Today

Kinetics Rate Laws

Finding the order of a reaction

Integrated Rate Laws

What is the concentration as a function of time?

The grand overview of all of the kinetics

$$aA + bB \longleftrightarrow cC + dD$$

measure in experiment

figure out from data

$$\frac{-\Delta[A]}{a\Delta t} = \frac{\Delta[C]}{c\Delta t} = \text{rate} = k[A]^x[B]^y$$

we are looking only at the rate of the "forward" reaction
This depends only on the concentration of the reactants

Four Factors that affect a reaction rate

1. Concentration of reactants

This is the "rate" law. It is found by looking at the data
It depends on the "mechanism"

$$2NO_2 \longrightarrow 2NO + O_2$$

for example rate = $k[NO_2]^2$
this reaction is 2nd order in NO_2

Four Factors that affect a reaction rate

2. Temperature

This changes the rate constant k

pre-factor

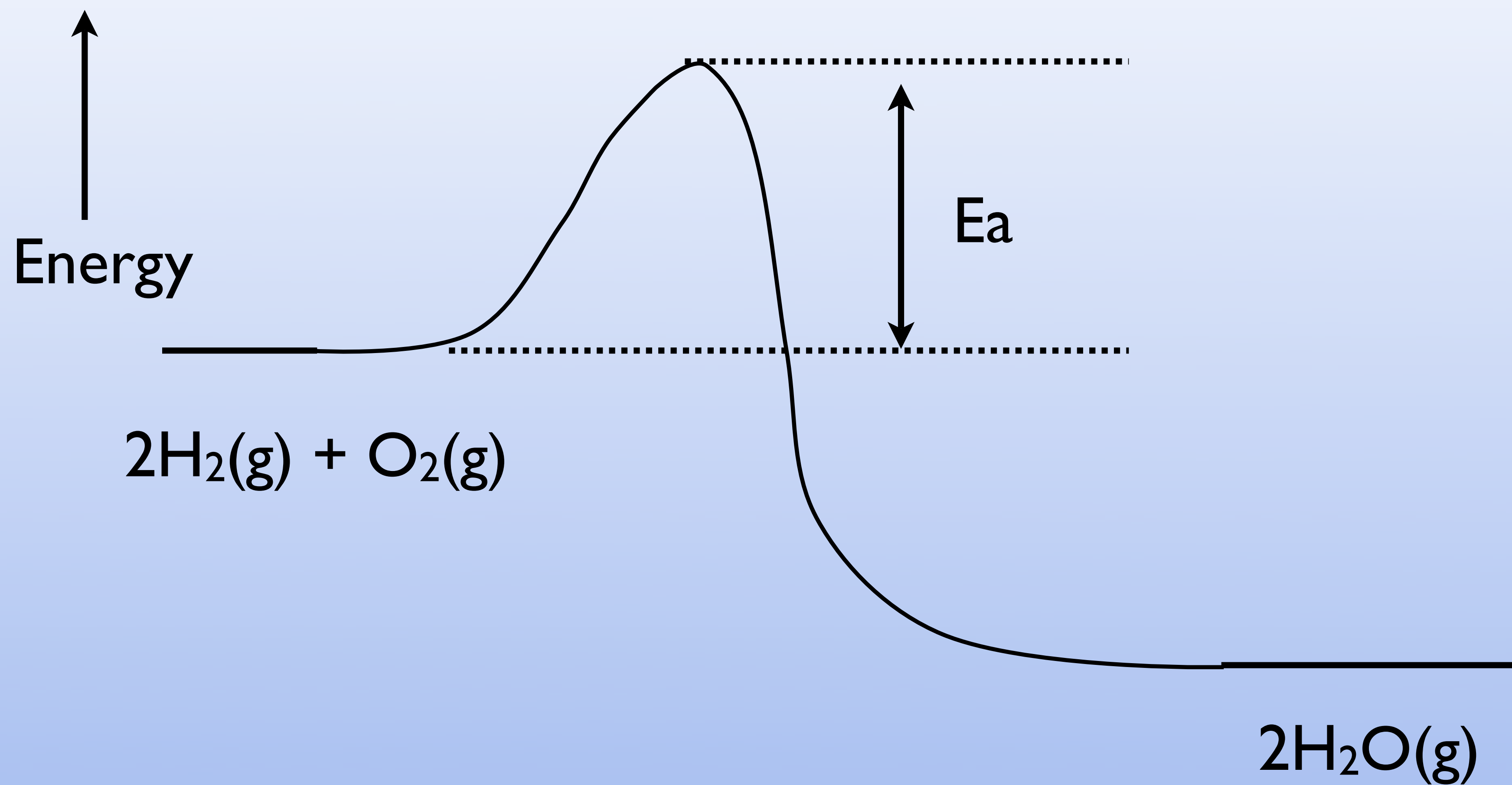
barrier

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

temperature

Arrhenius Law

The higher the temperature the more molecules that have enough energy to make it over the barrier


Energy
Ea
$2H_2(g) + O_2(g)$
$2H_2O(g)$

Four Factors that affect a reaction rate

3. Catalyst

This changes the rate constant k. Reduces E_a

pre-factor

barrier

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

temperature

Arrhenius Law

As the barrier is lower, the rate constant is larger

Four Factors that affect a reaction rate

4. Physical state (solid chunk, dust, gas, ...)

This changes the rate constant k. Changes A

pre-factor

barrier

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

temperature

Arrhenius Law

Prefactor A is the rate constant when T = infinity

Finding the rate law from initial rates

TABLE 15.4 Initial Rates from Three Experiments for the Reaction
$NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate ($mol\ L^{-1}\ s^{-1}$)
1	0.100 *M*	0.0050 *M*	1.35×10^{-7}
2	0.100 *M*	0.010 *M*	2.70×10^{-7}
3	0.200 *M*	0.010 *M*	5.40×10^{-7}

determine NO_2^- dependence from first two data points

determine NH_4^+ dependence from second two data points

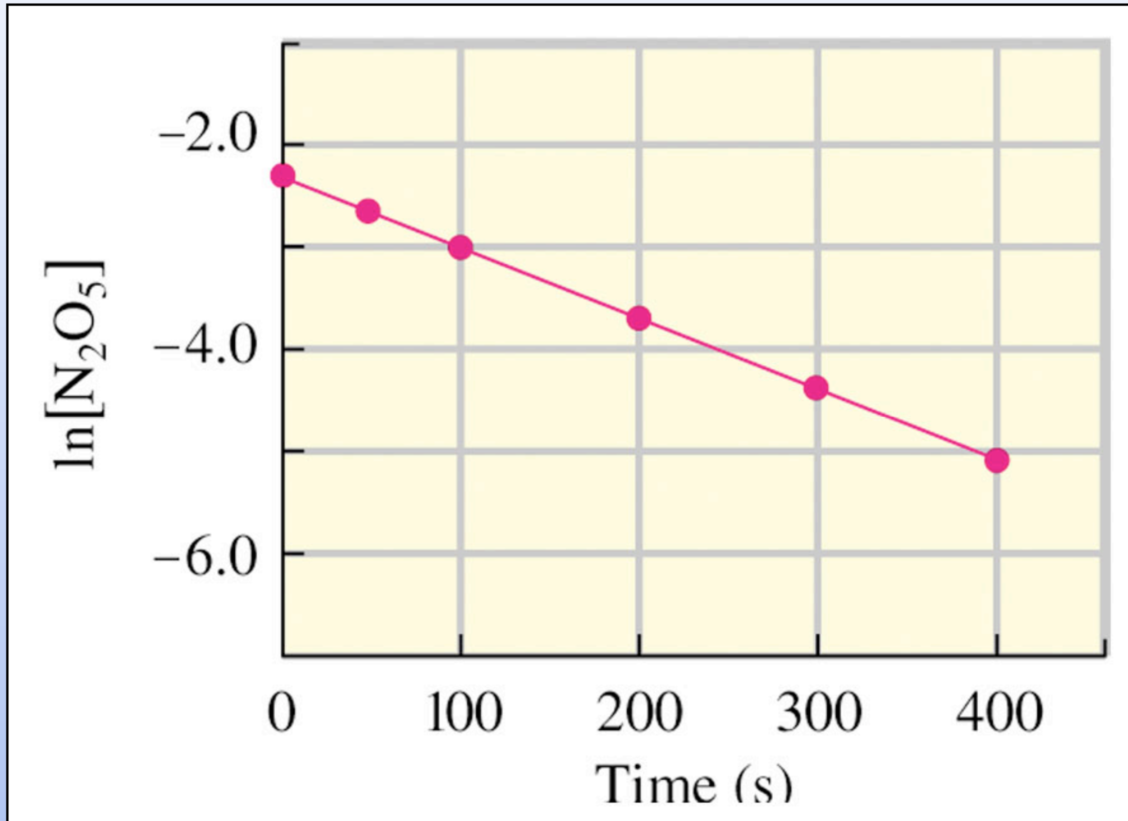
Integrated Rate Law

First Order

$$[A] = [A]_o e^{-kt}$$

$$\ln[A] = -kt + \ln[A]_o$$

So if you plot ln[A] vs time you get
a straight line with a slope of -k


ln[N2O5]
−2.0
−4.0
−6.0
0
100
200
300
400
Time (s)

Half life

TABLE 15.3 Concentration/Time Data for the Reaction $2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g)$ (at 45°C)

$[N_2O_5]$ (mol/L)	Time (s)
1.00	0
0.88	200
0.78	400
0.69	600
0.61	800
0.54	1000
0.48	1200
0.43	1400
0.38	1600
0.34	1800
0.30	2000

The half-life is the time at which half the initial concentration remains.

what is the half-life for the reaction at the right?

A. 200 s

B. 400 s

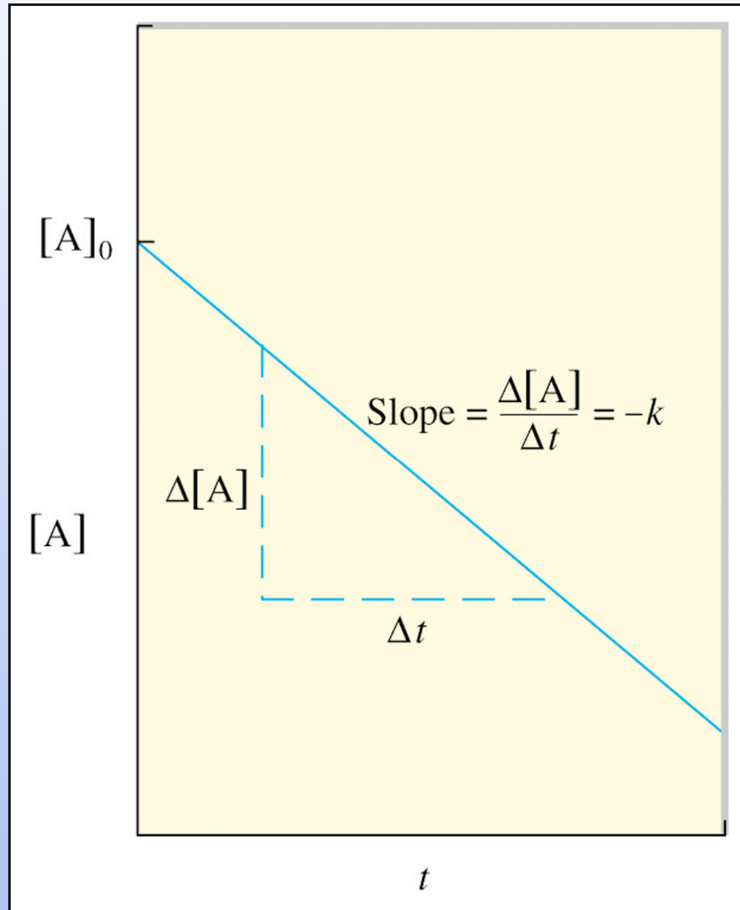
C. 1100 s

D. 1600 s

Zeroth Order

$$[A] = -kt + [A]_o$$

Plot of [A] vs time yields a straight line with a slope of -k

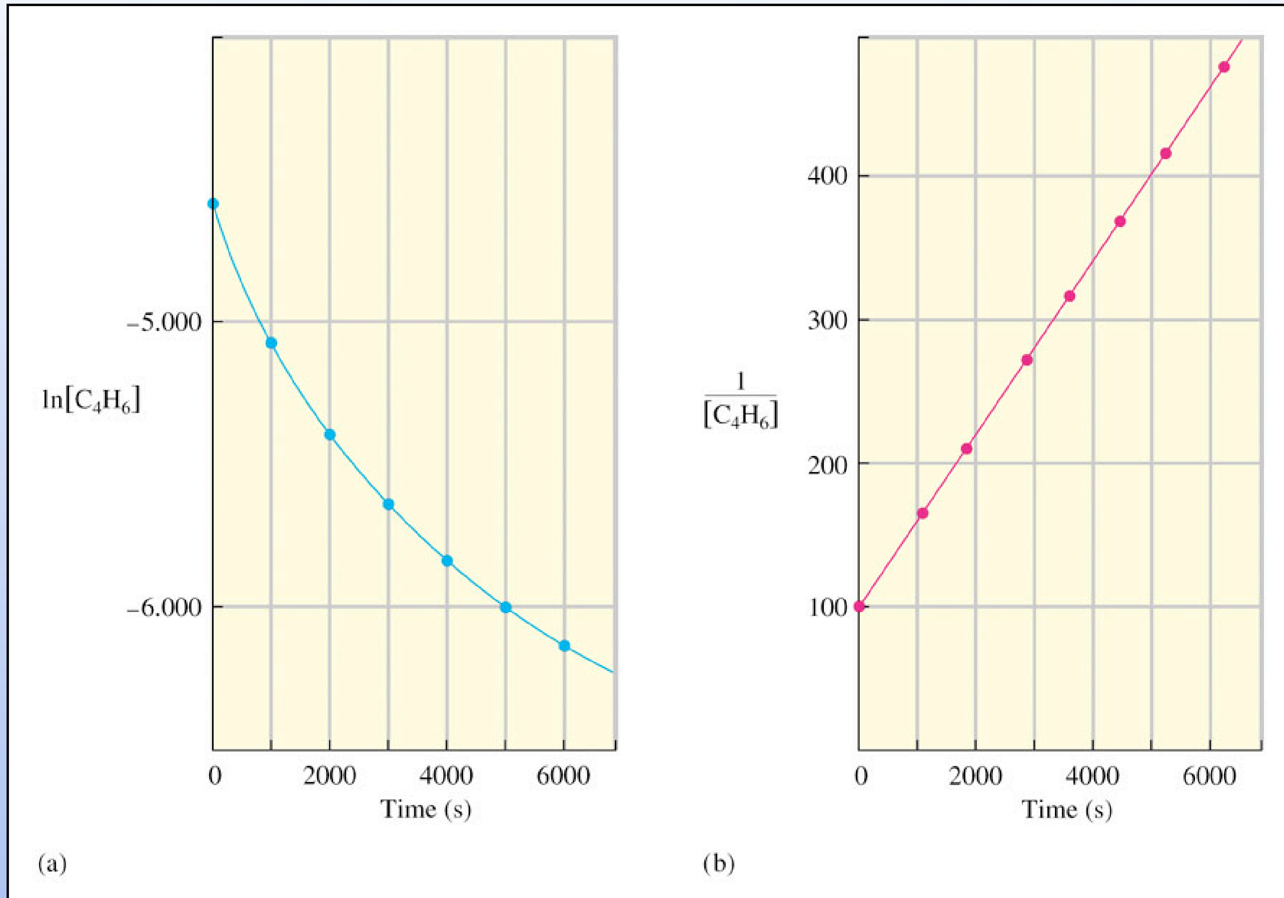

[A]$_0$
[A]
Δ[A]
Δt
Slope = $\frac{\Delta[A]}{\Delta t} = -k$
t

Integrated Rate Law

Second Order

$$1/[A] = kt + 1/[A]_o$$

So if you plot 1/[A] vs time you get
a straight line with a slope of k



ln[C4H6]
−5.000
−6.000
0
2000
4000
6000
Time (s)
(a)
1/[C4H6]
400
300
200
100
0
2000
4000
6000
Time (s)
(b)

TABLE 15.6 Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	First	Second
Rate law	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated rate law	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot needed to give a straight line	$[A]$ versus t	$\ln[A]$ versus t	$\frac{1}{[A]}$ versus t
Relationship of rate constant to the slope of straight line	Slope = $-k$	Slope = $-k$	Slope = k
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$