# 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

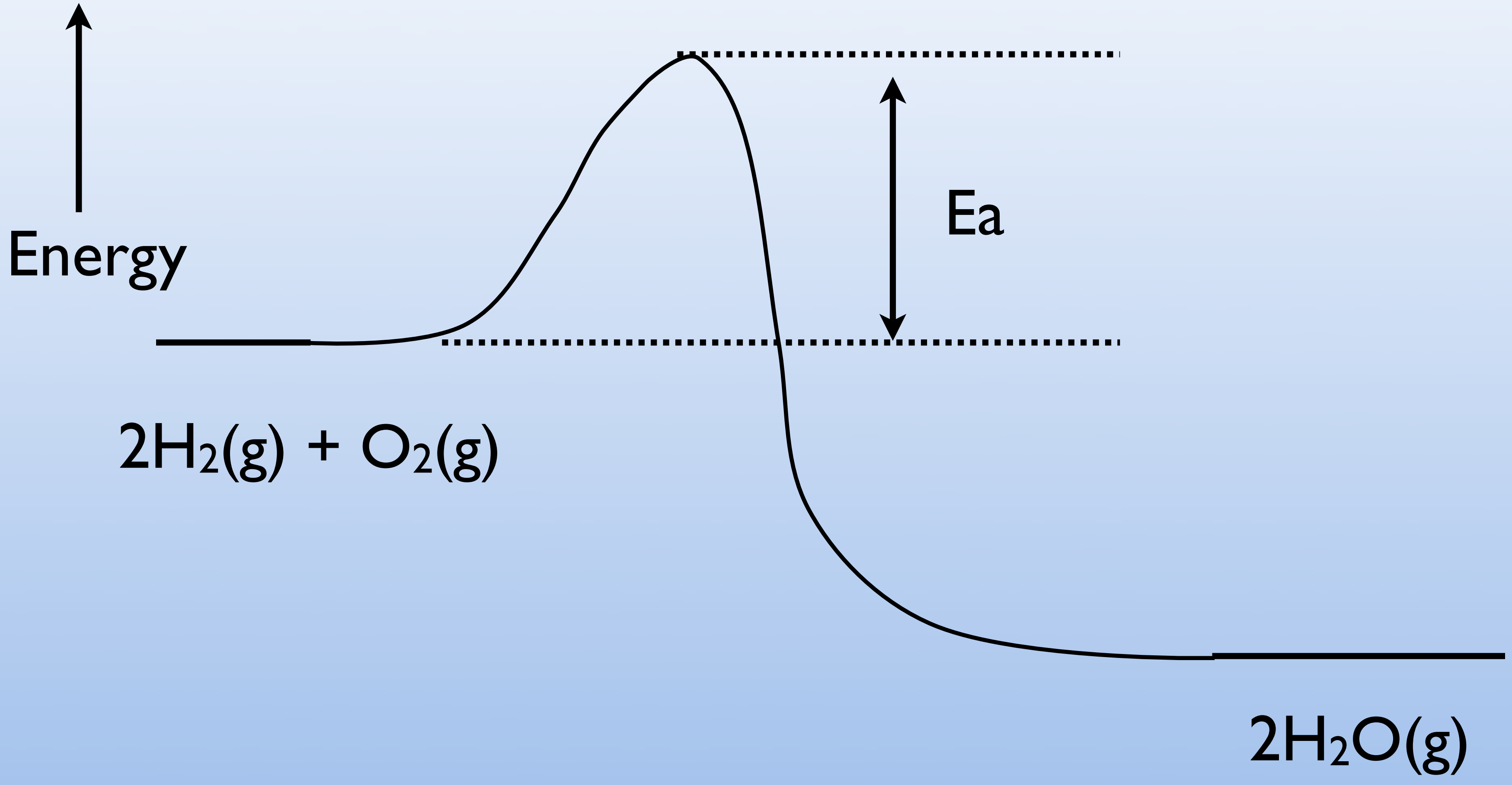
barrier

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

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

# Catalyst Demo

# 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

# Let's blow something up

# Which balloon reacted with a higher rate?

A. the first one

B. the second one

C. they were the same

# Which balloon contained both $H_2$ and $O_2$

A. the first one

B. the second one

# The rate for this reaction

A. depends on the concentration of oxygen

B. is independent of the concentration of oxygen

C. there is no way to know without more data

# Finding the rate law from initial rates

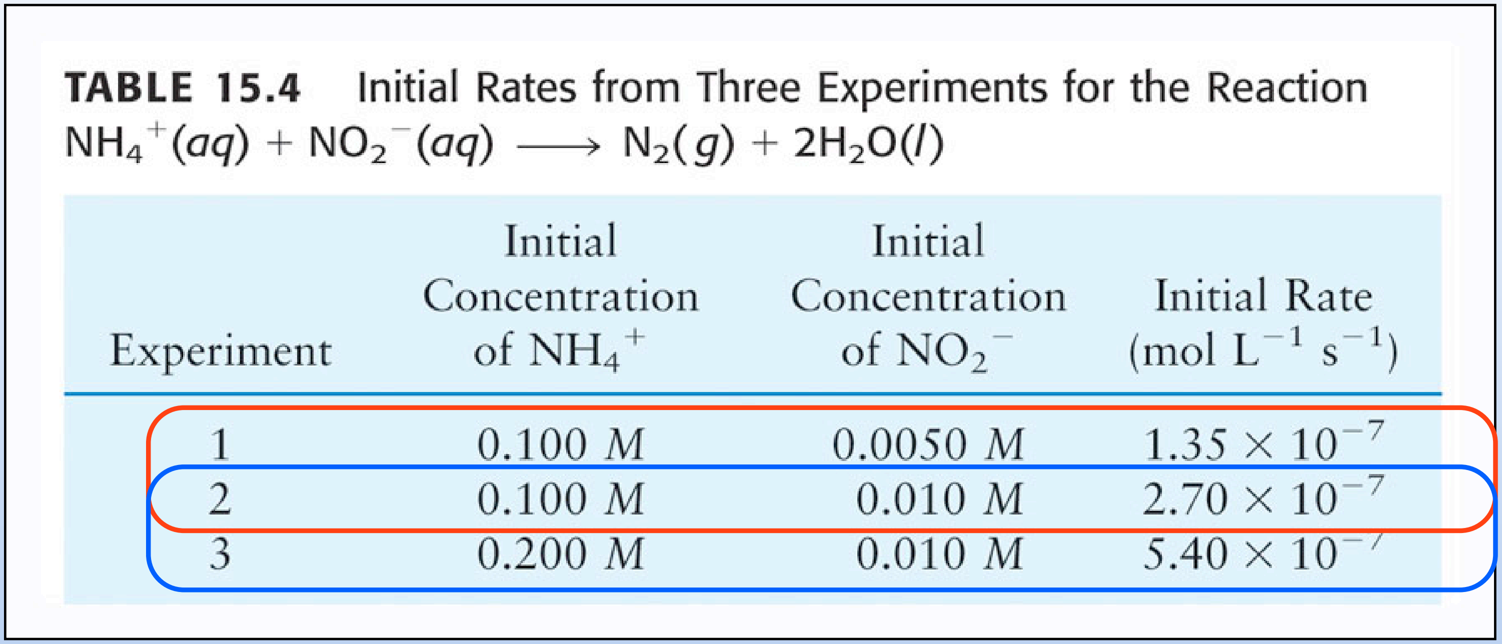


**TABLE 15.4** Initial Rates from Three Experiments for the Reaction $NH_4^+(aq) + NO_2^-(aq) \longrightarrow N_2(g) + 2H_2O(l)$

| 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* | $1.35 \times 10^{-7}$ |
| 2 | 0.100 *M* | 0.010 *M* | $2.70 \times 10^{-7}$ |
| 3 | 0.200 *M* | 0.010 *M* | $5.40 \times 10^{-7}$ |

determine $NO_2^-$ dependence from first two data points

determine $NH_4^+$ dependence from second two data points

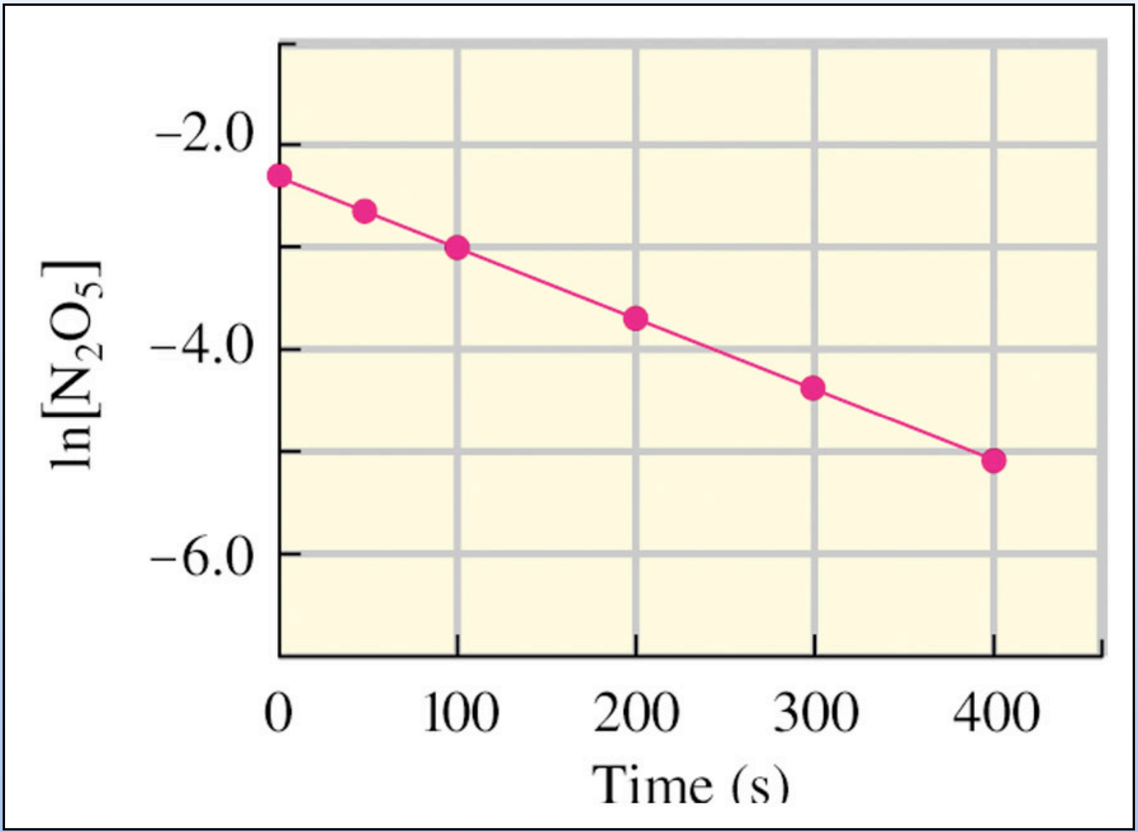
# Integrated Rate Law

## 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


−2.0
−4.0
−6.0
$\ln[N_2O_5]$
0
100
200
300
400
Time (s)

# Half life

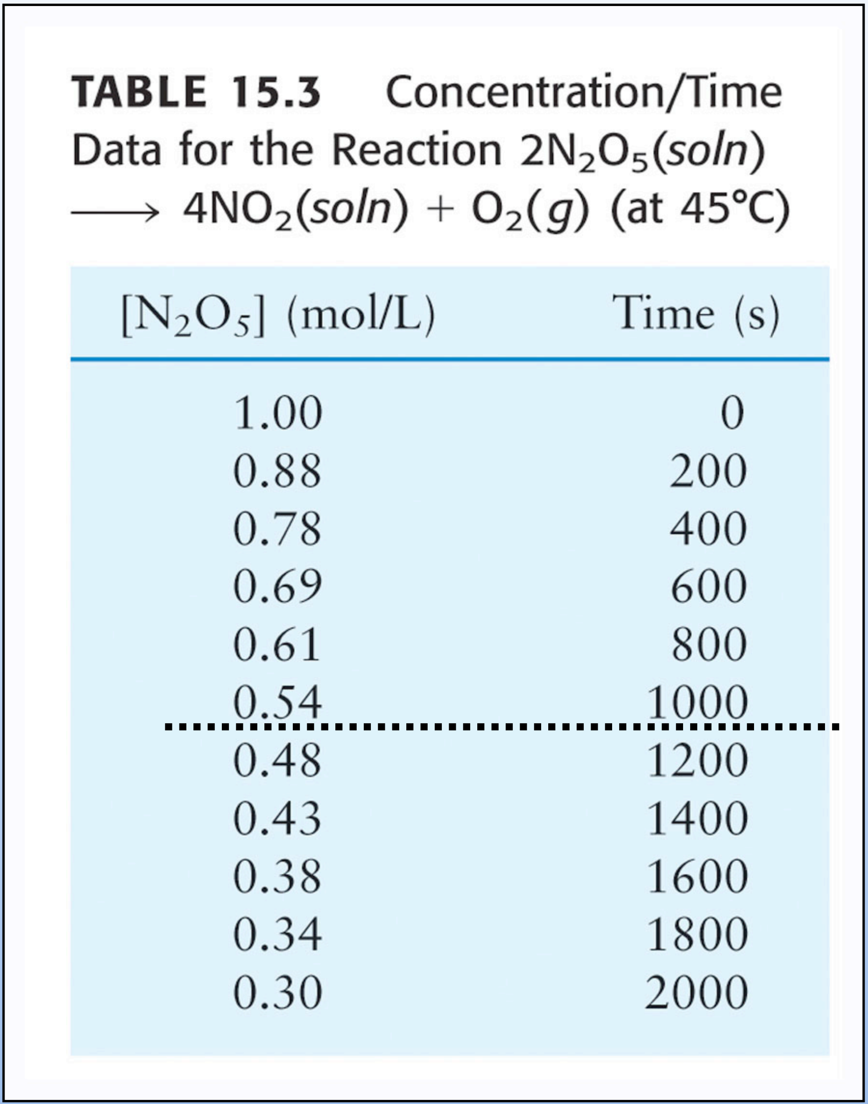


**TABLE 15.3** Concentration/Time Data for the Reaction $2N_2O_5(soln) \longrightarrow 4NO_2(soln) + O_2(g)$ (at 45°C)

| $[N_2O_5]$ (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

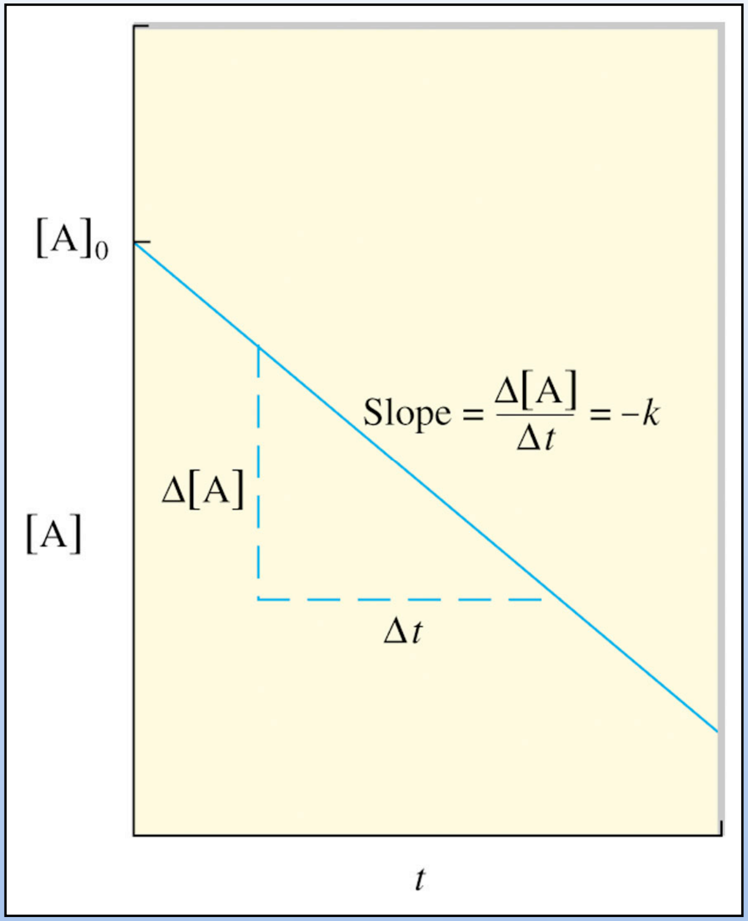
C. 1100 s

D. 1600 s

# Zeroth Order

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

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

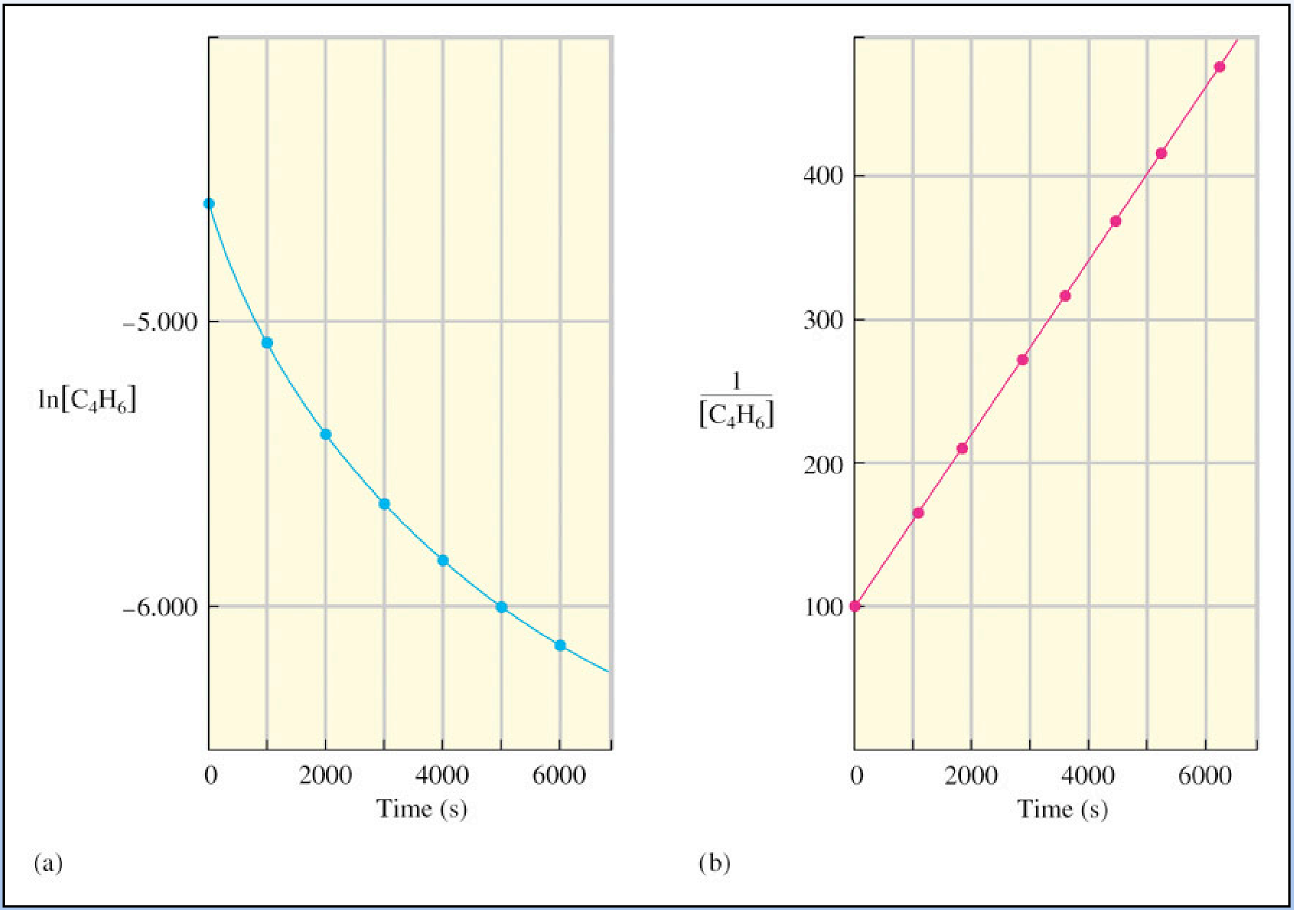

[A]$_0$
Slope = $\frac{\Delta[A]}{\Delta t} = -k$
Δ[A]
[A]
Δ$t$
$t$

# 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



$\ln[C_4H_6]$
−5.000
−6.000
0
2000
4000
6000
Time (s)
(a)
$\frac{1}{[C_4H_6]}$
400
300
200
100
0
2000
4000
6000
Time (s)
(b)

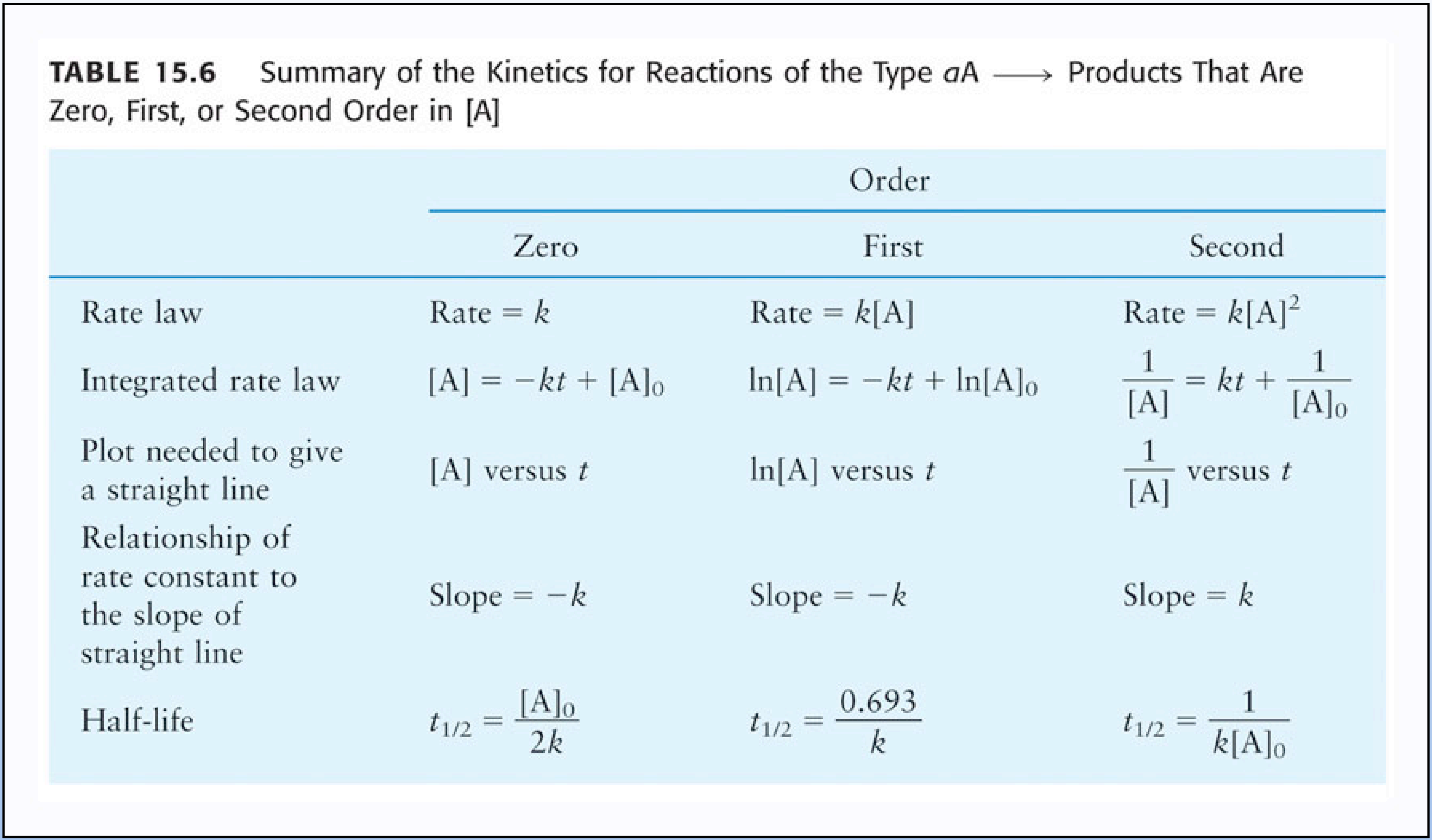


**TABLE 15.6** Summary of the Kinetics for Reactions of the Type $aA \longrightarrow$ Products That Are Zero, First, or Second Order in [A]

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