Deriving Rate Laws

Example: Derive the rate law and k for

$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$

from experimental data for rate of disappearance of CH_3CHO

Expt.	$[CH_3CHO]$ (mol/L)	Rate of disappearance of CH_3CHO (mol/L•sec)
1	0.10	0.020
2	0.20	0.081
3	0.30	0.182
4	0.40	0.318

Deriving Rate Laws

Rate of rxn = k $[CH_3CHO]^2$

Here the rate goes up by _____ when initial conc. doubles. Therefore, we say this reaction is _____ order.

Now determine the value of k. Use expt. #3 data—

0.182 mol/L•s = k (0.30 mol/L)^2

k = 2.0 (L / mol•s)

Using k you can calc. rate at other values of $[CH_3CHO]$ at same T.

Concentration / Time Relations

What is the concentration of reactant as function of time?

Consider FIRST ORDER REACTIONS

The rate law is

$$\text{Rate} = -\frac{\Delta[A]}{\Delta \text{time}} = k\,[A]$$

Concentration / Time Relations

Integrating -(Δ [A] / Δ time) = k [A], we get

$$\ln \frac{[A]}{[A]_o} = -k\,t$$

natural logarithm

[A] at time = 0

$[A] / [A]_0$ = fraction remaining after time t has elapsed.

This is the integrated first-order rate law.

Integrated Rate Laws

For a reaction with Reactant R becoming a Product P

R ---> P

	Rate Equation	Integrated Rate Law
First Order	$\frac{-\Delta[R]}{\Delta t} = k[R]$	$\ln\frac{[R]}{[R]_o} = -kt$
Second Order	$\frac{-\Delta[R]}{\Delta t} = k[R]^2$	$\frac{1}{[R]_t} - \frac{1}{[R]_0} = kt$
Zero Order	$\frac{-\Delta[R]}{\Delta t} = k[R]^0$	$[R]_0 - [R]_t = kt$

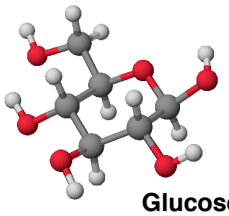
Concentration / Time Relations

Sucrose decomposes to simpler sugars like glucose

Rate of disappearance of sucrose = k [sucrose]

If k = 0.21 hr^{-1} and [sucrose] = 0.010 M

How long to drop 90% (to 0.0010 M)?



Glucose

Concentration / Time Relations

Rate of disappearance of sucrose = k [sucrose], k = 0.21 hr^{-1}. If initial [sucrose] = 0.010 M, how long to drop 90% or to 0.0010 M?

Use the first order integrated rate law

$$\ln\left(\frac{0.0010\ M}{0.010\ M}\right) = -(0.21\ hr^{-1})\ t$$

$$\ln(0.100) = -2.3 = -(0.21\ hr^{-1}) \cdot time$$

time = 11 hours