Today

Kinetics

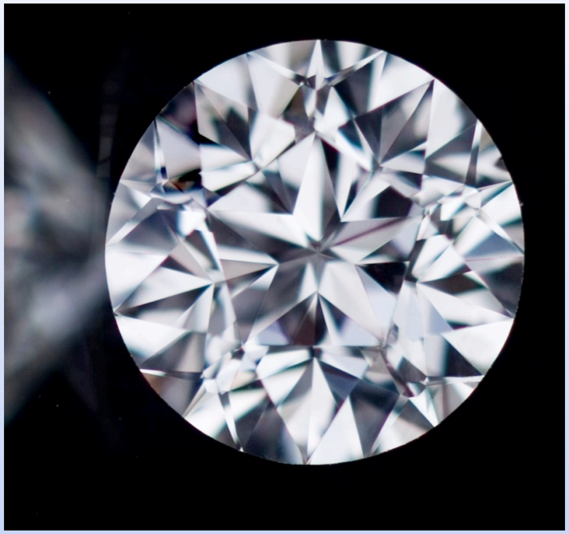
How fast are reactions?

What are the rates?

What affects the rate of reactions?

1. Nature of the reactants
2. Concentration of the reactants
3. Temperature
4. Presence of a Catalyst

Thermodynamics vs. Kinetics



Diamond

→

Graphite

$\Delta_R G° = -3 \text{ kJ mol}^{-1}$

Graphite is lower in free energy than Diamond

Reaction of Diamond to Graphite is spontaneous

THE REACTION IS JUST VERY VERY SLOW

Thermodynamics

Compares Free energy of reactants and products
This is the ideal case assuming everything can find its lowest energy state (time is irrelevant)

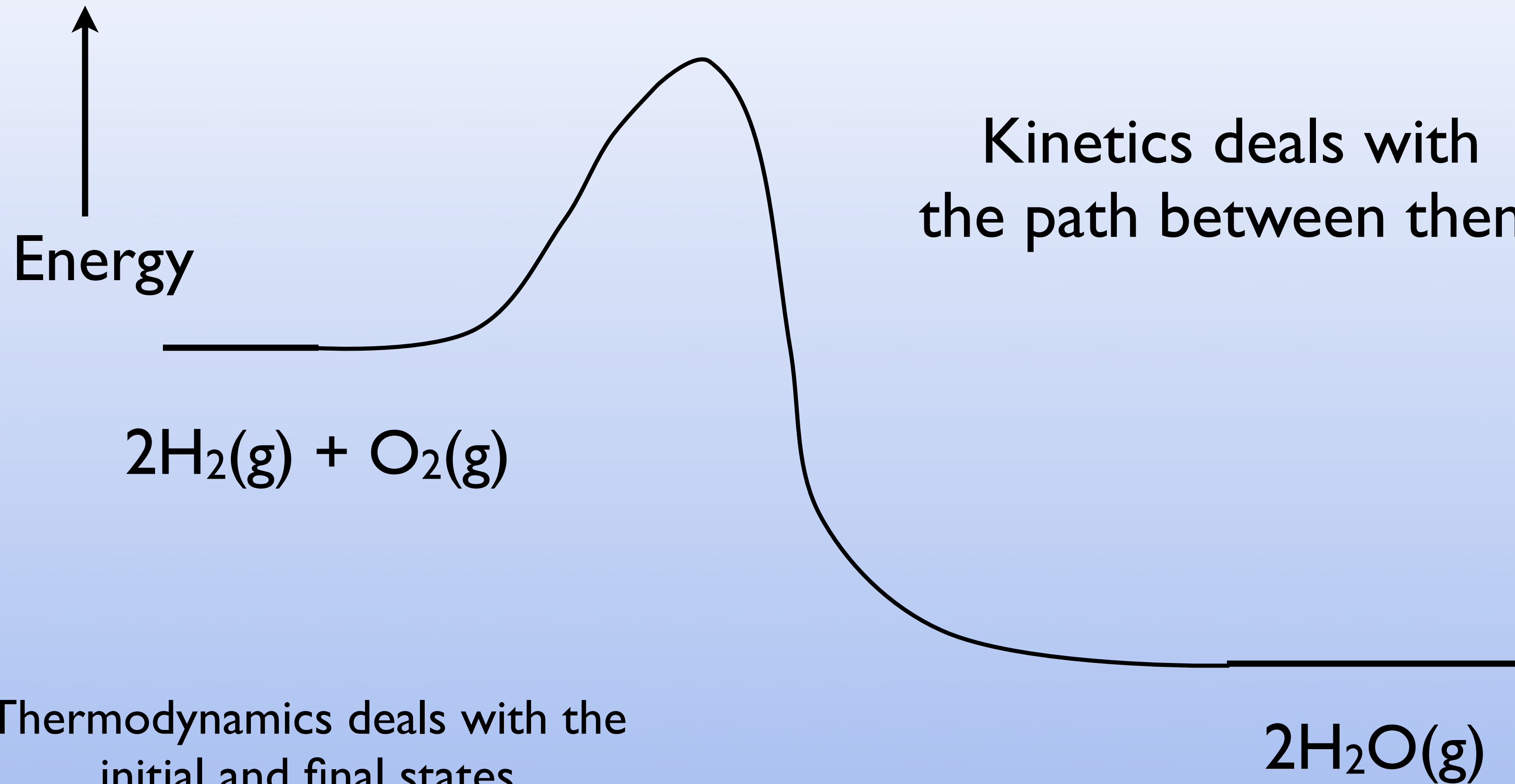
Diamonds are unstable

Kinetics

What is actually happening
How long does it take convert reactants to products

Diamonds are "kinetically trapped" in the unstable state

What prevents reactions form going "downhill" in energy?



Kinetics deals with the path between them

Thermodynamics deals with the initial and final states

Why is there a "barrier"?

You have to break the "old" bonds before you can form the "new" ones

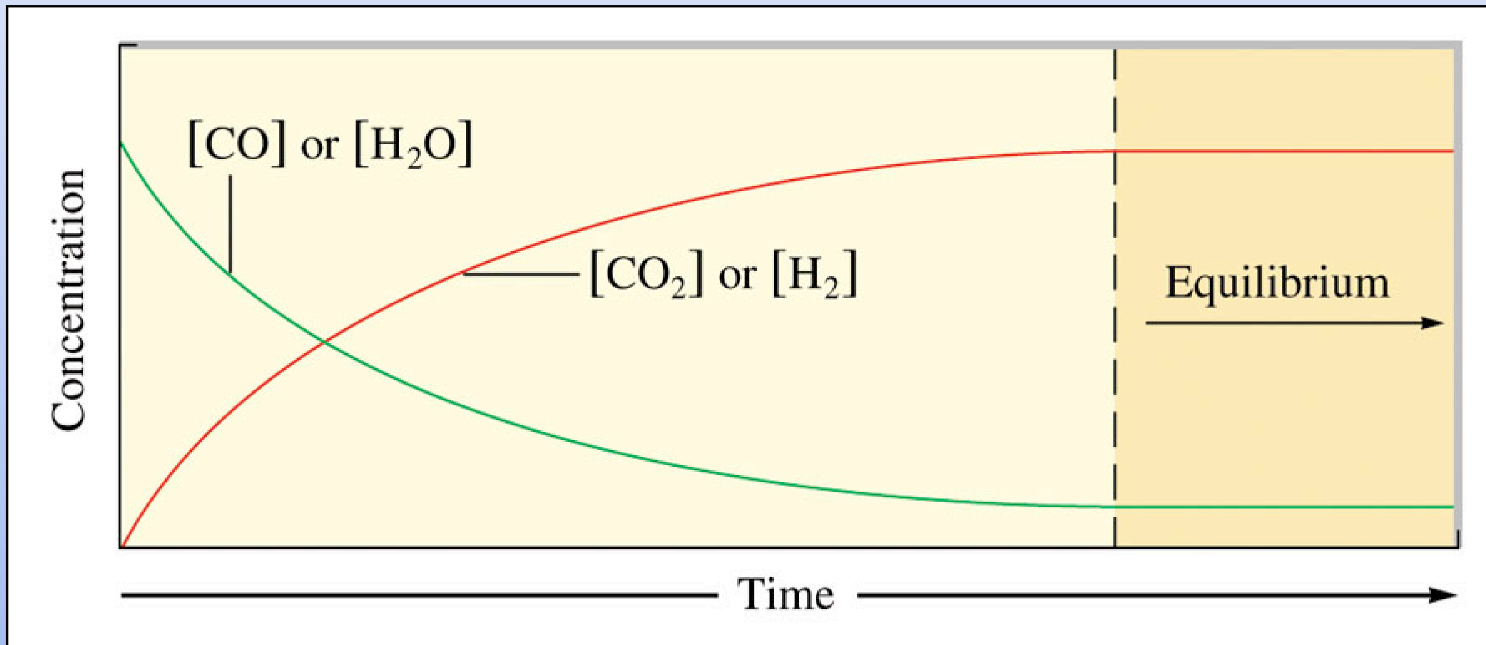
How do you speed up a reaction?

Raise the temperature
(more molecules over the barrier)
Add a catalyst
(lower the barrier)

How do we know how fast a reaction is?

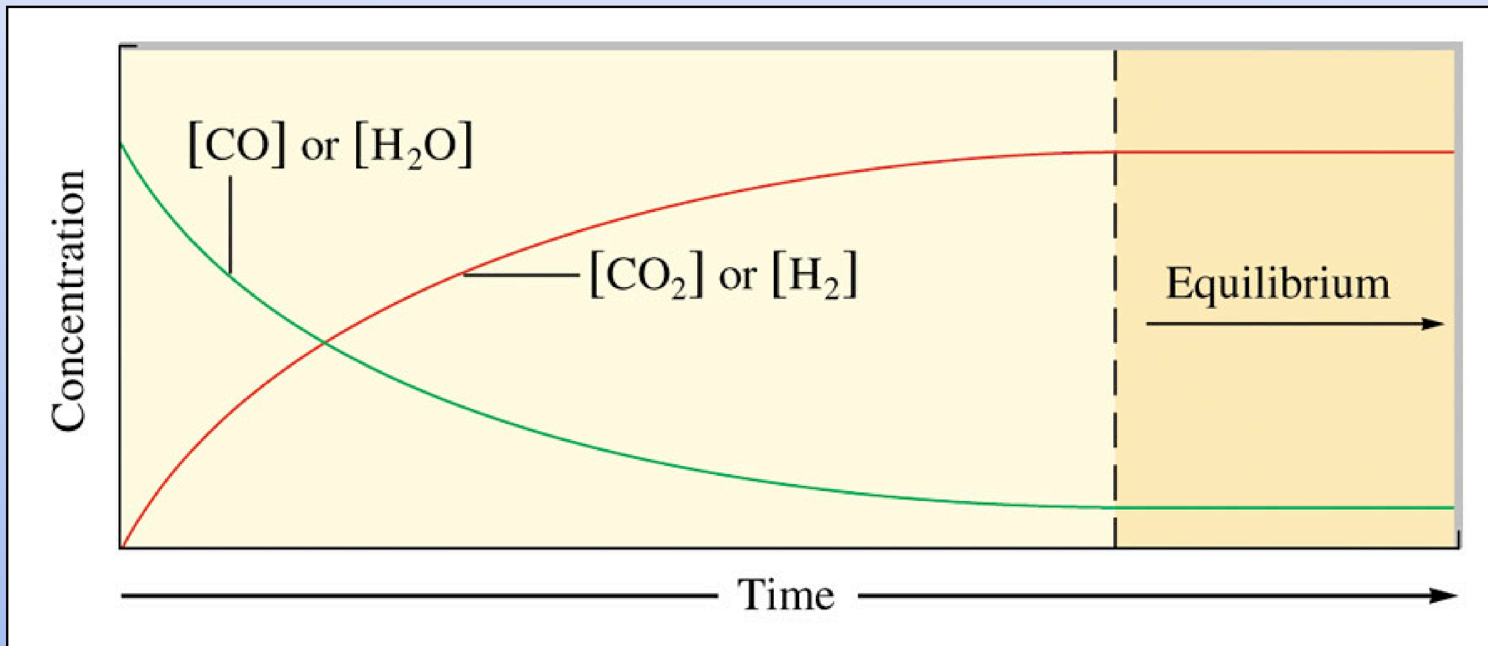
We look at the rate

Rate is change per time
Reaction rate is change in concentration per time



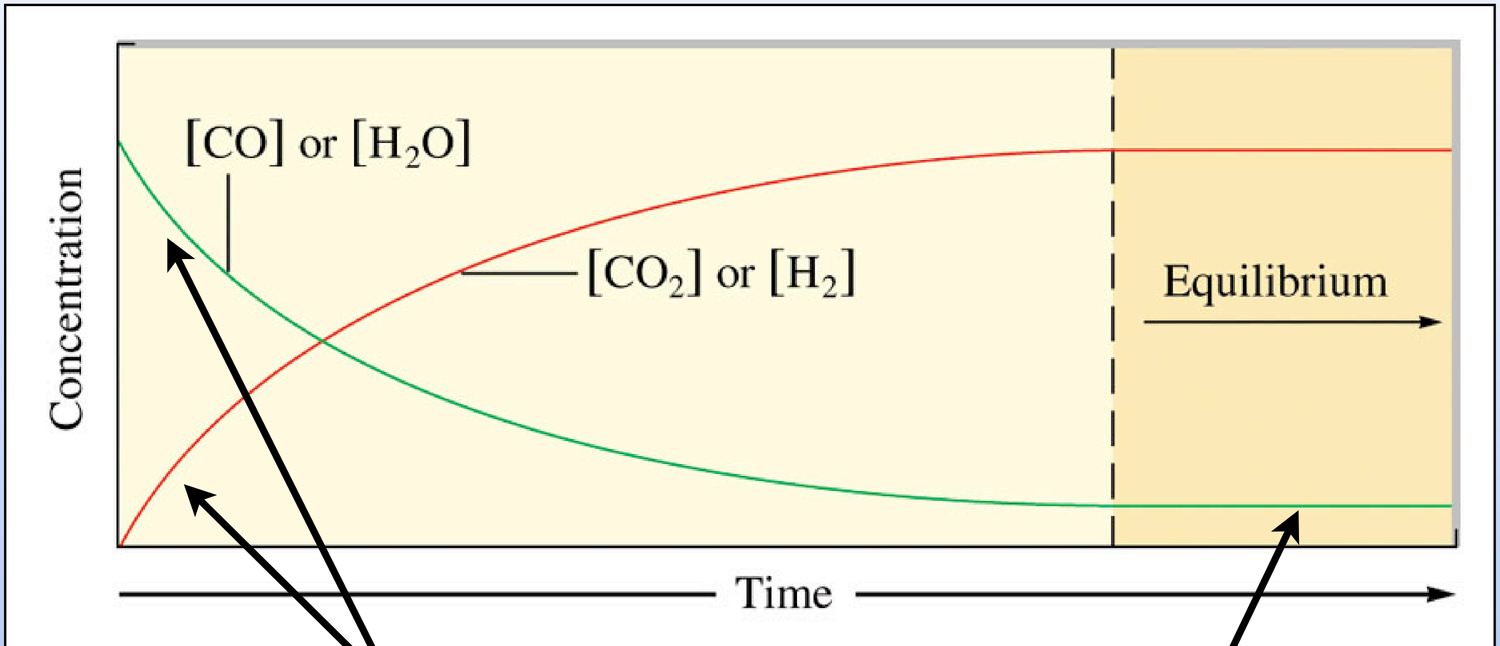
For this reaction

A. the rate for all the species is constant
B. the rate if largest at the start of the reaction
C. the rate is largest at equilibrium
D. the rate is randomly fluctuating



Rate is change in concentration per unit time

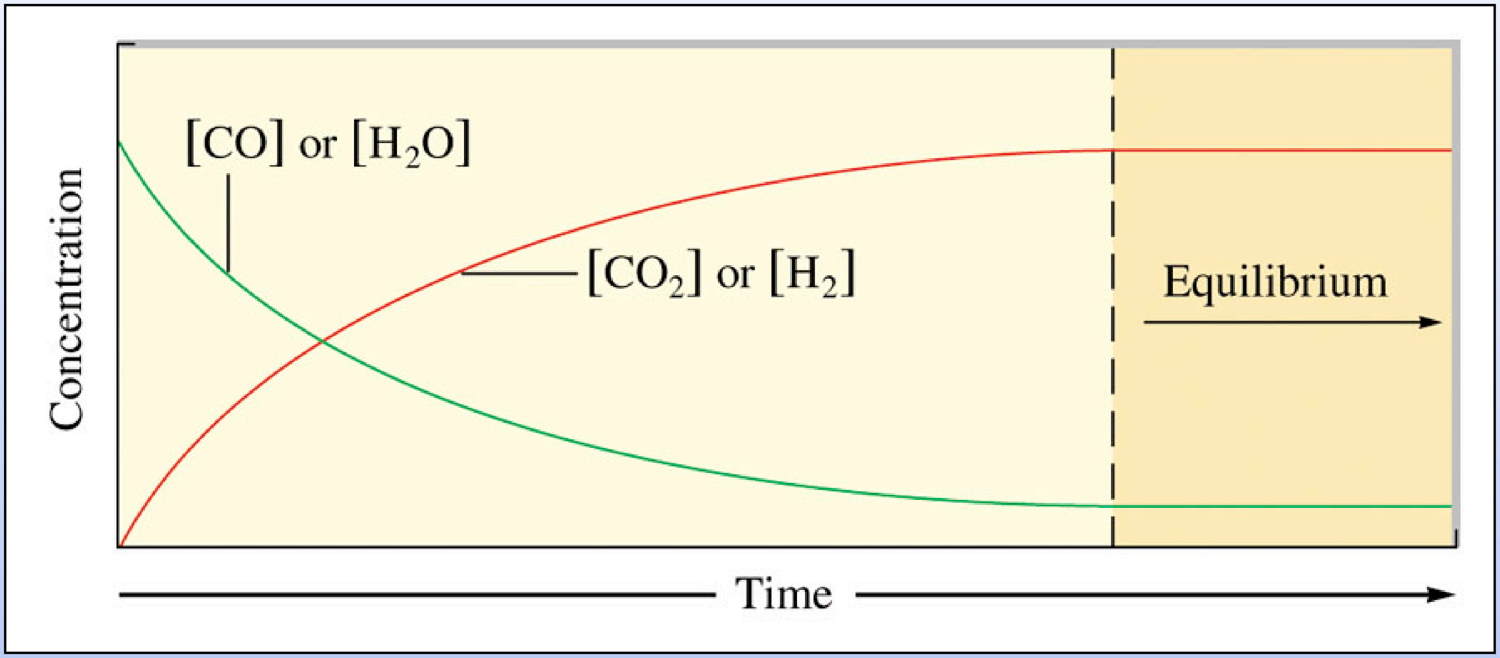
Rate is the slope of the graph of concentration vs time



Steepest slow at the start

at equilibrium rate = 0 (reaction has stopped)

$CO(g) + H_2O(g) \longleftrightarrow CO_2(g) + H_2(g)$



If you know the rate of one reactant or product you know them all

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

reactant decrease

Change

Rate of consumption of H_2

$$= -\frac{\Delta[H_2]}{\Delta t} = -\frac{d[H_2]}{dt}$$

products increase

Rate of formation of H_2O

$$= +\frac{\Delta[H_2O]}{\Delta t} = +\frac{d[H_20]}{dt}$$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$$

Rate of consumption of H_2	=	2 x the Rate of consumption of O_2	=	Rate of formation of H_2O

H_2 and H_2O has rates that are faster since 2 moles reaction for each 1 mole of O_2

For this reactions

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

the rate of production of NH_3 is

A. 2 times the rates of consumption of H_2

B. 1.5 times the rate of consumption of H_2

C. 2/3 times the rate of consumption of H_2

2x N_2 2/3x H_2

For this reactions

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\text{Rate} = -\frac{1}{1}\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d[H_2]}{dt} = +\frac{1}{2}\frac{d[NH_3]}{dt}$$

Generic Reaction

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

Characterizing rates

We want the slope

$$\frac{d[C]}{dt} \sim \frac{\Delta[C]}{\Delta t}$$

Note

Rate is changing with concentration

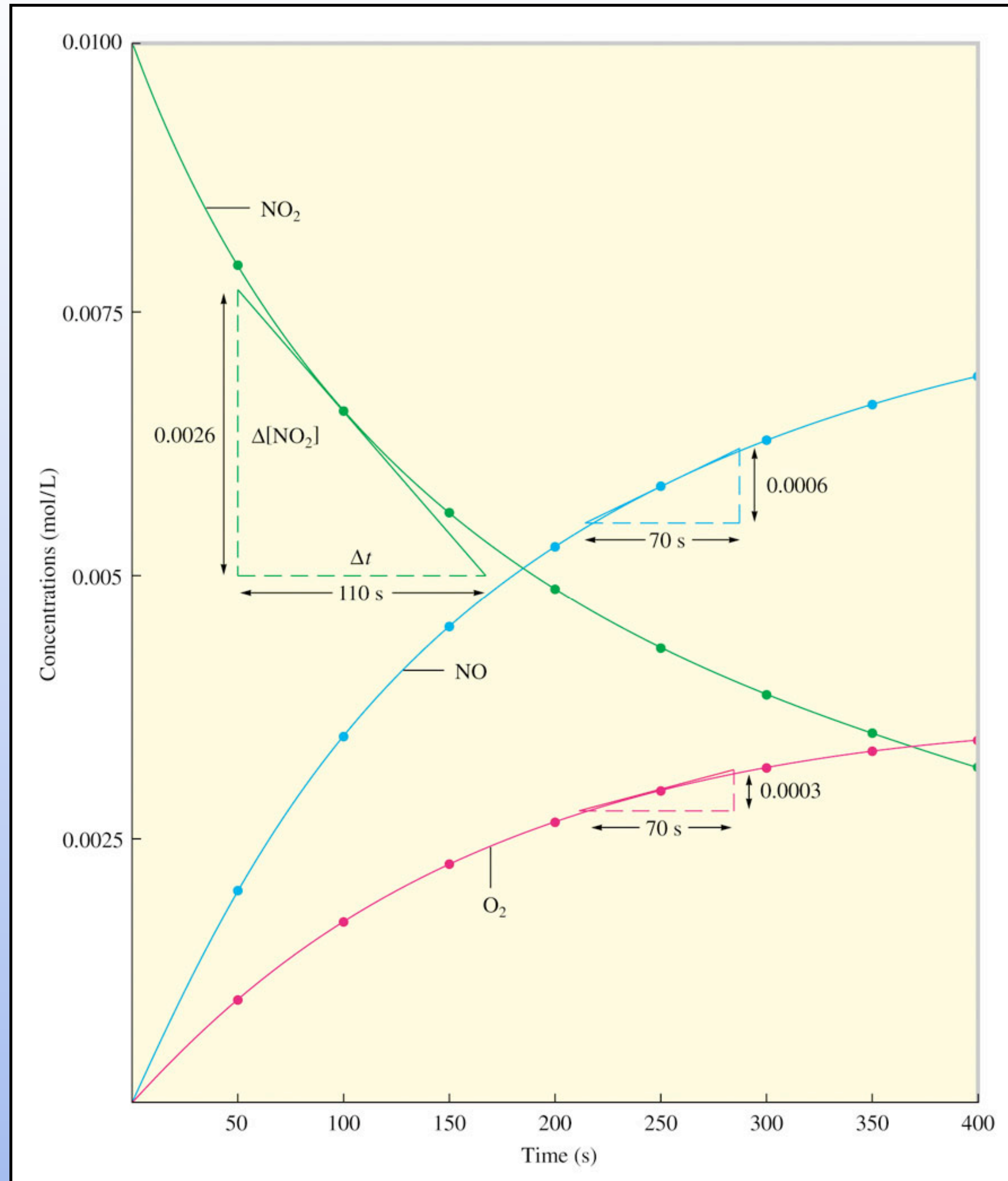


TABLE 15.1 Concentrations of Reactant and Products as a Function of Time for the Reaction $2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$ (at 300°C)

	Concentration (mol/L)		
Time (± 1 s)	NO_2	NO	O_2
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033
400	0.0031	0.0069	0.0035

Rate Laws

How does the rate depend on the concentrations?

Rate is some function of the concentration of the reactant molecules

What is the function?

$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

unknown constant

$$\text{Rate} = k[NO_2]^n$$

unknown exponent

k is the "rate constant"

n is the "reaction order" with respect to NO_2