not empirical*)

Development of mathematical relationships based on experimental observation

Arrhenius equation had physical meaning and fit experimental data

Temperature Dependence of Rate

Arrhenius Relationship

$$k = Ae^{-E/RT}$$

Take natural logarithm \ln of both sides of equation

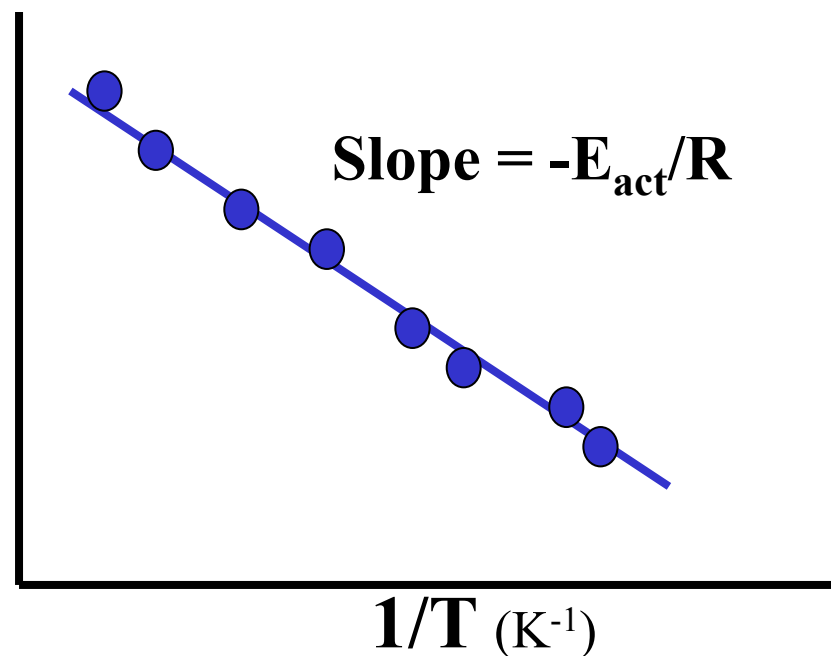
$$\ln k = \ln A - E_{\text{act}}/RT$$

$$Y = b + mX$$

$\ln k$

Units of R to match units of E
 $R = 8.314510 \text{ J/K-mol}$

Why do we try to make graphs take on a linear form?



Temperature Dependence of Rate

Simple Arrhenius Equation - $k = Ae^{-E/RT}$

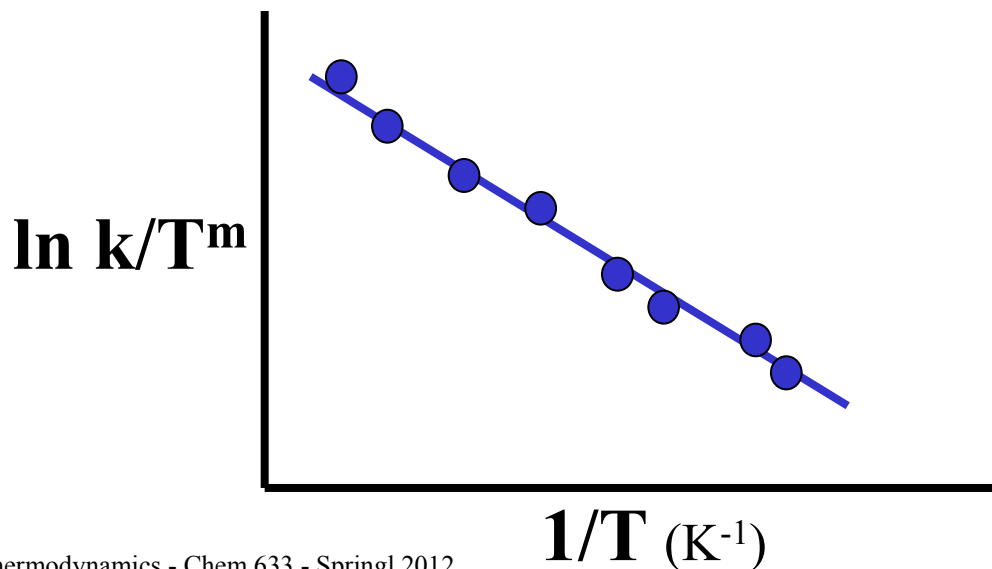
E and A are not functions of Temperature

Better fit over a wide temperature range – add “correction” terms

$$k = AT^m e^{-E/RT} \longrightarrow \ln k = \ln A + m \ln T - E_a/RT$$

“m” is an empirical constant determined from experimental data

If $m=0$ then E_a is independent of temp.
Value of m can tell something about nature of structure of Transition State



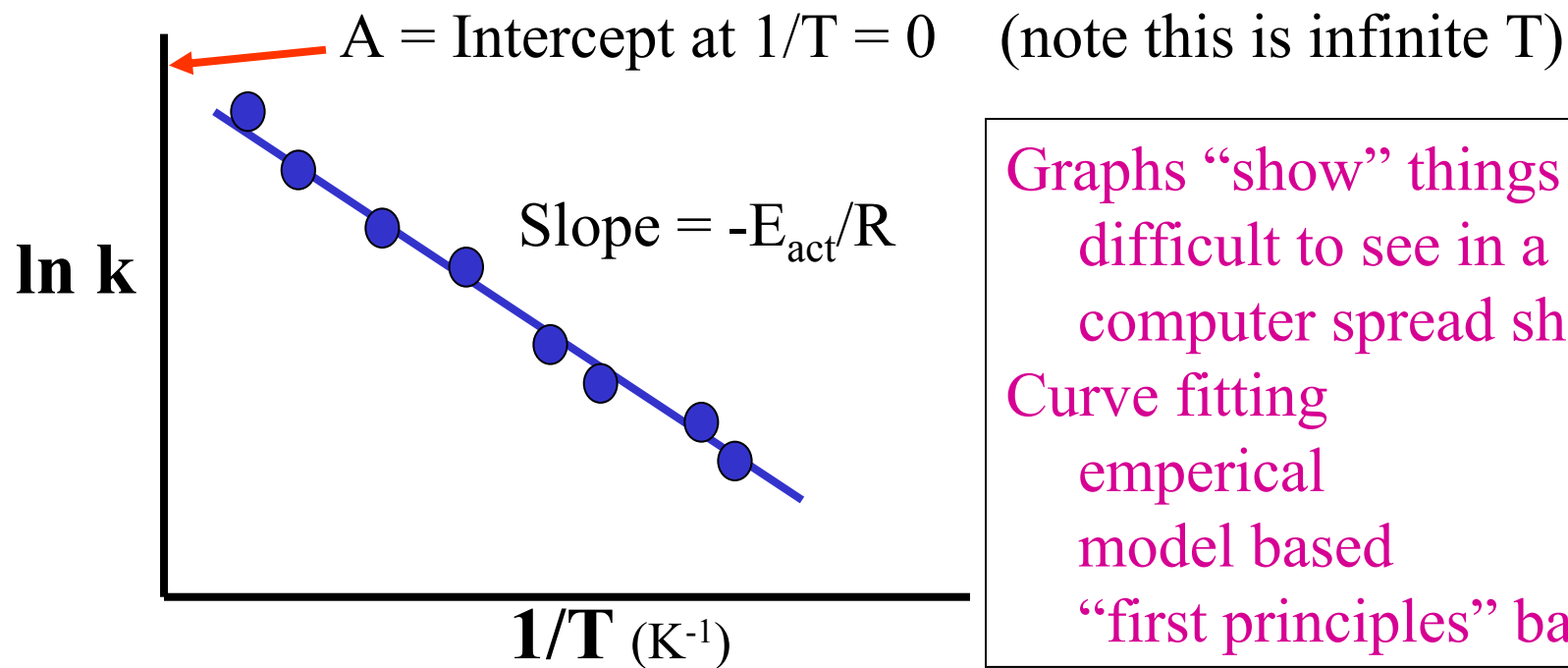
Solution to Arrhenius Equation

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

Unknowns

E_{act} Activation Energy
 A pre-exponential term

Experimental Data - rate or rate constant and temp in K



Solution to Arrhenius Equation

$$k = Ae^{-E/RT}$$

$$\ln k = \ln A - E_{\text{act}}/RT$$

Two data point solution - (2 data points only has a lot of error)

$$\ln k = \ln A - E_{\text{act}}/RT$$

2 points k_1 at T_1 and k_2 at T_2

two simultaneous equations

$$\ln k_1 + E_{\text{act}}/RT_1 = \ln k_2 + E_{\text{act}}/RT_2 \quad \text{eliminate A term}$$

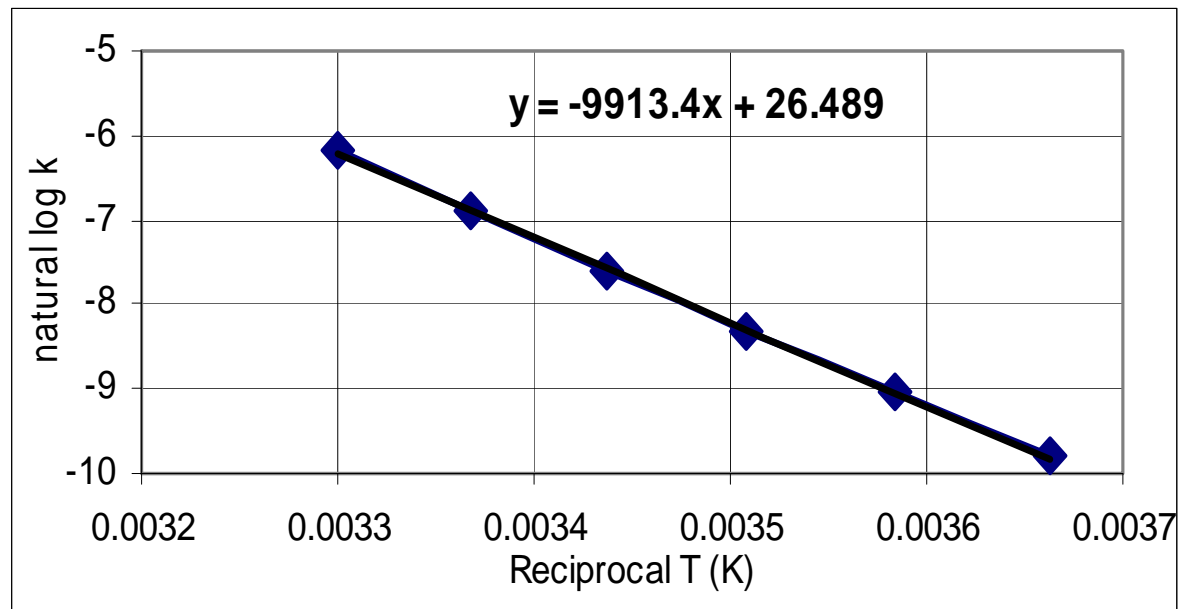
solve for E_{act} go back and solve for pre-exponential A

If you have the data, graphical analysis will
show error scatter
reduce error
show trends

Example Experiment - Arrhenius

Reaction of methyl iodide with sodium ethanoate forming methyl ethyl ether and sodium iodide - *Hecht & Conrad-Z Phys Chem, 3, 450 (1889)*

Temp C	rate const
0	5.60E-05
6	1.18E-04
12	2.45E-04
18	4.88E-04
24	1.00E-03
30	2.08E-03



$$E = 9913 \times 8.31 = 82400 \text{ J/mol} = 82.4 \text{ kJ/mol}$$

$$A = e^{26.489} = 3.2 \times 10^{11}$$

$$\ln(x) = 2.303 \log(x)$$

a lot of “older” data is in \log_{10} rather than \ln_e – Why?

Value of Arrhenius Constants

Tables of “Eact” and “A” values are in numerous data bases for many reactions and steps in reactions. Volumes of data exist. (see National Institute of Standards and Technology NIST web sites

With “Eact” and “A” you can calculate the rate constant “k” at any temperature over the range for which the “Eact” and “A” values are considered valid.

Valuable for “modeling” multi-step processes where the temperature is not constant.

$\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$	300 – 6000	23.28	~ 0
$\text{CH}_3 + \text{C}_8\text{H}_8 \rightarrow \text{CH}_4 + \text{C}_8\text{H}_7$	456 – 600	17.04	38.5
$\text{BH}_3 + \text{BH}_3\text{CO} \rightarrow \text{CO} + \text{B}_2\text{H}_6$	273 – 333	19.34	29.3
$\text{PH}_3 + \text{B}_2\text{H}_6 \rightarrow \text{PH}_3\text{BH}_3 + \text{BH}_3$	249 – 273	14.97	47.7
$\text{CO} + \text{O}_2 \rightarrow \text{O} + \text{CO}_2$	2400 – 3000	21.97	213.4
$\text{F}_2 + \text{ClO}_2 \rightarrow \text{F} + \text{FClO}_2$	227 – 247	16.37	33.5

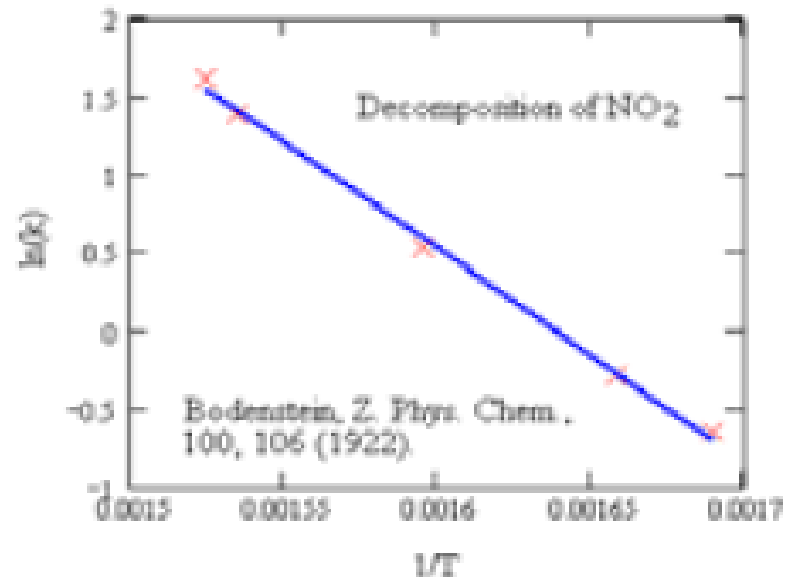
Temperature dependence of rate constants

$$k(T) = A \exp(-E_a / RT)$$

◆ Empirical theory of Arrhenius gives a useful way to parameterize rate constants

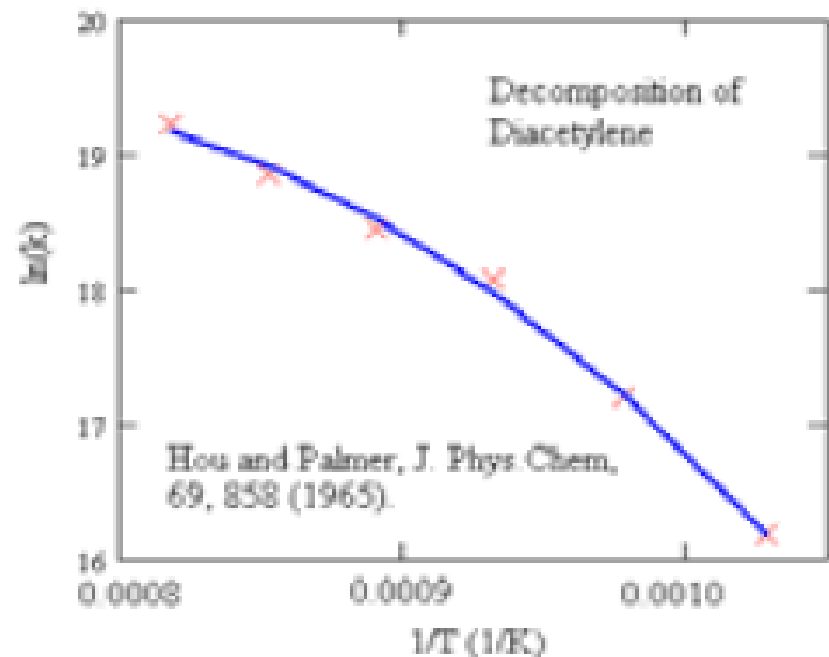
- $A \equiv$ pre-exponential factor
- $E_a \equiv$ activation energy

◆ Often seen in analysis of kinetic data



Non-Arrhenius behavior

- ◆ Arrhenius behavior is empirical
- ◆ For some reactions the temperature dependence of the rate constant is not exponential
- ◆ Theory does not easily predict Arrhenius form
- ◆ Amazing that Arrhenius behavior is so often seen

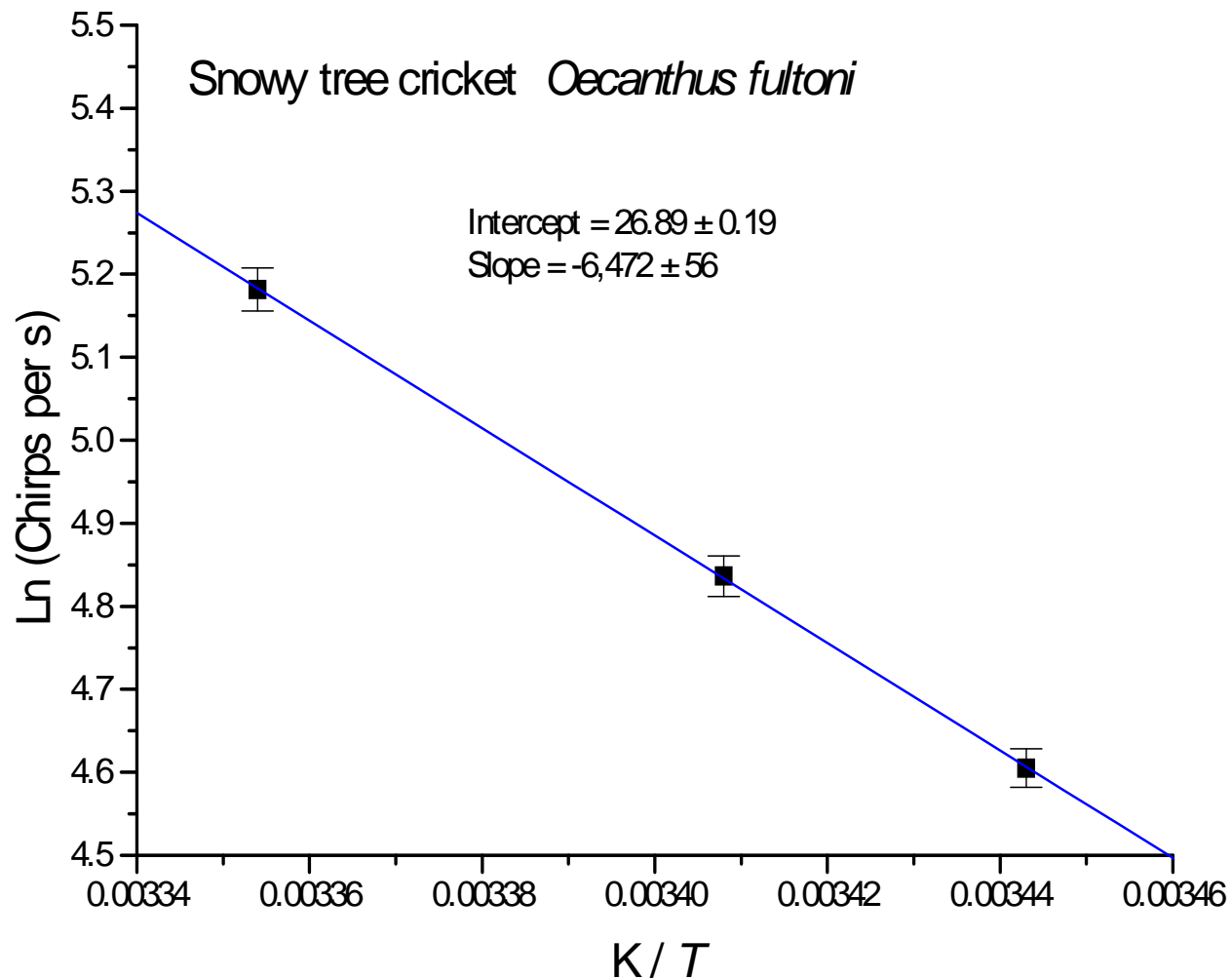


Non-Arrhenius behavior suggests possibility that reaction is a series of elementary processes, like two steps with different Eact

Unconventional Applications of Arrhenius Theory



some examples



Data from Keith Laidler, *J Chem Educ* 49, 343 (1972)
 T 17.3—25.0 C, chirp rates of 100 to 178 min^{-1}

Unconventional Application of Arrhenius Theory

- Many complex processes follow pseudo-Arrhenius behavior
- If a process is the composite of many simple processes, each of which follows Arrhenius behavior, then the net process follows Arrhenius-"like" behavior
- Useful to develop mathematical expressions that predict behavior
- Useful for complex models
- Complex reaction with many steps

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

$$\ln k = \ln A - E_{\text{act}}/RT$$

$$\text{Rate} = A' \cdot e^{-E/RT}$$

$$\ln k = \ln A' - E_{\text{act}}/RT$$

$$\text{Something proportional to Rate} = A'' \cdot e^{-E/RT}$$

A, A', A'' are functions of frequency of collisions

Sample Problem – Arrhenius Theory

A second order process $A + B \rightarrow$ products has a rate constant of 1.0×10^{-2} M/sec at 25°C . And 3.0×10^{-2} M/sec at 50°C .

What is the Activation Energy? What is the pre-exponential term A?

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

$$\ln k = \ln A - E_{\text{act}}/RT$$

$\ln A$ for data set 1 must equal $\ln A$ for data set 2 – use algebra to solve for E

Two Point Solution

$$\ln k_1 + E_{\text{act}}/RT_1 = \ln k_2 + E_{\text{act}}/RT_2$$

DATA-

$$k_1 = 1.0 \times 10^{-2}$$

$$T_1 = 298 \text{ K}$$

$$k_2 = 3 \times 10^{-2}$$

$$T_2 = 323 \text{ K}$$

$$R = 8.3145 \text{ J/K-mol}$$

$$R = 1.9872 \text{ cal/K-mol}$$

$$\text{Solve for } E_{\text{act}} = 35600 \text{ J/mol}$$

$$E_{\text{act}} = \mathbf{35.6 \text{ kJ/mol}}$$

Substitute in E_{act} and solve for A

$$A = \mathbf{1.7 \times 10^4} \text{ (units of "k")}$$

With only 2 points it is meaningless to generate a graph.

Sample Problem – Arrhenius Theory – cont'd

Based on the data in the problem on the previous slide, how long does it take for the concentration of reactant to drop from 1.0 M each A and B to 0.1M each (ie drop 10x) at 25 C and at 50 C?

1.0×10^{-2} M/sec at 25°C, 3.0×10^{-2} M/sec at 50°C. Second Order Reaction goes 3x faster at 50°C than at 25°C. (see slide set 2)

If $A_0 = B_0$ Then $d[A]/dt = -k[A]^2$ or $1/(At) = kt + 1/(A_0)$

Substitute into $1/(At) = kt + 1/(A_0)$

at 25°C it takes 900 sec or 15 min to drop from 1 M to 0.1 M

at 50°C it takes 300 sec or 5 min to drop from 1 M to 0.1 M

Improved/Modified Arrhenius Equation

$$k = AT^m e^{-E/RT}$$

$$\ln k = \ln A + m \ln T - E_a/RT$$

- Some theoretical models (later) use or predict values for “m”
- Large values of “A” dominate and variations in “m” have little effect
- “m” leads to curvature in Arrhenius plots (ln rate vs 1/T)

Another approach to deal with “non-pure” Arrhenius behavior

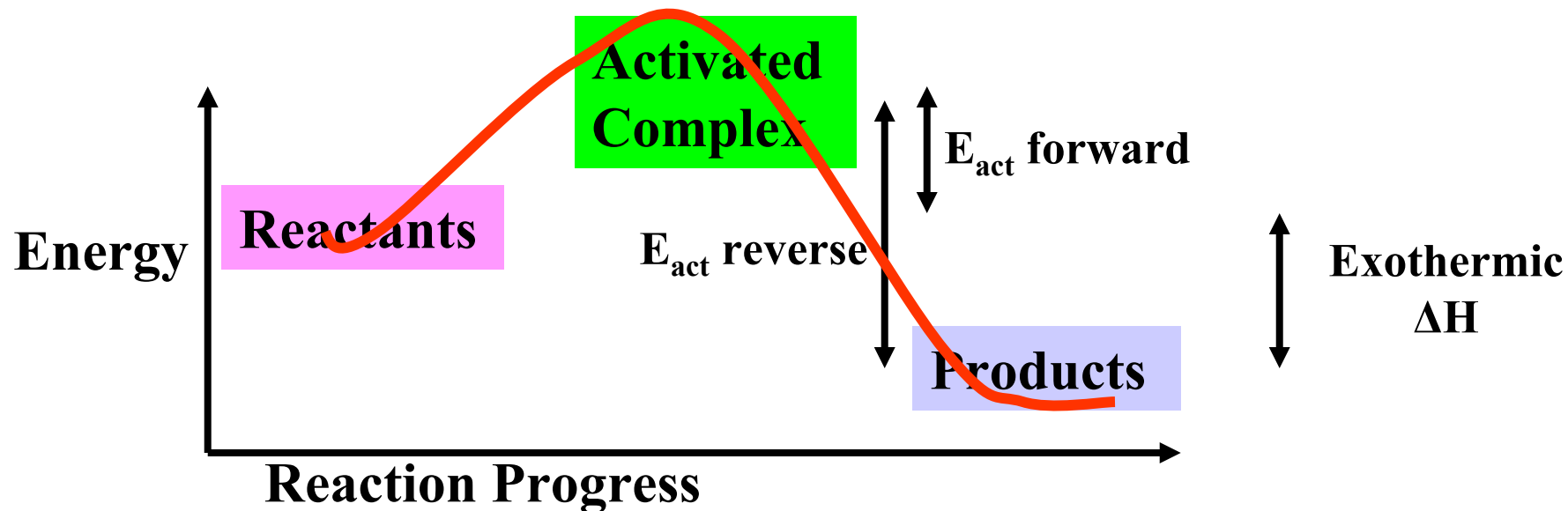
$$E_{\text{act}} = E_0 + RT$$

where E_0 is hypothetical Activation Energy at absolute zero

If traditional Arrhenius graph show curvature rather than linear
Then probably E_{act} is a function of temperature

There are several empirical equations commonly used to fit data

Activation Energy Concept



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



Activation Energy gained by multiple collisions - statistical

Molecular Kinetic Energy

- **Where do molecules get the energy required to exceed E_{act} ?**
- Environmental energy is only $\sim RT$ and E_{act} may be greater than RT

Kinetic Energy of Molecules

- Rotational
- Vibrational
- Translational

Translational Energy

- 3 degrees of freedom x, y, z
- kinetic energy of translation = $1/2kT$ per degree of freedom
- Kinetic energy is directly proportional to temperature
- Total average kinetic energy of translation = $3/2kT$
 - At 25°C (298K) 888 cal/mol 3700 J/mol 3.7 kJ/mol
 - For 1 molecule 6.17×10^{-14} erg

Multiple collisions can accumulate energy (statistically) and some molecules can exceed E_{act}
--drastically fewer molecules have enough energy to cross barrier as E_{act} increases and/or T decreases (Boltzman Statistics)

Molecular Motion

Gas Phase Systems-

average kinetic energy = $3/2kT$

based on Maxwell Boltzman Statistics

Average Speed $c = \sqrt{8RT/\pi M}$

Most Probable Speed = $\sqrt{2RT/M}$

Root Mean Square Speed = $\sqrt{3RT/M}$

Mean Free Path Between Collisions = $L = 1/2\sigma^2N^*$

σ = collision diameter N^* = number of molecules/unit Volume
(*in a vacuum N^* is small so L is large*)

Number of collisions per molecule per second = $2\pi\sigma^2cN^*$

Collisions are an integral part of what controls reaction kinetics

A Feel For Molecular Motion

speed of sound
at sea level =
340.29 m / s

Molecular Speeds			
<u>molecule</u>	<u>speed at 25°C</u>		<u>speed at 1000°C</u>
H ₂	1770 m/s		3660 m/sec
He	1260		2600
N ₂	470	1060mph	970 2190mph
CO ₂	380		780
Hg	180		370

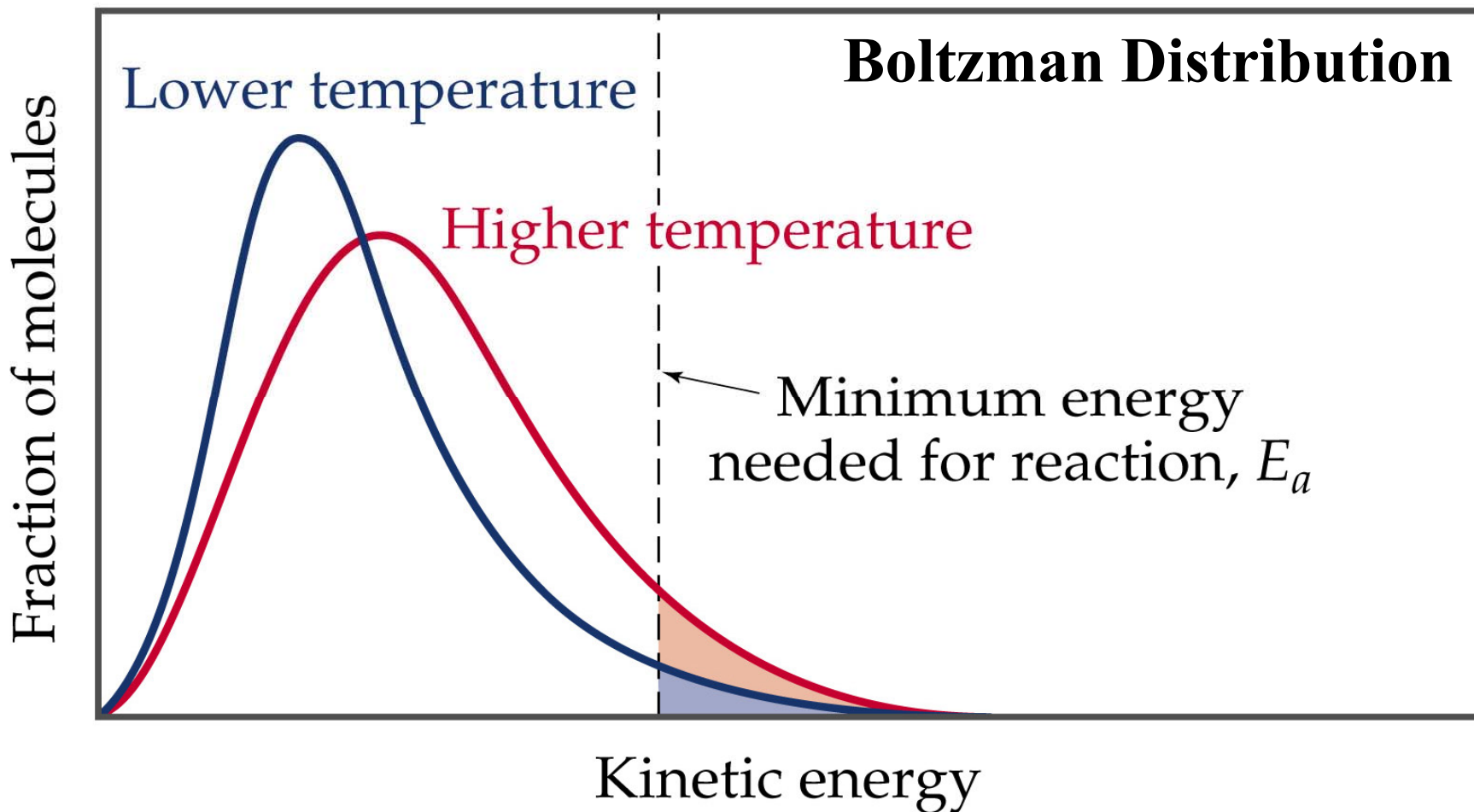
At 25°C and 1 atm pressure Nitrogen N₂

- gas density $N^* = 2.46 \times 10^{25}$ per m³
- mean free path $L = 6.56 \times 10^{-8}$ meters
- collision frequency = $Z_1 = 7.24 \times 10^9$ collisions/sec for a molecule
- collision frequency = $Z_{11} = 8.9 \times 10^{34}$ collisions/m³-sec

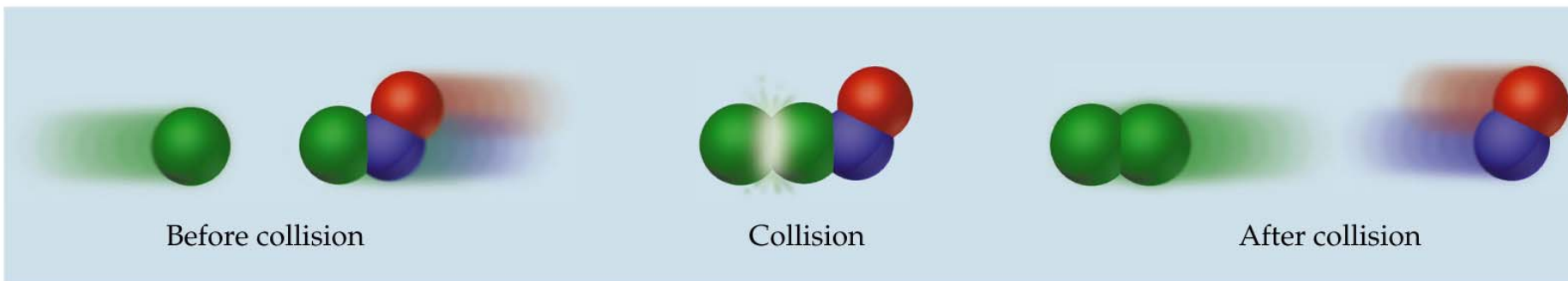
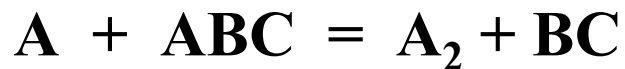
There is a relationship between frequency of collision, rate of reaction and the Arrhenius pre-exponential term “A”

Effect of Temperature on Rate

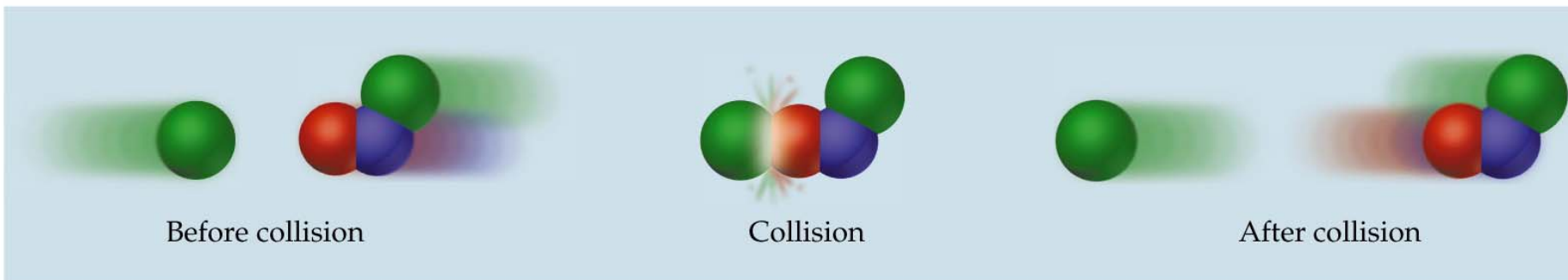
$$k = Ae^{-E/RT} \quad \text{or} \quad \ln k = \ln A - E_{\text{act}}/RT$$



Orientation Factor



(a) Effective collision

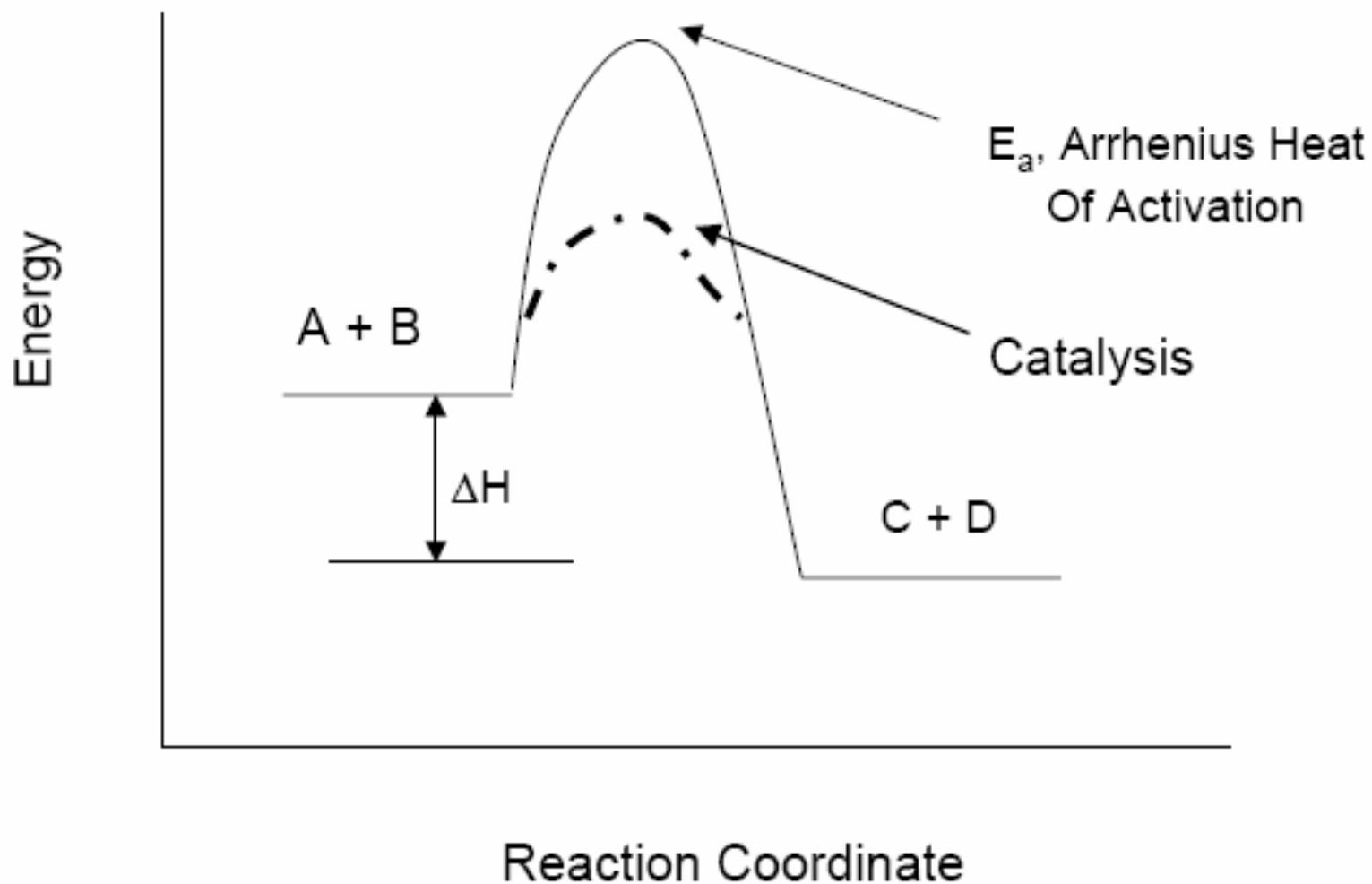


(b) Ineffective collision

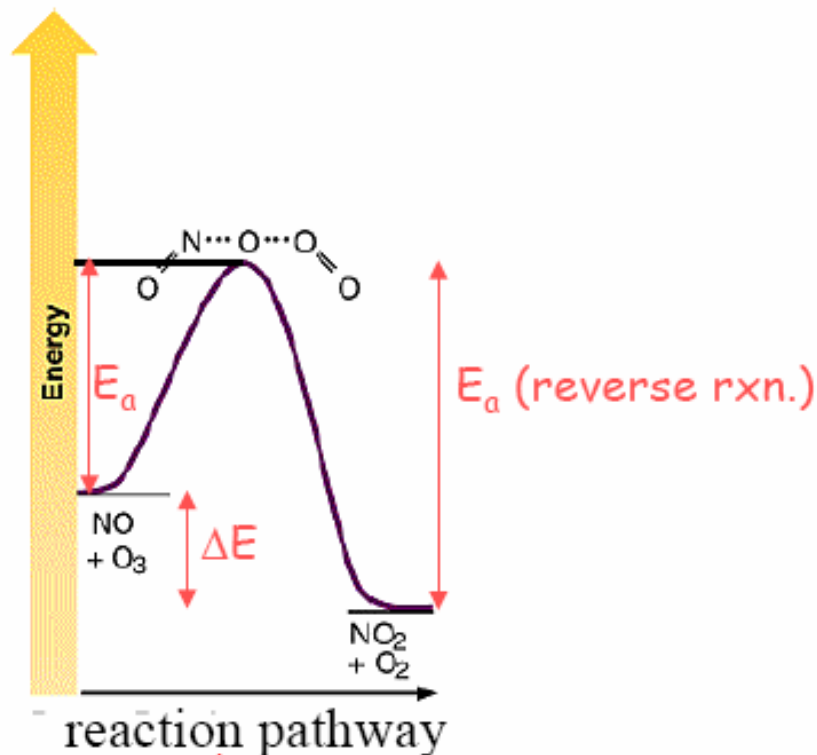
Collision orientation affects the “A” term not the E term

$$k = A e^{-E/RT} \quad \text{or} \quad \ln k = \ln A - E_{\text{act}}/RT$$

Chemical Reaction Profile

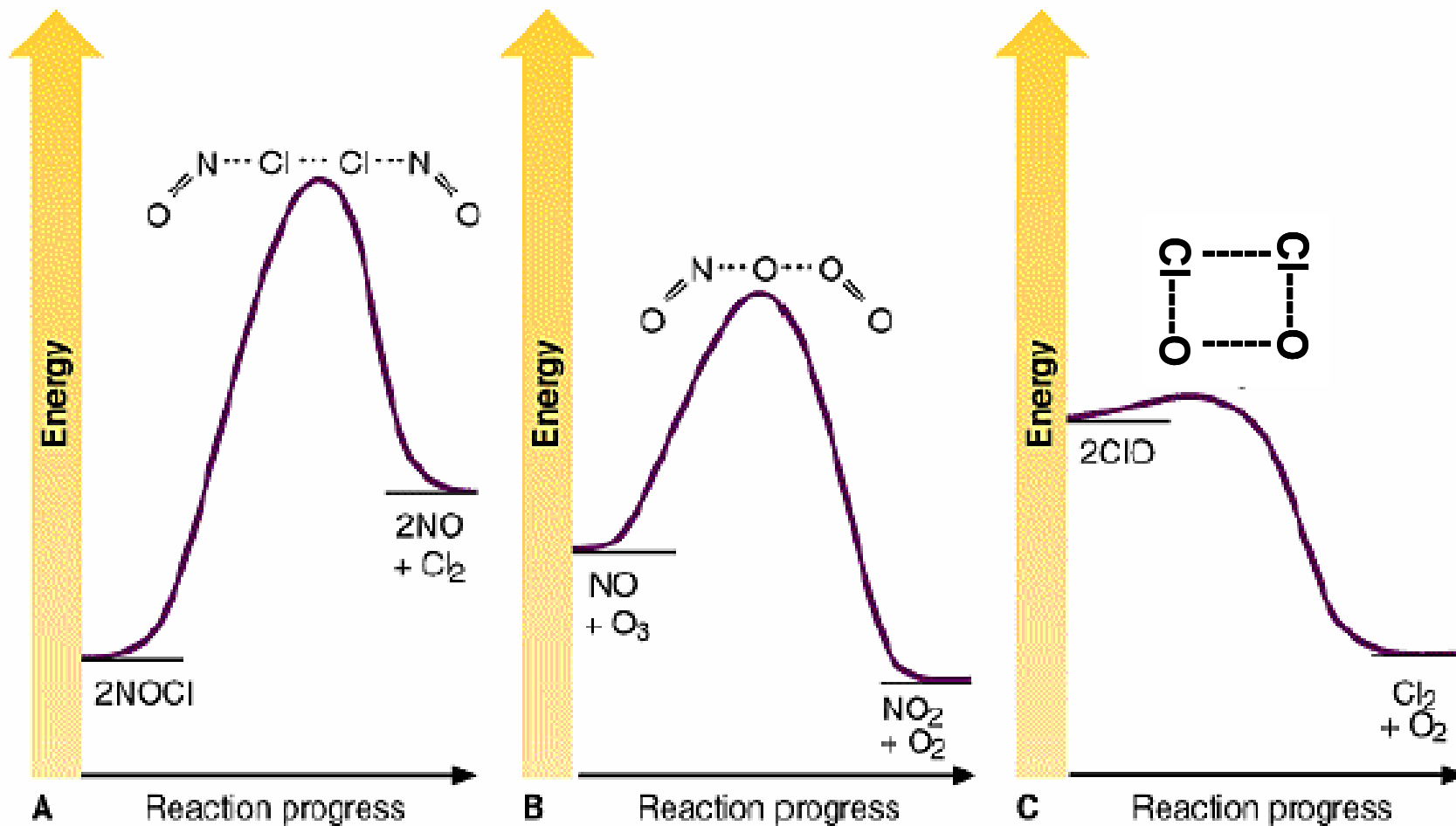


Energy Requirements

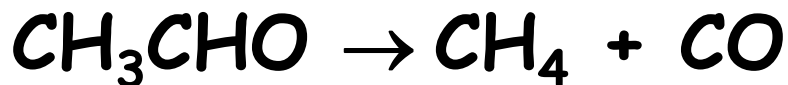


- Energy barrier to reaction that must be overcome
Usually referred to as activation energy (E_a)
- ΔE is the net internal energy change
- Note
 E_a (forward reaction) \neq E_a (reverse reaction)
 ΔE (forward reaction) = $-\Delta E$ (reverse reaction)

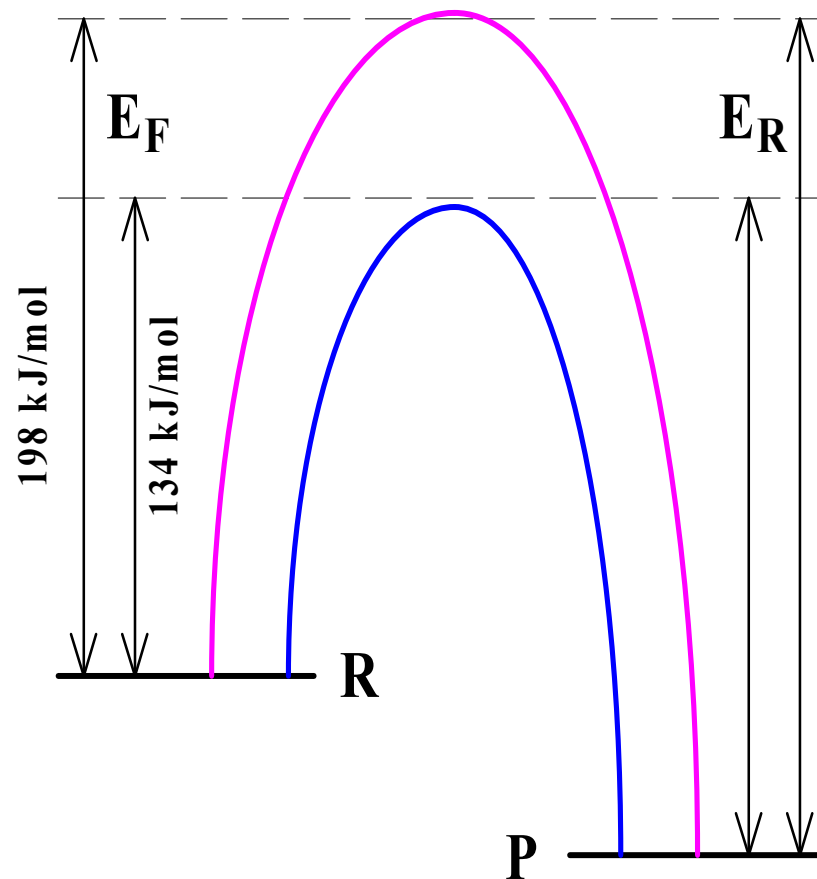
Reaction-Specific Energy Requirements



Reaction profile diagram



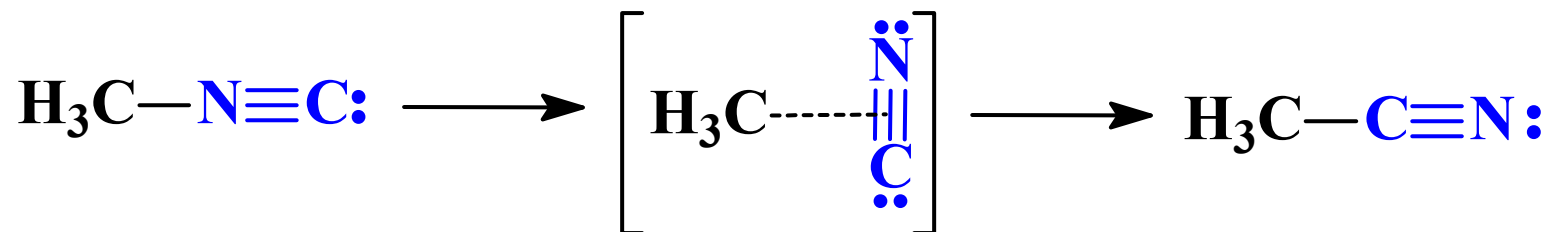
- $E_F = 198$ kJ/mol
- Add some iodine as catalyst $E_F = 134$ kJ/mol
 - Modest reduction in barrier
 - Massive increase in rate
- At 773 K catalysed rxn is **20,000** times faster
 - $D(\text{C-C})=340$, $D(\text{C-H})=420$
 - But $D(\text{I-I})=153$ kJ/mol



Use Arrhenius equation to see the effect of activation energy on rate
At home set up an excel spreadsheet and “experiment” with numbers

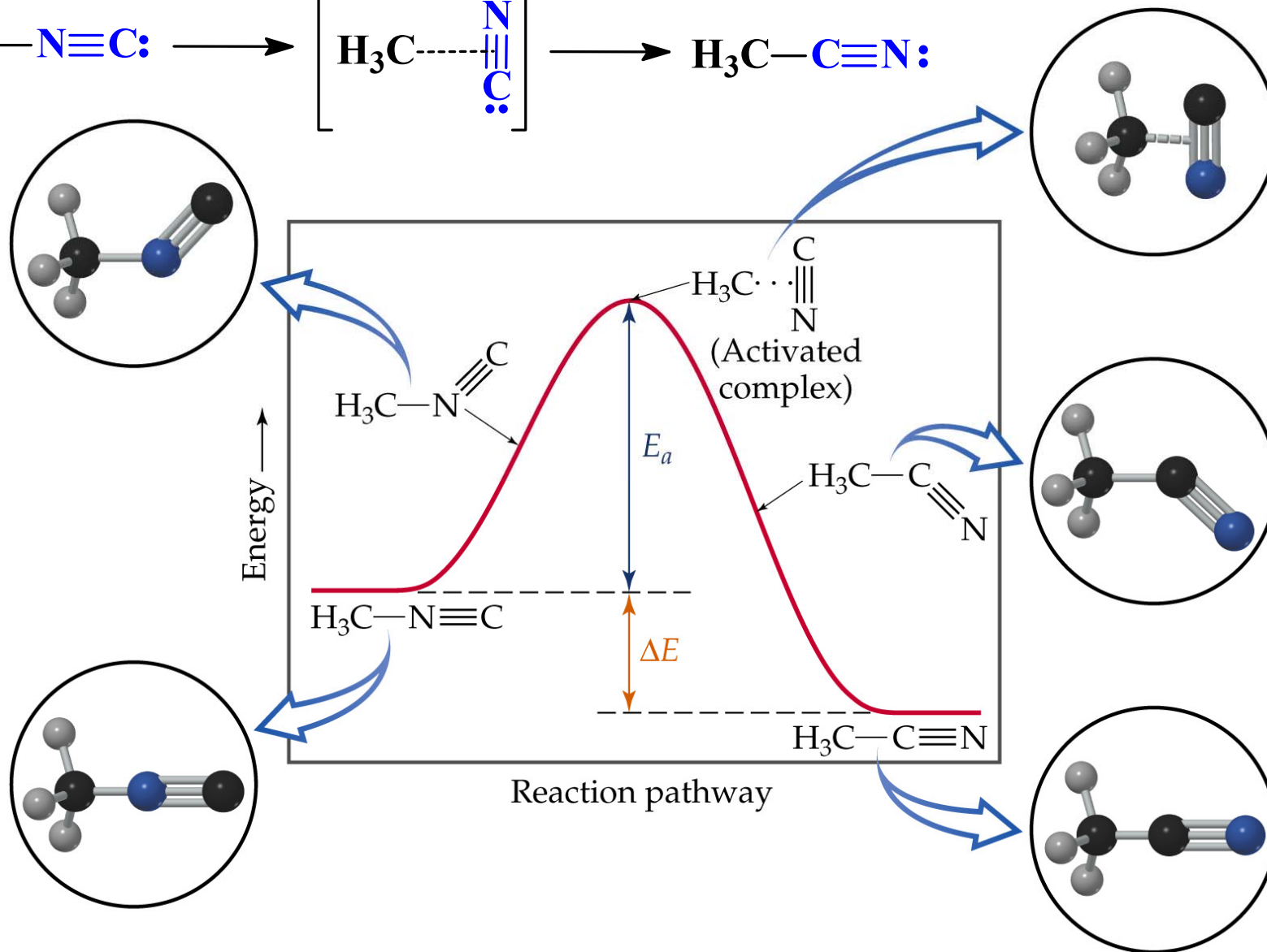
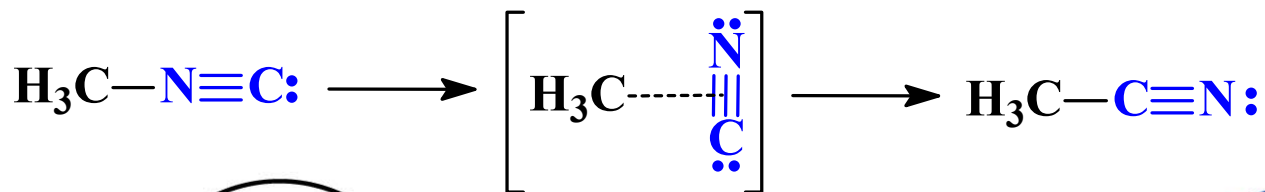
Activation Energy and the Transition State

- Consider the rearrangement of methyl isonitrile:



- In $\text{H}_3\text{C}-\text{N}\equiv\text{C}$, the $\text{C}-\text{N}\equiv\text{C}$ bond bends until the $\text{C}-\text{N}$ bond breaks and the $\text{N}\equiv\text{C}$ portion is perpendicular to the H_3C portion. This structure is called the activated complex or transition state.
- The energy required for the above twist and break is the activation energy, E_a .
- Once the $\text{C}-\text{N}$ bond is broken, the $\text{N}\equiv\text{C}$ portion can continue to rotate forming a $\text{C}-\text{C}\equiv\text{N}$ bond.

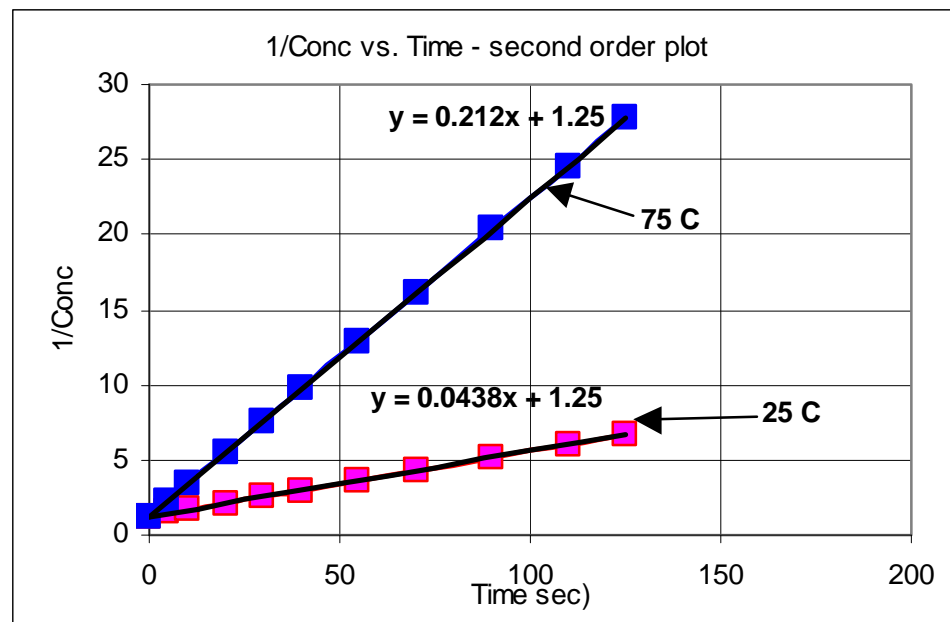
Activation Energy



Sample Problem

The following concentration vs. time data was measured for a reaction at 25°C and again at 75°C. What is the order, rate constant and Arrhenius Activation Energy?

time sec	at 25 C		at 75 C	
	conc M	1/conc	conc	1/conc
0	0.800	1.25	0.800	1.25
5	0.681	1.47	0.433	2.31
10	0.593	1.69	0.297	3.37
20	0.471	2.13	0.182	5.49
30	0.390	2.56	0.131	7.61
40	0.333	3.00	0.103	9.73
55	0.274	3.66	0.077	12.91
70	0.232	4.31	0.062	16.09
90	0.193	5.19	0.049	20.33
110	0.165	6.06	0.041	24.57
125	0.149	6.72	0.036	27.75
	k=	0.0438	k2=	0.212
		1/M-sec		1/M-sec



Much more accurate to take data at several temperatures and not just two

(continued on next slide)

Sample Problem *contd*

temp	temp K	1/temp K	k	lnk
25	298	0.003356	0.04375	-3.12926
75	348	0.002874	0.212	-1.55117
slope from graph ==		-3273		
Eact=slope x R =		27198.63 J/mol		
		27.2 kJ/mol		

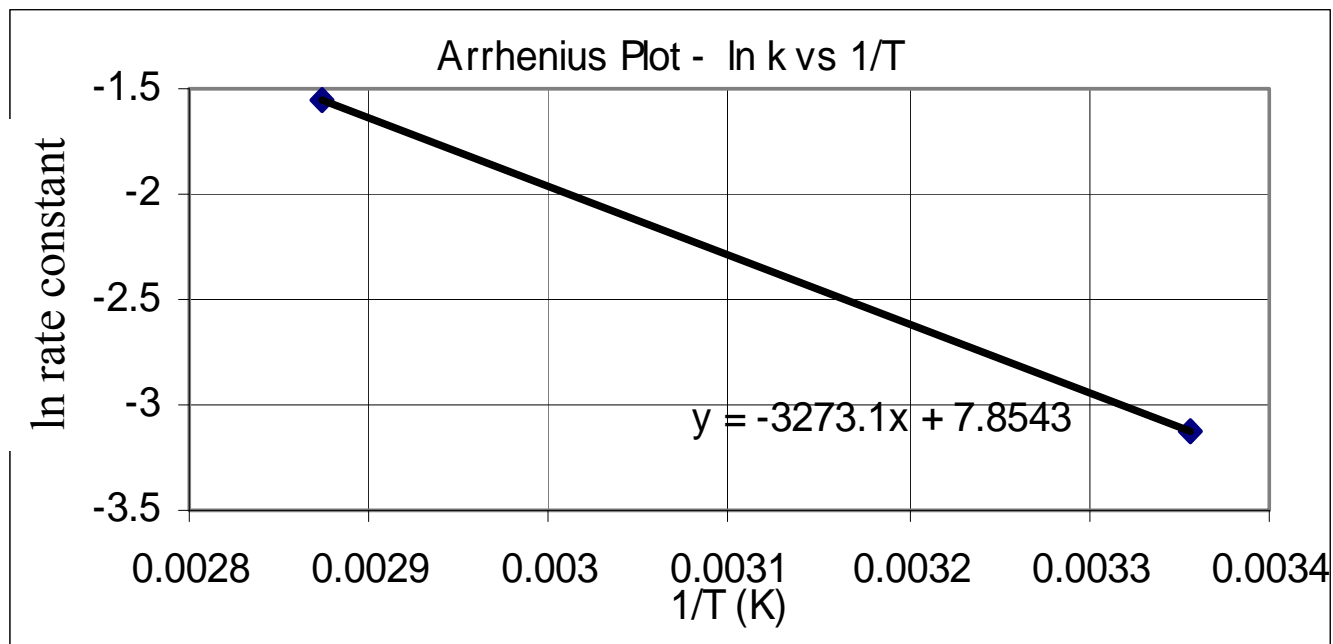
$$k = Ae^{-E/RT}$$

pre-exponential is A

$$\ln(A) = 7.854$$

$$\text{so } A = e^{+7.854} = 2576$$

often \ln rate rather than \ln rate constant is plotted on y-axis since they are proportional to each other you get the same slope (not the same intercept)

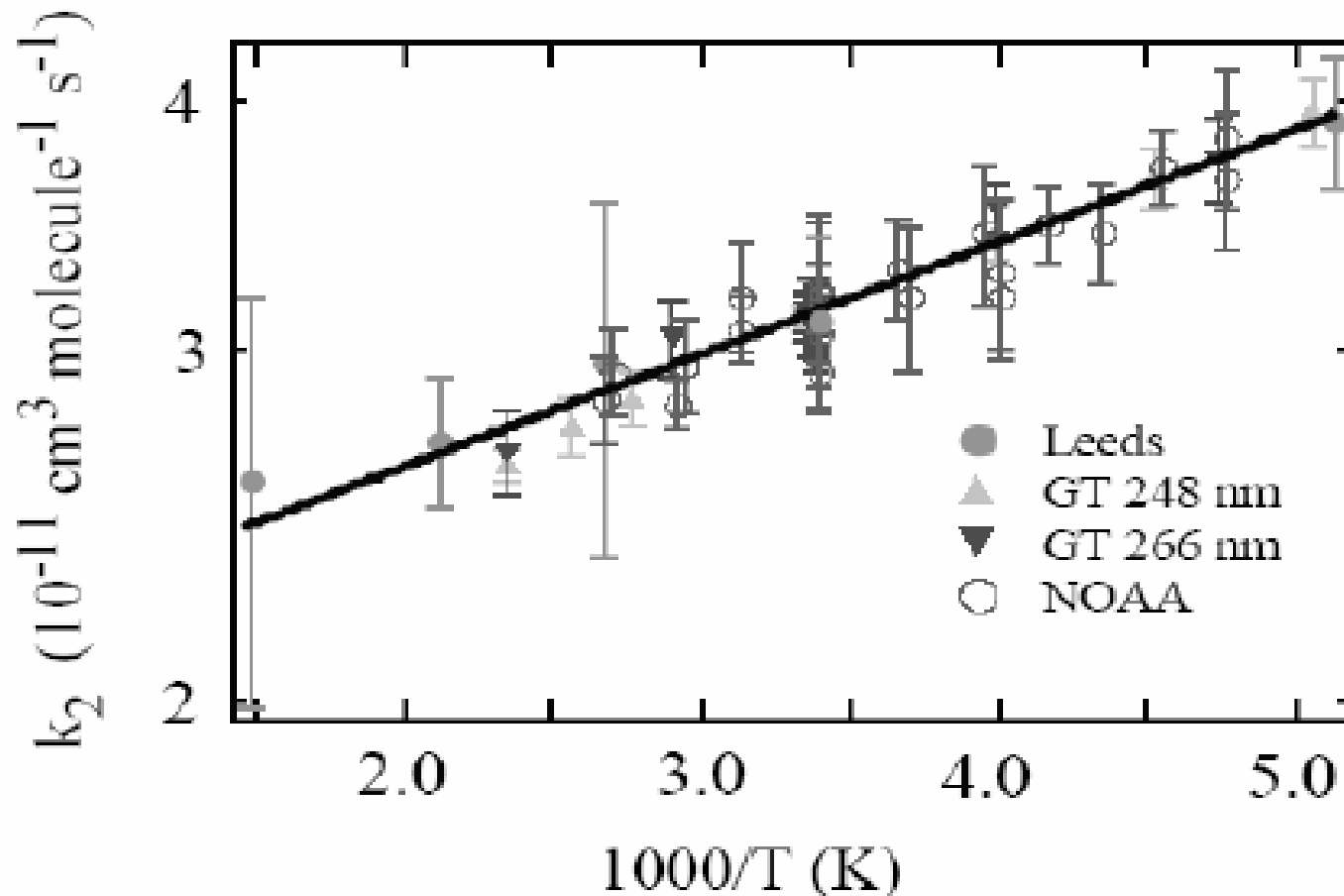


Example of Arrhenius Plot

Measurements of rate coefficient for $O(^1D) + N_2$

Plotted on log scale, so fit to Arrhenius expression appears as line

Note that this is example of negative activation energy



From
Ravishankara
et al., *GRL*,
VOL. 29, NO.
15, 1745,
2002

A

Arrhenius eqn. $k=A \exp\{-E/RT\}$

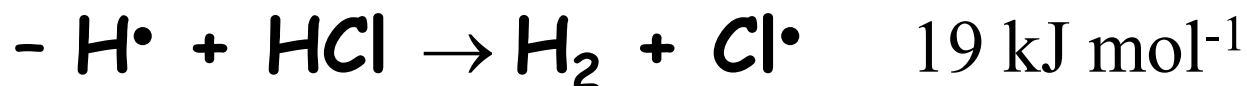
Useful *linear* form: $\ln k = -(E/R)(1/T) + \ln A$

- Plot $\ln k$ along Y-axis *vs* $(1/T)$ along X-axis

Slope is *negative* $-(E/R)$; intercept = $\ln A$

- Experimental E s range from 0 to +400 kJ mol⁻¹

Examples of Activation Energies:



Examples of Experimental Activation Energies

Reaction	Range	$\ln A$	E_a
$H + D_2 \rightarrow HD + H$	300 – 750	24.61	39.3
$H + HCl \rightarrow H_2 + Cl$	200 – 500	23.85	14.6
$H + HBr \rightarrow H_2 + Br$	1000 - 1700	25.42	15.5
$O + O_3 \rightarrow 2 O_2$	273 – 900	23.21	20.0
$N + NO \rightarrow N_2 + O$	300 – 6000	23.28	~ 0
$CH_3 + C_6H_6 \rightarrow CH_4 + C_6H_5$	456 – 600	17.04	38.5
$BH_3 + BH_3CO \rightarrow CO + B_2H_6$	273 – 333	19.34	29.3
$PH_3 + B_2H_6 \rightarrow PH_3BH_3 + BH_3$	249 – 273	14.97	47.7
$CO + O_2 \rightarrow O + CO_2$	2400 – 3000	21.97	213.4
$F_2 + ClO_2 \rightarrow F + FClO_2$	227 – 247	16.37	33.5

(a) The range of validity is expressed in kelvins.
 (b) A is in $dm^3 mol^{-1} s^{-1}$.
 (c) E_a is in $kJ mol^{-1}$.

Careful of units! A can be any inverse conc inverse time

Problem Example

Using the data in the previous slide – The initial concentration of O atoms and ozone O₃ gas in a container (maybe like the earth's stratosphere) at 25°C are each 0.0001 molar. How long would it take for the concentration of O₃ to drop to ½ of this amount? How long if the temperature were 100°C?

Use Arrhenius relationship and values of A and E_{act} to find K at each temperature. Using those k's use a second order kinetic rate equation to solve.

$k = Ae^{-E/RT}$ or $\ln k = \ln A - E_{act}/RT$ watch units!

at 298K $\ln k = 23.21 - 20,000 \text{ kJ}/(\text{mol}/8.31 \text{ J/K-mole} \times 298) = 15.134$

$k @ 298\text{K} = 3.7 \times 10^6 \text{ M}^{-1}\text{sec}^{-1}$ $k @ 373\text{K} = 1.9 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$

(reaction goes a little over 5 times faster at 100°C than 25°C)

Problem Example - continued

$$k @298K = 3.7 \times 10^6 \text{ M}^{-1}\text{sec}^{-1} \quad k @373K = 1.9 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$$

second order $dx/dt = k[A_0 - x][B_0 - x]$ x =amount reacted in time t

here $A_0 = B_0$ (we are lucky! the arithmetic is easier)

$$d[A]/dt = -k[A]^2 \quad \text{or} \quad 1/(A_t) = kt + 1/(A_0)$$

How long for the concentration of O_3 (and O) to drop $1/2$?

$A_0 = 0.0001 \text{ M}$ and $A_t = 0.00005 \text{ M}$ we know k so solve for time t

$$1/0.00005 = 3.7 \times 10^6 (\text{time}) + 1/0.0001$$

solve for time

time for conc of ozone to drop to $1/2$ initial conc at $25^\circ\text{C} = 0.0027 \text{ sec}$

at 100°C it should take about 0.0005 seconds

try it if initial conc of O and O_3 are not equal to each other (this is far more realistic case)

discuss importance of ozone in earth's stratosphere