Chemistry 1B, Fall 2016
Topic 23

Chemistry 1B

Fall 2016

Topic 23
[more] Chemical Kinetics

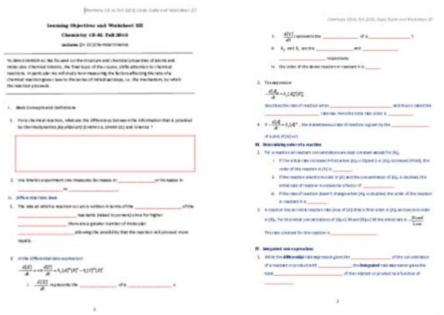
goals for topic 23

- kinetics and mechanism of chemical reaction
- energy profile and reaction coordinate
- activation energy and temperature dependence of rate constant
- catalysis

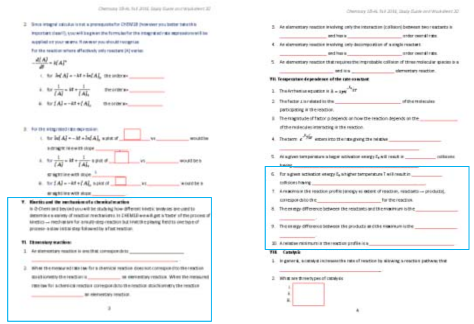
chemical kinetics

elementary reactions
reaction mechanisms
reaction energy profile and the reaction coordinate diagram

have already covered worksheet 10 sections I-IV



this video and : worksheet 10 sections I-VI and VII (6-10)



goals for video 13

- elementary reactions
- kinetics and the mechanism of a chemical reaction
- energy profile and reaction coordinate

Chemistry 1B, Fall 2016
Topic 23

kinetics and mechanism of reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ at T< 500K

if the reaction was a collision between a NO_2 molecule and a CO molecule one might expect for the differential rate law:

$$-\frac{d[NO_2]}{dt} = k[NO_2][CO] \quad \times$$

but the observed rate of reaction is:

$$-\frac{d[NO_2]}{dt} = k[NO_2]^2$$

You might ask ?

elementary reactions

the observed kinetics $-\frac{d[NO_2]}{dt} = k[NO_2]^2$

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ at T< 500K

is not consistent with this stoichiometric equation in representing the actual molecular collisions involved in the reaction

ok?? but first let's look at reactions where the stoichiometric equation DOES represent the actual collision process. these are called ELEMENTARY REACTIONS

kinetics and mechanism of reaction

back to the question: so what's up DOC ??

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ at T< 500K

answer: the above (stoichiometric) equation NO_2 colliding with CO does NOT represent the molecular mechanism (molecular steps of the reaction)

in actuality: the reaction takes place in two steps

$NO_2(g) + \cancel{NO_2}(g) \rightarrow NO(g) + \cancel{NO_3}(g)$ *slow*

$\cancel{NO_3}(g) + CO(g) \rightarrow CO_2(g) + \cancel{NO_2}(g)$ *fast*

net reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ *overall reaction*

mechanism of the reaction

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ *overall reaction (T<500K)*

$NO_2(g) + NO_2(g) \xrightarrow{k_{slow}} NO(g) + NO_3(g)$ *slow*

$NO_3(g) + CO(g) \xrightarrow{k_{fast}} CO_2(g) + NO_2(g)$ *fast*

- The two steps are the actual molecular processes by which the reaction occurs and is the **MECHANISM** the reaction
- They represent **ELEMENTARY** reactions
- The combination of elementary reactions must sum to the overall stoichiometry
- Species [e.g. NO_3 (g)] appearing in the steps of the mechanism, but not the overall reaction are **REACTION INTERMEDIATES**

how to get rate law from mechanism of the reaction

T<500K

$NO_2(g) + NO_2(g) \xrightarrow{k_{slow}} NO(g) + NO_3(g)$ *slow*

$NO_3(g) + CO(g) \xrightarrow{k_{fast}} CO_2(g) + NO_2(g)$ *fast*

- rates for individual steps come directly from the stoichiometry of the **ELEMENTARY** reactions
- how to combine rates of elementary reactions to get overall rate equation
  LOTS OF TRICKS (but we don't have time for many)
- our **ONE** example will be **slow** reaction followed by **rapid** reaction (like above reaction)

how to get rate law from mechanism of the reaction

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

T<500K

$2\ NO_2(g) \xrightarrow{k_{slow}} NO(g) + NO_3(g)$ *slow*

$NO_3(g) + CO(g) \xrightarrow{k_{fast}} CO_2(g) + NO_2(g)$ *fast*

since these are ELEMENTARY reactions:

$$\boxed{-\frac{d[NO_2]}{dt} = k_{slow}[NO_2]^2} = +2\frac{d[NO_3]}{dt} \quad \textbf{slow}$$

$$-\frac{d[CO]}{dt} = k_{fast}[NO_3][CO] \quad \textbf{fast}$$

- since $k_{fast} >> k_{slow}$ as soon as slow reaction produces NO_3 the fast reaction occurs
- the total rate is the just the rate of the slow step
  total rate= $k_{slow}\,[NO_2]^2$ *(2nd order in NO_2, 0th order in CO)*

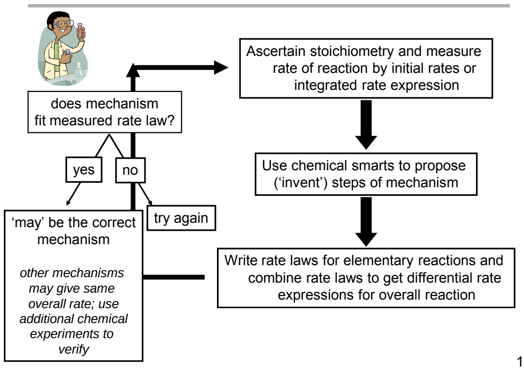
from slide #5: the observed rate of reaction is: $-\frac{d[NO_2]}{dt} = k[NO_2]^2$

Chemistry 1B, Fall 2016
Topic 23

factoids about rate laws and mechanisms

- in general the rate law cannot be written in terms of the stoichiometric coefficients of the overall reaction
- the rate law for an elementary reaction **IS** determined by the molecularity (stoichiometry) of the individual step
- the overall rate law is obtained from combining rate laws of elementary reactions
- an overall reaction where the measured rate law and the stoichiometric coefficients 'match' **MAY** or **MAY NOT** be an elementary reaction

the actual process of determining mechanism of a reaction



Ascertain stoichiometry and measure rate of reaction by initial rates or integrated rate expression

Use chemical smarts to propose ('invent') steps of mechanism

Write rate laws for elementary reactions and combine rate laws to get differential rate expressions for overall reaction

does mechanism fit measured rate law?

yes

no

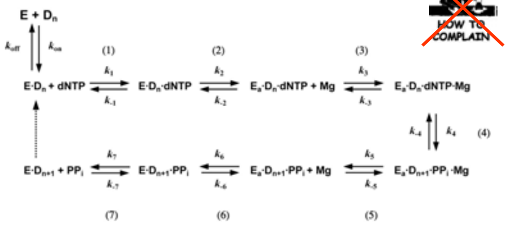
'may' be the correct mechanism

other mechanisms may give same overall rate; use additional chemical experiments to verify

try again

DNA synthesizer kinetics

and your thought Chem 1B kinetics was complicated !!



$k_{on} = 1.2 \times 10^7\ M^{-1}\cdot s^{-1}$, $k_{off} = 0.06\ s^{-1}$, $k_1 = 1.25 \times 10^7\ M^{-1}\cdot s^{-1}$, $k_{-1} = 250\ s^{-1}$, $k_2 = 50\ s^{-1}$, $k_{-2} = 3\ s^{-1}$, $k_3 = 9.5 \times 10^5\ M^{-1}\cdot s^{-1}$, $k_{-3} = 100\ s^{-1}$, $k_4 = 150\ s^{-1}$, $k_{-4} = 40\ s^{-1}$, $k_5 = 100\ s^{-1}$, $k_{-5} = 9.5 \times 10^5\ M^{-1}\cdot s^{-1}$, $k_6 = 4\ s^{-1}$, $k_{-6} = 4\ s^{-1}$, $k_7 = 60\ s^{-1}$, $k_{-7} = 1.45 \times 10^4\ M^{-1}\cdot s^{-1}$.)

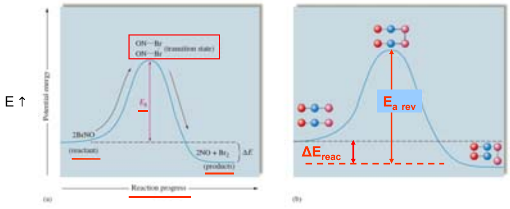
Pourmand N et al. PNAS 2006;103:6466-6470

PNAS

the reaction coordinate and course of a chemical reaction

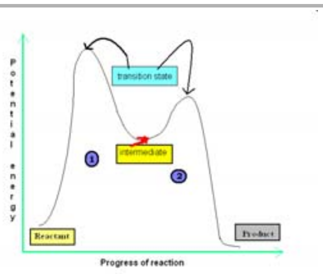
elementary reaction
$2BrNO \rightarrow 2NO + Br_2$

molecularity ?
bimolecular



- energy vs reaction coordinate (progress of reaction reactants –products)
- transition state (maxima of E vs reaction coordinate)
  [N---Br bonds breaking, Br---Br bond forming]
- activation energy ($E_a = E_{\text{transition state}} - E_{\text{reactants}}$)
- reverse activation energy ($E_{a\ rev} = E_{\text{transition state}} - E_{\text{products}}$)
- $\Delta E_{\text{reaction}}$ (ΔH)= ($E_{\text{products}} - E_{\text{reactants}}$)

multi-step reaction



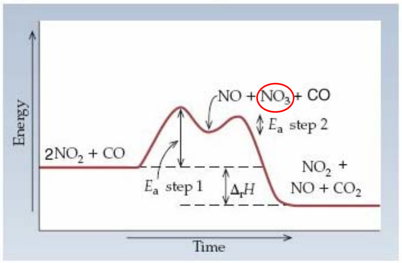
('stable') **Reaction Intermediate** is at a relative minimum along curve

http://chemwiki.ucdavis.edu/@api/deki/files/916/=intermediate.bmp

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ at T< 500K

$NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ ***slow***

$NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g)$ ***fast***



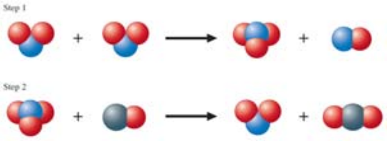
Chemistry 1B, Fall 2016
Topic 23

our
last
video !!

onto more kinetics !!!

Zumdahl figure 15.8 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

$NO_2(g) + NO_2(g) \longrightarrow NO_3(g) + NO(g)$ ***slow***



$NO_3(g) + CO(g) \longrightarrow CO_2(g) + NO_2(g)$ ***fast***

elementary reactions

- an elementary reaction represents the molecules 'colliding' in an actual step of the overall reaction
- the rate law for an elementary reaction **is** determined by the stoichiometry of the elementary reaction (the order of each reactant is its stoichiometric coefficient)
- the overall order of an elementary reaction is its **molecularity**
- the 'sum' of the individual elementary reactions must yield the equation for the overall reaction

***elementary** reactions and 'molecularity'*

elementary reaction	*molecularity*
${}^{14}_{6}C \xrightarrow{k_1} {}^{14}_{7}N + \beta\,(particle)$ nuclear decay $-\frac{d\left[{}^{14}_{6}C\right]}{dt} = k_1\left[{}^{14}_{6}C\right]$ first-order	**unimolecular**
$O_3(g) + NO(g) \xrightarrow{k_2} O_2(g) + NO_2(g)$ $-\frac{d[O_3(g)]}{dt} = k_2[O_3][NO]$ second-order	**bimolecular**
$2Cl\bullet(g) + Cl_2(g) \xrightarrow{k_3} 2Cl_2(g)$ $-\frac{d[Cl_2(g)]}{dt} = k_3[Cl\bullet]^2[Cl_2]$ third-order	**termolecular** *improbable*

elementary or not ???

if A + 2B → C **IS** an elementary reaction
then

$$-\frac{d[A]}{dt} = k[A][B]^2$$ termolecular TRUE

---

if the measured rate law for A + 2B → C is

$$-\frac{d[A]}{dt} = k[A][B]^2$$ third order

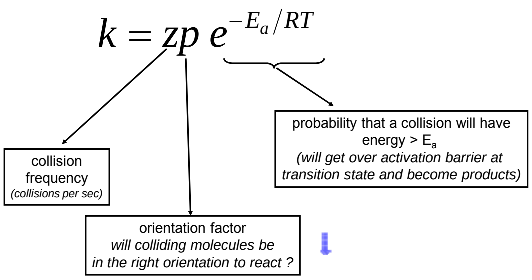
then

A + 2B → C **MAY** or **MAY NOT** be an elementary reaction TRUE

a multi-step mechanism for reaction may have a set of elementary reactions that coincidentally leads to the third-order rate law

- Temperature dependence of rate constant
- Catalysis

collision theory and effect of temperature on rate constant



$$k = zp\, \underbrace{e^{-E_a/RT}}$$

collision frequency
(collisions per sec)

orientation factor
will colliding molecules be in the right orientation to react ?

probability that a collision will have energy > E_a
(will get over activation barrier at transition state and become products)

Arrhenius equation

$$k = \underbrace{zp}\, e^{-E_a/RT}$$

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

'pre exponential' factor
(slight dependence on T will be ignored)

Svante August Arrhenius (19 February 1859 – 2 October 1927) was a Swedish scientist, originally a physicist, but often referred to as a chemist, and one of the founders of the science of physical chemistry.

temperature dependence of rate constant (HW 10 #69 Z15.73)

$$k_{T_2} = A\, e^{-E_a/RT_2}$$

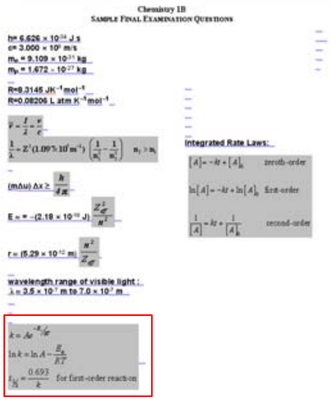
$$k_{T_1} = A\, e^{-E_a/RT_1}$$

$$\frac{k_{T_2}}{k_{T_1}} = \frac{e^{-E_a/RT_2}}{e^{-E_a/RT_1}} = e^{-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

$$k_{T_2} = k_{T_1}\, e^{-\frac{E_a}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

$$\ln k_{T_2} = \ln k_{T_1} + \frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$ eqn 15.11

know k_{T1} and $E_a \Rightarrow$ get k_{T2} or measure k_{T1} and $k_{T2} \Rightarrow$ get E_a



Chemistry 1B
SAMPLE FINAL EXAMINATION QUESTIONS

h= 6.626 × 10^{-34} J s
c= 3.000 × 10^{8} m/s
m_e = 9.109 × 10^{-31} kg
m_p = 1.672 × 10^{-27} kg

R=8.3145 JK^{-1}mol^{-1}
R=0.08206 L atm K^{-1}mol^{-1}

$\tilde{\nu} = \frac{f}{\lambda} = \frac{\nu}{c}$

$\frac{1}{\lambda} = Z^2(1.097\times10^7\,\mathrm{m}^{-1})\left(\frac{1}{n_1^2}-\frac{1}{n_2^2}\right) \quad n_2 > n_1$

$(m\Delta u)\,\Delta x \geq \frac{h}{4\pi}$

$E_n = -(2.18\times10^{-18}\,\mathrm{J})\,\frac{Z_{eff}^2}{n^2}$

$r = (5.29\times10^{-12}\,\mathrm{m})\,\frac{n^2}{Z_{eff}}$

wavelength range of visible light :
λ = 3.5 × 10^{-7} m to 7.0 × 10^{-7} m

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

$\ln k = \ln A - \frac{E_a}{RT}$

$t_{1/2} = \frac{0.693}{k}$ for first-order reaction

Integrated Rate Laws:

$[A] = -kt + [A]_0$ zeroth-order

$\ln[A] = -kt + \ln[A]_0$ first-order

$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$ second-order

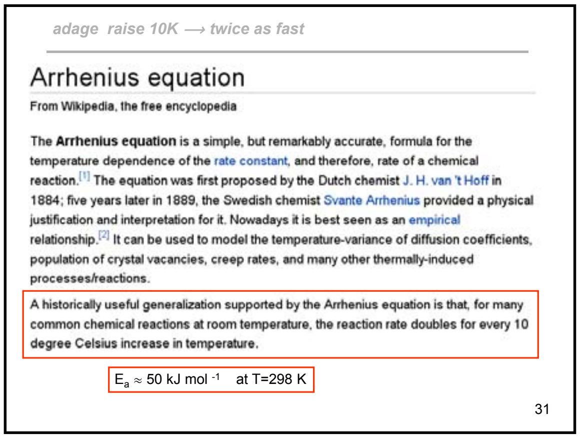
Example (by request)

A first-order reaction with activation energy E_a=50 kJ mol^{-1} has a rate constant of k_{300}=3.0 × 10^{-1} sec^{-1} at 300K.

What is the rate constant at 310K?

What is the ratio of k_{310}/k_{300} ?

Chemistry 1B, Fall 2016
Topic 23



adage raise 10K ⟶ twice as fast

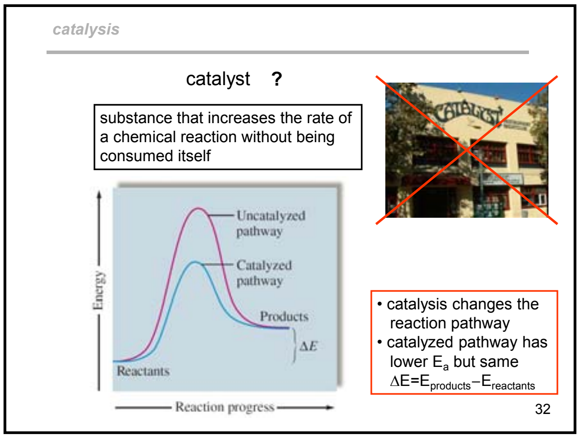
Arrhenius equation

From Wikipedia, the free encyclopedia

The **Arrhenius equation** is a simple, but remarkably accurate, formula for the temperature dependence of the rate constant, and therefore, rate of a chemical reaction.[1] The equation was first proposed by the Dutch chemist J. H. van 't Hoff in 1884; five years later in 1889, the Swedish chemist Svante Arrhenius provided a physical justification and interpretation for it. Nowadays it is best seen as an empirical relationship.[2] It can be used to model the temperature-variance of diffusion coefficients, population of crystal vacancies, creep rates, and many other thermally-induced processes/reactions.

A historically useful generalization supported by the Arrhenius equation is that, for many common chemical reactions at room temperature, the reaction rate doubles for every 10 degree Celsius increase in temperature.

$E_a \approx 50$ kJ mol^{-1} at T=298 K

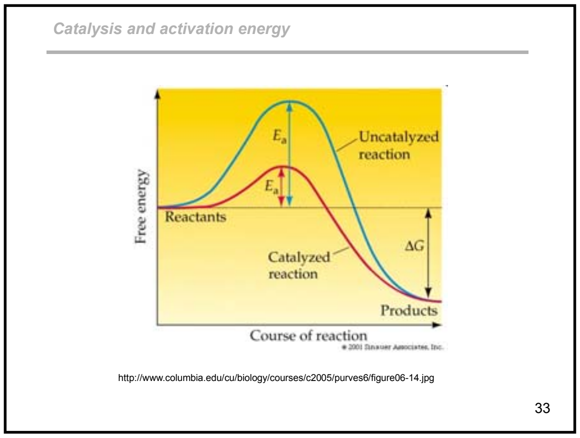


catalysis

catalyst ?

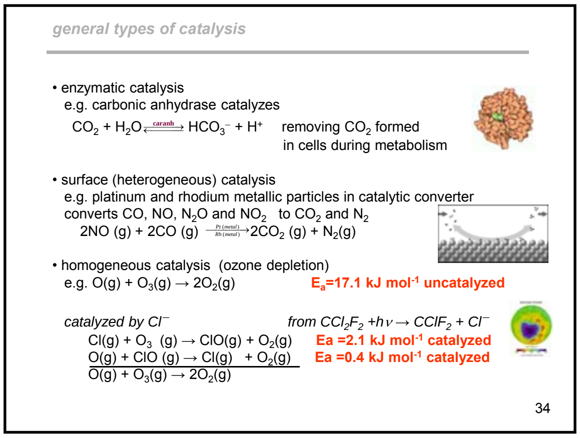
substance that increases the rate of a chemical reaction without being consumed itself

- catalysis changes the reaction pathway
- catalyzed pathway has lower E_a but same $\Delta E = E_{products} - E_{reactants}$



Catalysis and activation energy

http://www.columbia.edu/cu/biology/courses/c2005/purves6/figure06-14.jpg



general types of catalysis

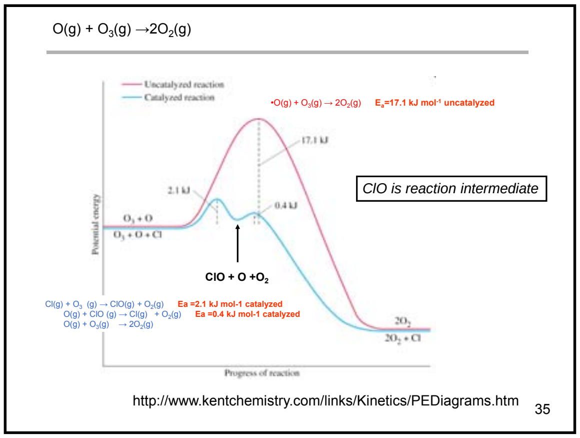
- enzymatic catalysis
  e.g. carbonic anhydrase catalyzes
  $CO_2 + H_2O \xrightleftharpoons{caranh} HCO_3^- + H^+$ removing CO_2 formed in cells during metabolism
- surface (heterogeneous) catalysis
  e.g. platinum and rhodium metallic particles in catalytic converter converts CO, NO, N_2O and NO_2 to CO_2 and N_2
  $2NO(g) + 2CO(g) \xrightarrow[Rh\,(metal)]{Pt\,(metal)} 2CO_2(g) + N_2(g)$
- homogeneous catalysis (ozone depletion)
  e.g. $O(g) + O_3(g) \rightarrow 2O_2(g)$ **E_a=17.1 kJ mol^{-1} uncatalyzed**

catalyzed by Cl^- *from $CCl_2F_2 + h\nu \rightarrow CClF_2 + Cl^-$*

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ **Ea =2.1 kJ mol^{-1} catalyzed**

$O(g) + ClO(g) \rightarrow Cl(g) + O_2(g)$ **Ea =0.4 kJ mol^{-1} catalyzed**

$O(g) + O_3(g) \rightarrow 2O_2(g)$



$O(g) + O_3(g) \rightarrow 2O_2(g)$

•$O(g) + O_3(g) \rightarrow 2O_2(g)$ **E_a=17.1 kJ mol^{-1} uncatalyzed**

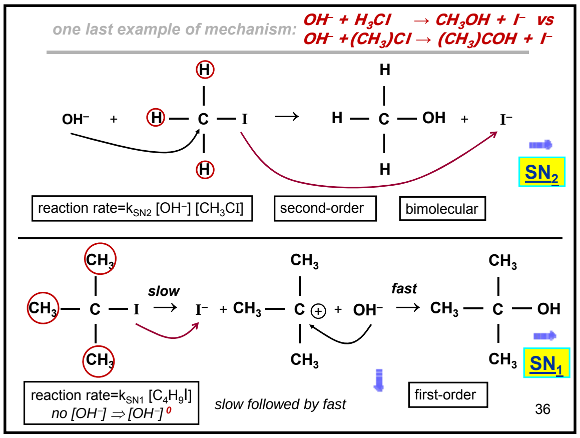
ClO is reaction intermediate

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$ **Ea =2.1 kJ mol-1 catalyzed**

$O(g) + ClO(g) \rightarrow Cl(g) + O_2(g)$ **Ea =0.4 kJ mol-1 catalyzed**

$O(g) + O_3(g) \rightarrow 2O_2(g)$

http://www.kentchemistry.com/links/Kinetics/PEDiagrams.htm



one last example of mechanism: ***$OH^- + H_3CI \rightarrow CH_3OH + I^-$ vs***
$OH^- + (CH_3)CI \rightarrow (CH_3)COH + I^-$

reaction rate=k_{SN2} [OH^-] [CH_3CI]

second-order

bimolecular

reaction rate=k_{SN1} [C_4H_9I]
no [OH^-] ⇒ [OH^-]^0

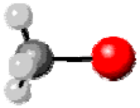
slow followed by fast

first-order

Chemistry 1B, Fall 2016
Topic 23

chemical kinetics (chapter 15)

N≡C⁻ ⟶ **H_3C-I**

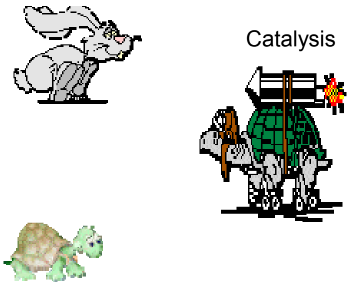


N≡C-CH_3 + I^-

Kinetics: How **fast** a reaction proceeds, **and the molecular steps involved in a reaction [*the mechanism of a reaction*].**

http://www.bluffton.edu/~bergerd/classes/CEM221/sn-e/SN2_alternate.html

kinetic measurements: how fast will a reaction proceed



Catalysis

goals for lecture 23

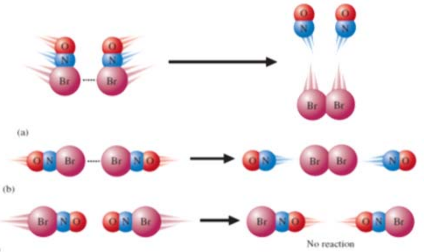
- ☑ kinetics and mechanism of chemical reaction
- ☑ energy profile and reaction coordinate
- ☑ activation energy and temperature dependence of rate constant
- ☑ catalysis

FINIS !!!

BUT ONE MORE THING ➡

p the orientation factor (2 ONBr ⟶ 2NO +Br_2)

what relative orientation of two ONBr molecules will lead to a reaction ?
(Br------Br bond formation)



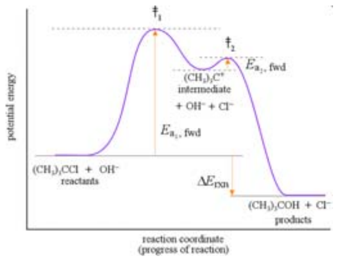
yes

yes

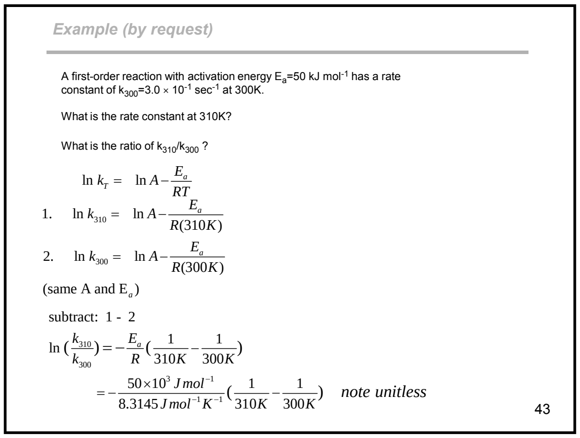
no

the more 'particular' the reaction is about alignment of colliding molecule the smaller the p factor

two-step, slow then fast, first-order with reaction intermediate HW#10 probs 67 and 68



http://guweb2.gonzaga.edu/faculty/cronk/CHEM240/images/reaction_coordinate_SN1.gif



Example (by request)

A first-order reaction with activation energy E_a=50 kJ mol^{-1} has a rate constant of k_{300}=3.0 × 10^{-1} sec^{-1} at 300K.

What is the rate constant at 310K?

What is the ratio of k_{310}/k_{300} ?

$$\ln k_T = \ln A - \frac{E_a}{RT}$$

1. $\ln k_{310} = \ln A - \dfrac{E_a}{R(310K)}$

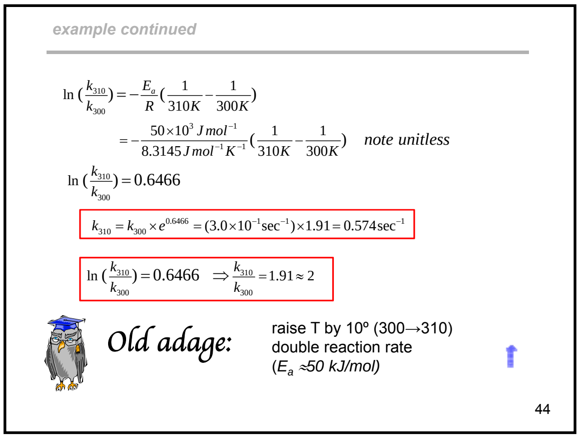
2. $\ln k_{300} = \ln A - \dfrac{E_a}{R(300K)}$

(same A and E_a)

subtract: 1 - 2

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = -\frac{E_a}{R}\left(\frac{1}{310K} - \frac{1}{300K}\right)$$

$$= -\frac{50\times10^3\ J\,mol^{-1}}{8.3145\,J\,mol^{-1}K^{-1}}\left(\frac{1}{310K} - \frac{1}{300K}\right) \quad \textit{note unitless}$$



example continued

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = -\frac{E_a}{R}\left(\frac{1}{310K} - \frac{1}{300K}\right)$$

$$= -\frac{50\times10^3\ J\,mol^{-1}}{8.3145\,J\,mol^{-1}K^{-1}}\left(\frac{1}{310K} - \frac{1}{300K}\right) \quad \textit{note unitless}$$

$$\ln\left(\frac{k_{310}}{k_{300}}\right) = 0.6466$$

$$\boxed{k_{310} = k_{300} \times e^{0.6466} = (3.0\times10^{-1}\sec^{-1})\times1.91 = 0.574\sec^{-1}}$$

$$\boxed{\ln\left(\frac{k_{310}}{k_{300}}\right) = 0.6466 \quad \Rightarrow \frac{k_{310}}{k_{300}} = 1.91 \approx 2}$$

Old adage:

raise T by 10º (300→310)
double reaction rate
(*E_a ≈50 kJ/mol)*