

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



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

I. Concentration of reactants

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



for example $\text{rate} = k[\text{NO}_2]^2$
this reaction is 2nd order in NO_2

Four Factors that affect a reaction rate

2. Temperature

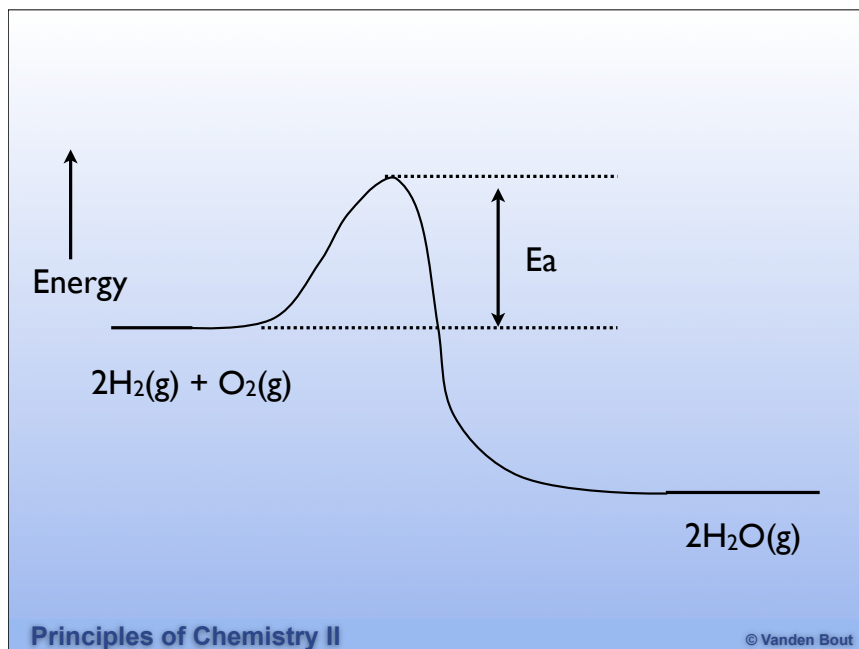
This changes the rate constant k

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

pre-factor barrier temperature

Arrhenius Law

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



Four Factors that affect a reaction rate

3. Catalyst

This changes the rate constant k . Reduces E_a

pre-factor barrier temperature

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

Arrhenius Law

As the barrier is lower, the rate constant is larger

Principles of Chemistry II © Vanden Bout

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 temperature

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

Arrhenius Law

Prefactor A is the rate constant when $T = \text{infinity}$

Principles of Chemistry II © Vanden Bout

Finding the rate law from initial rates

TABLE 15.4 Initial Rates from Three Experiments for the Reaction $\text{NH}_4^+(aq) + \text{NO}_2^-(aq) \rightarrow \text{N}_2(g) + 2\text{H}_2\text{O}(l)$

Experiment	Initial Concentration of NH_4^+	Initial Concentration of NO_2^-	Initial Rate ($\text{mol L}^{-1} \text{s}^{-1}$)
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

Principles of Chemistry II © Vanden Bout

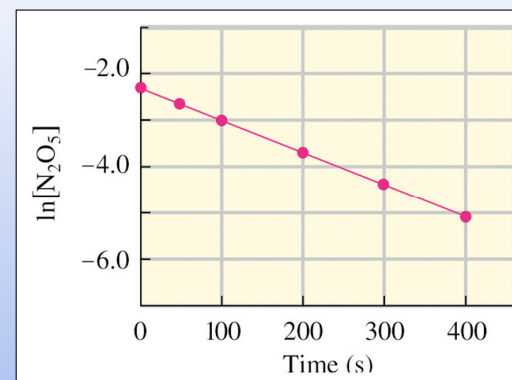
Integrated Rate Law

First Order

$$[A] = [A]_0 e^{-kt}$$

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

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



Half life

TABLE 15.3 Concentration/Time Data for the Reaction $2\text{N}_2\text{O}_5(\text{soln}) \rightarrow 4\text{NO}_2(\text{soln}) + \text{O}_2(\text{g})$ (at 45°C)

[N ₂ O 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.

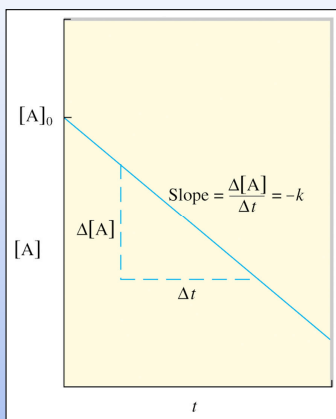
what is the half-life for the reaction at the right?

- A. 200 s
- B. 400 s
- C. 1100 s
- D. 1600 s

Zeroth Order

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

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



Integrated Rate Law

Second Order

$$1/[A] = kt + 1/[A]_0$$

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

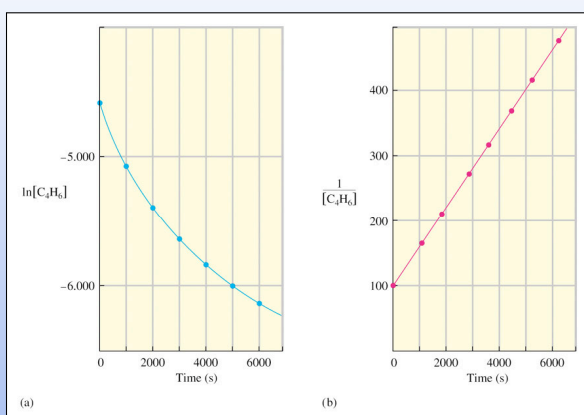


TABLE 15.6 Summary of the Kinetics for Reactions of the Type $aA \rightarrow$ Products That Are Zero, First, or Second Order in $[A]$

	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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$