

## Lecture #18: Thursday March 23<sup>rd</sup>

- I. Integrated Rate Laws
- II. Temperature Dependence of Rxn Rates
- III. Two Chemical Kinetic Theories
- IV. Catalysis
- IV. Reaction Mechanisms
  - A. Elementary Reactions

### I. Integrated Rate Laws

#### A. Determination of order & rate constant

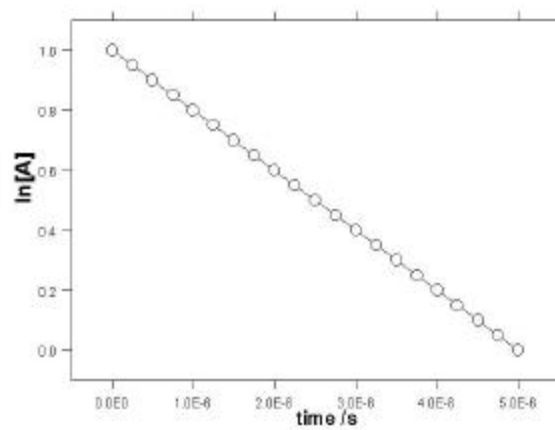
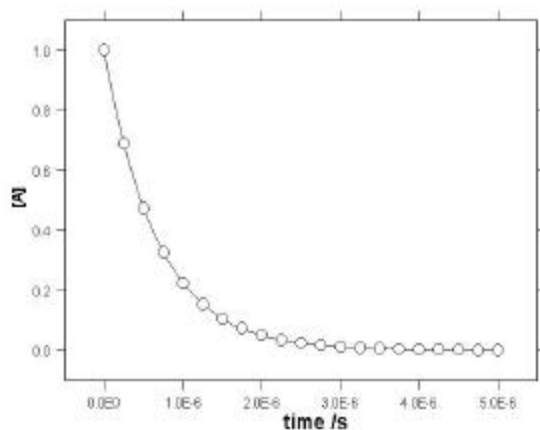
For overall reactions, to determine order: know what function of concentration vs time yields

line.  $\ln [A]$  vs  $t$  and  $\frac{1}{[A]}$  vs  $t$ , for 1<sup>st</sup> and 2<sup>nd</sup> order respectively

Start with  $-\frac{d[A]}{dt} = k[A]^a$  where  $a = 1$  or  $2$

**1<sup>st</sup> order wrt [A]:**  $[A] = [A]_0 e^{-kt}$      $\ln[A] = \ln[A]_0 - kt$  **MEMORIZE THIS EQUATION**

1<sup>st</sup> order rxns show exp'l decay of [A], If plot of  $\ln[A]$  vs  $t$  is line, it first order in [A]  
slope is  $-k$ .



For example if the following data of  $[N_2O_5]$  is as follows, show that the rxn is first order wrt  $[N_2O_5]$ , furthermore find  $k$ :

$t / s$	0	200	400	600	1000
$[N_2O_5]$ $mol L^{-1}$	0.110	0.073	0.048	0.032	0.014
$\ln [N_2O_5]$	-2.207	-2.617	-3.037	-3.442	-4.269

You can prove this is first order in  $[N_2O_5]$  by plotting or by showing that the slope is virtually constant between any 2 points:

slope between points 1&2 =  $-2.617 - (-2.207) / [200 - 0] = -2.05E-3 L mol^{-1} s^{-1} = -k$

slope between points 4&5 =  $-4.269 - (-3.442) / [1000 - 600] = -2.07E-3 mol^{-1} s^{-1} = -k$

Thus slopes approximately the same,  $k = 2.05E-3 L mol^{-1} s^{-1}$

An example of a 1<sup>st</sup> order "reaction" is noted in the following energy deactivation process:

"Singlet oxygen quenching of tris(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>) and *N,N*'-diphenyl-*N,N*'-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) "

Wade N. Sisk and William L. Lawrence [Journal of Photochemistry and Photobiology A: Chemistry](#)  
[Volume 163, Issue 3](#) , 21 May 2004, Pages 439-443

2<sup>nd</sup> order wrt [A]:  $\frac{1}{[A]} = \frac{1}{[A]_0} + kt$  **MEMORIZE THIS EQUATION**

Plot  $\frac{1}{[A]}$  vs t and if this yields a line, the rate is 2<sup>nd</sup> order with respect to [A].

An example of a 2<sup>nd</sup> order reaction is noted in the following in which  $\frac{[A]_0}{[A]}$  was plotted vs time:

"The concentration dependence of the normalized photostability of 1,3,5,7,8-pentamethyl-2,6-di-*t*-butylpyrromethene-difluoroborate complex (PM-597) methanol solutions"

Wade N. Sisk and Wesley Sanders [Journal of Photochemistry and Photobiology A: Chemistry](#)  
[Volume 167, Issues 2-3](#) , 1 October 2004, Pages 185-189

## B. Half Lives

$\tau_{?}$  is the time it takes for the concentration of a species to go to ? of its initial value:

Time for [A] → ? [A]<sub>0</sub>

For a first order rxn:  $\ln([A]/[A]_0) = -kt$ , for half-life:  $\ln(? [A]_0/[A]_0) = -k\tau_{?}$

$$\text{Thus: } \tau_{?} = \frac{\ln \frac{1}{?}}{-k} = \frac{\ln ?}{k}$$

2<sup>nd</sup> order rxn:  $1/[A] = 1/[A]_0 + kt$ ,  $2/[A]_0 = 1/[A]_0 + k\tau_{?}$  thus  $\tau_{?} = 1/k\{2/[A]_0 - 1/[A]_0\} = 1/k[A]_0$

Example: If the rate constant of a particular first order rxn is  $3.57\text{E-}5 \text{ s}^{-1}$  , what is the half life in hours?

## II. Temperature Dependence of Rxn Rates

$k = A \exp(-E_{\text{act}}/RT)$  explained by Boltzmann

**MEMORIZE THIS EQUATION**

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

Thus if we plot the (ln k) vs. 1/T , the slope of such a line yields the activation energy, E<sub>a</sub> and preexponential factor A. These equations are known as *Arrhenius* equations.

Example. Determine the activation energy in KJ mol<sup>-1</sup> for cyclopentadiene dissociation rate in which the following (T,k) information was obtained:

Temp °C	170.0	180.1	185.2	189.9
k s <sup>-1</sup>	1.92x10 <sup>-4</sup>	4.61x10 <sup>-4</sup>	7.1X10 <sup>-4</sup>	10.52x10 <sup>-4</sup>

### III. Two Chemical Kinetic Theories

#### A. Collision Theory

Collisions in which reactants have sufficient energy leads to product.

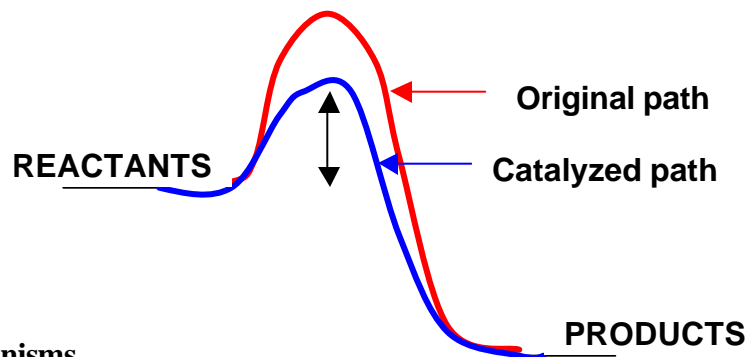
Rate of rxn = collision rate (proportional to concentration)  $\times$  fraction of collisions that react (fraction with  $KE > E_{act} = \exp\{-E_{act}/RT\}$ )  
 $= [B][C] \times \exp\{-E_{act}/RT\} = [B][C]k$  where  $k$  is proportional to  $\exp\{-E_{act}/RT\}$

#### B. Activated Complex Theory (Transition State Theory)

Reactants go through an activated complex (including solvent) at the maximum (crucial configuration is transition state). These are not rxn intermediates.  $A + B \leftrightarrow (AB)^\ddagger \rightarrow \text{products}$   
The advantage over collision theory is that this is applicable to solution phase as well as gas phase.

### IV. Catalysis

A **catalyst** is a substance that increases the rate of rxn without being consumed. If the catalyst is in the same phase as the reactant it is a **homogeneous catalyst**, if in a different phase – it's a **heterogeneous catalyst**. A catalyst provides a different pathway for reaction with a lower activation barrier than the uncatalyzed reaction. *The catalyst does NOT lower the activation barrier, rather it provides a lower barrier pathway!* The catalyst may allow previous Hi T rxns to occur at moderate T



### V. Reaction Mechanisms

#### A. Elementary Rxns

Elementary rxns are the “steps” of a rxn mechanism. These rxns occur molecularly as they are written. These should be written with the phase (s,l, g) designated.

i.e.  $H + Br_2 \rightarrow HBr + Br$

Molecularity of elementary rxns is the number of molecules coming together to react.

unimolecular (molecularity = 1, i.e.  $NO_2 \rightarrow NO + O$ )

bimolecular (molecularity = 2, i.e.  $H + Br_2 \rightarrow HBr + Br$ )

When one writes the rate expression for an elementary rxn, the coefficients become the “order” and “reciprocal coefficients”.

For example:  $O + O \rightarrow O_2$  which can be written as  $2O \rightarrow O_2$

- ?  $d[O]/dt = -k[O]^2$ , if this was not an elementary step, we could only write - ?  $d[O]/dt = -k[O]^\alpha$