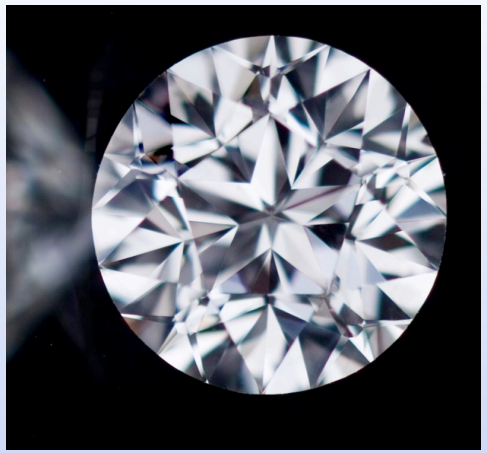
Today

Kinetics

How fast are reactions?
What are the rates?

Interconversion of two forms of carbon



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

Diamond

Graphite

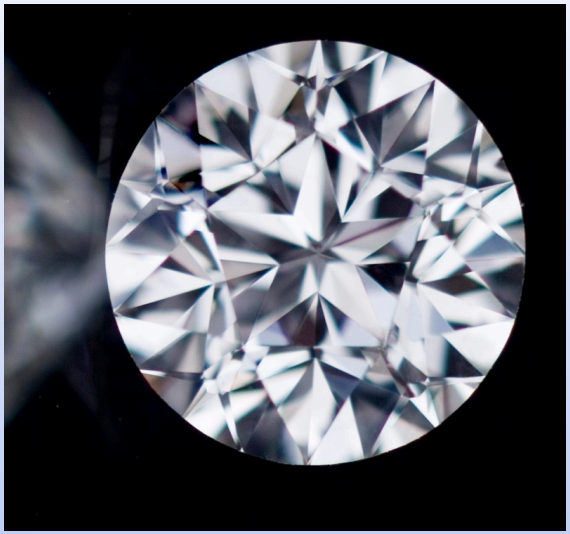
If you own diamond jewelry,
why should you not worry about this reaction?

A. we know diamond is more stable from $\Delta_R G°$

B. the reaction is extremely slow

C. the reaction will only happen if we add energy

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

Kinetics

To understand how fast a reaction proceeds we need to think about what is actually happening during the reaction

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

What actually happens?

Presumably somehow the reactants have to physically interact before there can be any chemistry

(assuming we are not doing this in a electrochemical cell)

Let's look at some reactions

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \quad \Delta_R G° = -147 \text{ kJ mol}^{-1}$$

$$Cu(s) + 2H^+(aq) \longrightarrow Cu^{2+}(aq) + H_2(g) \quad \Delta_R G° = +65 \text{ kJ mol}^{-1}$$

which will be faster to react?

A. Zn

B. Cu

C. no way to since, since kinetics doesn't have anything to do with thermodynamics

Let's look at some reactions

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

which will be faster to react?

A. Zn dust

B. Zn chunks

C. they will react at the same rate (they're both Zn)

Let's look at some reactions

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

which will be faster to react?

A. higher concentration HCl

B. lower concentration HCl

C. they will react at the same rate (they're both strong acids)

What can affect the rate of reactions?

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

First you have to get the reactants together

Often we have two species that need to interact (physical contact) before there can be a chemcial reaction (bond breaking/forming)

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How do you speed up a reaction?

More interactions

"Nature" of the reactanct
(more surface area for solids)

Higher concentrations
(more collisions for species in solution)

What prevents reactions form going "downhill" in energy?

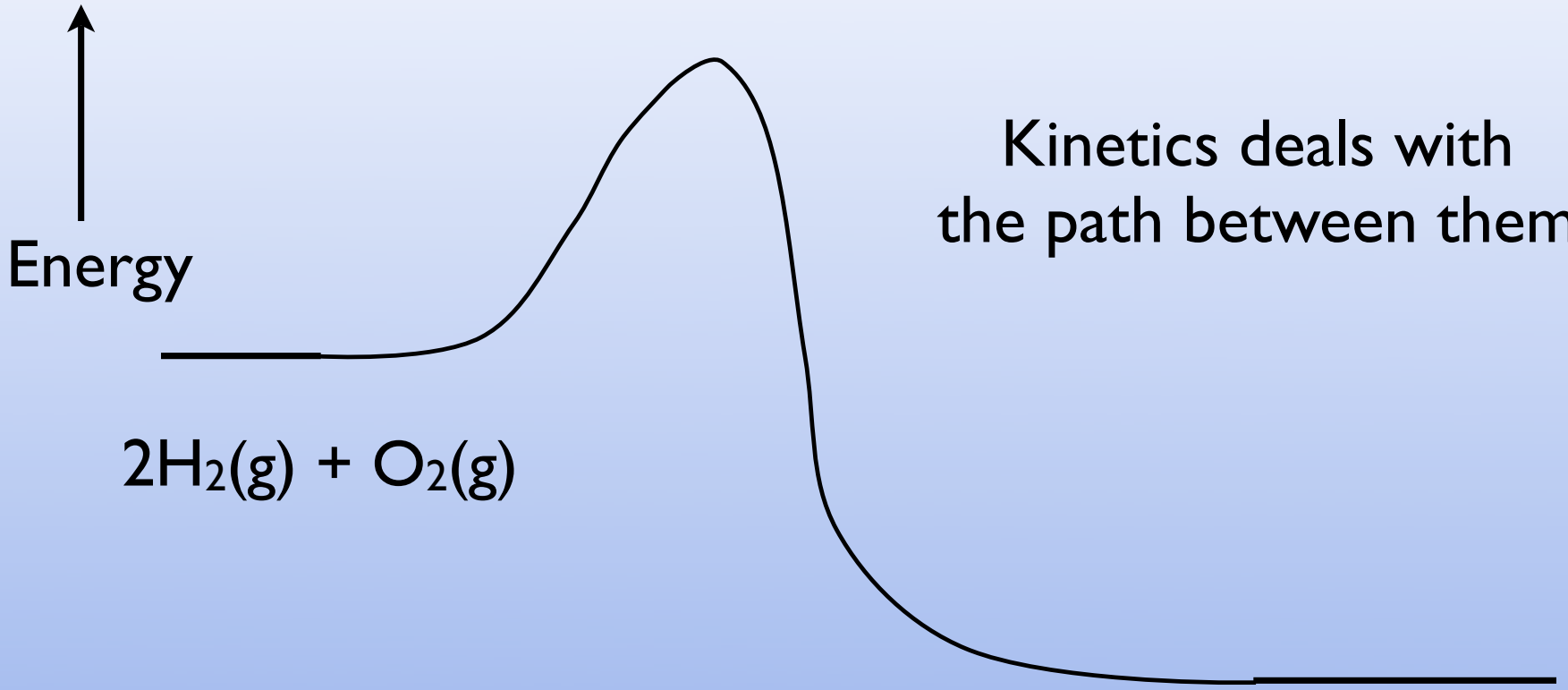
Energy

$2H_2(g) + O_2(g)$

Thermodynamics deals with the initial and final states

$2H_2O(g)$

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

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?

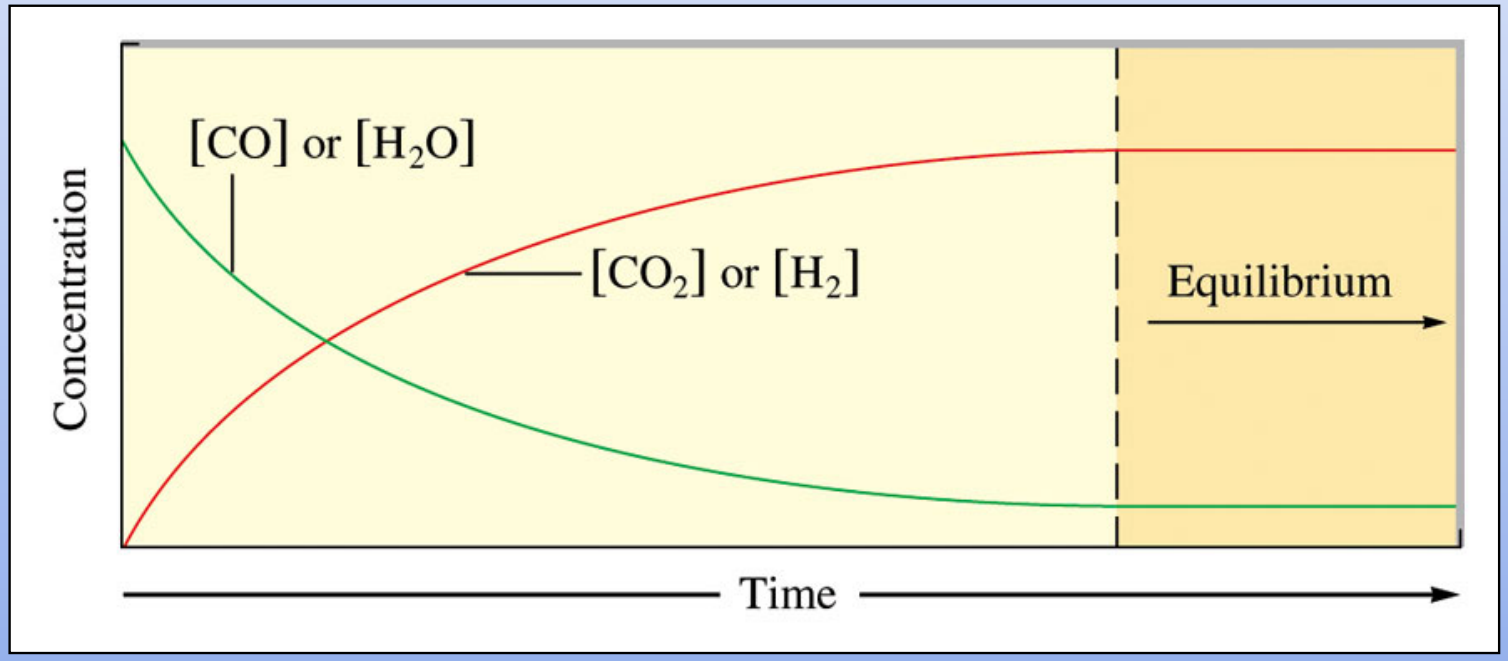
Raise the temperature
(more molecules over the barrier)

Add a catalyst
(lower the barrier)

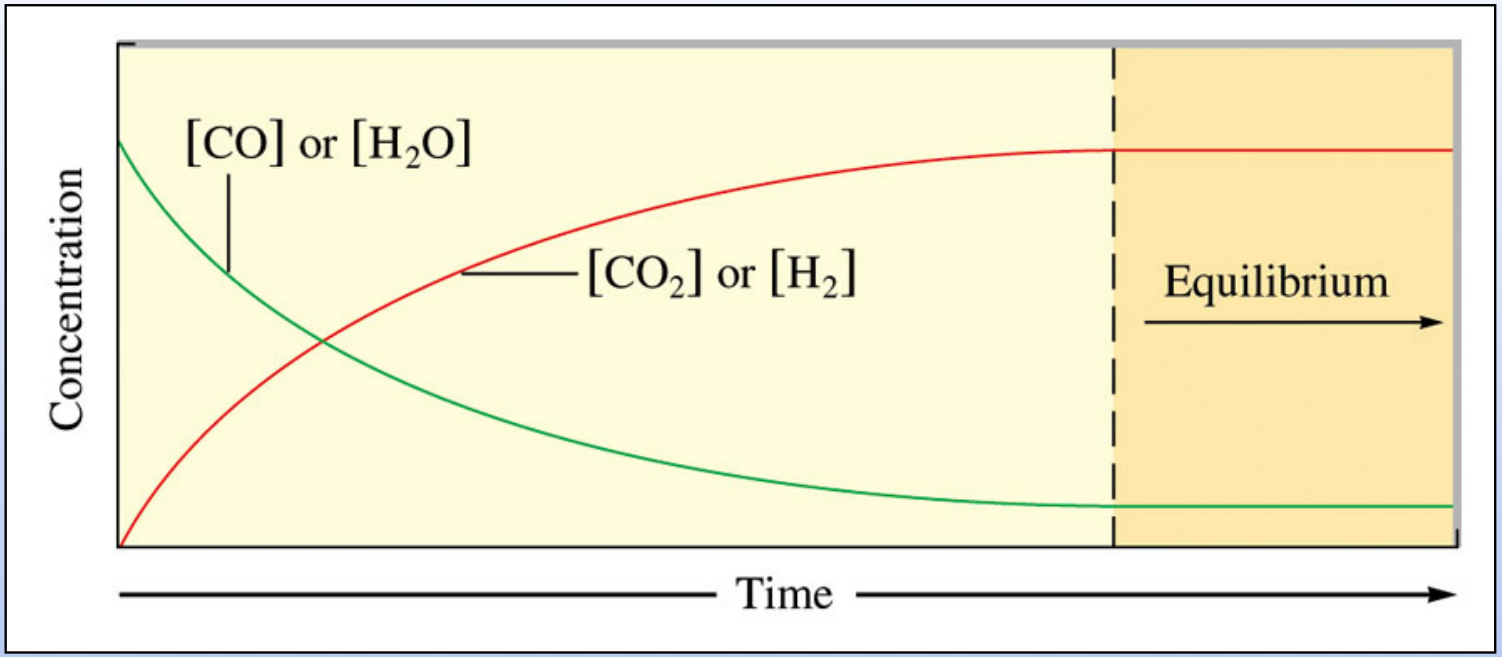
How do we know how fast a reaction is?

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

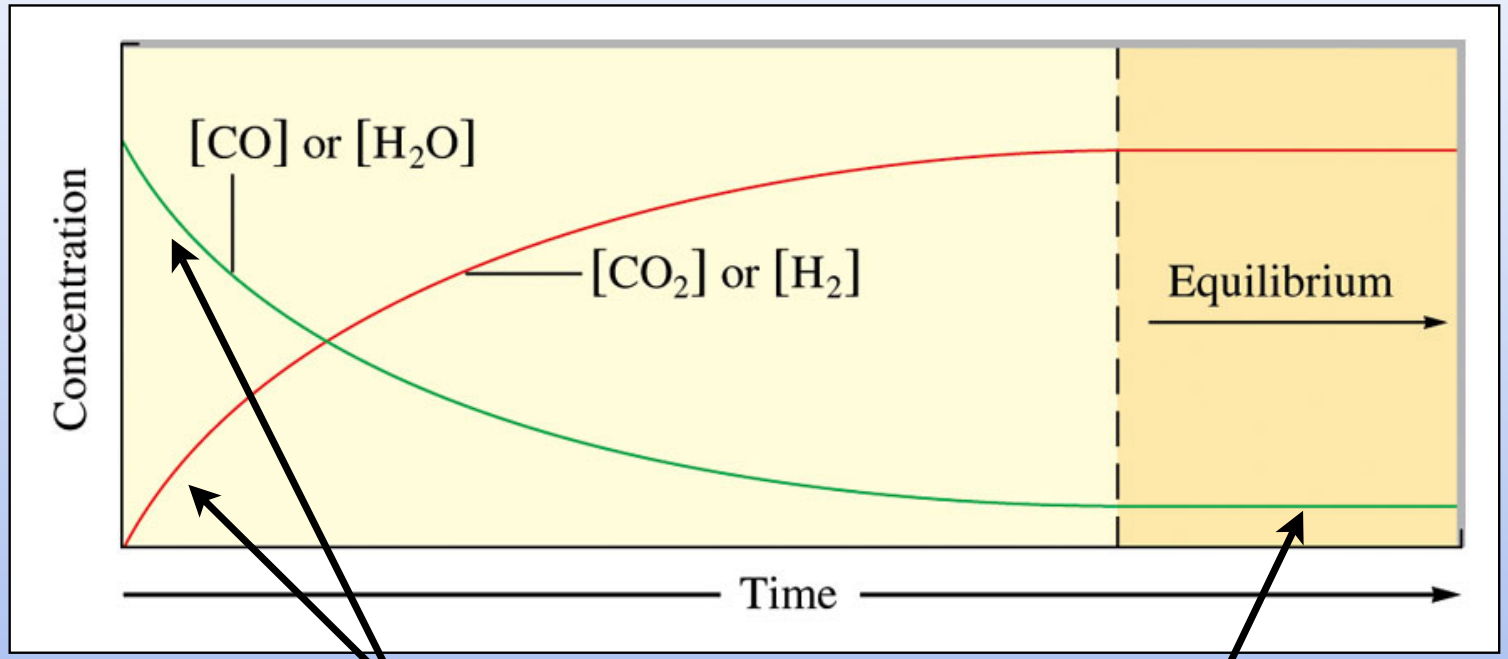
B. the rate if largest at the start of the reaction

C. the rate is largest at equilibrium

D. the rate is randomly fluctuating

Rate is change in concentration per unit time

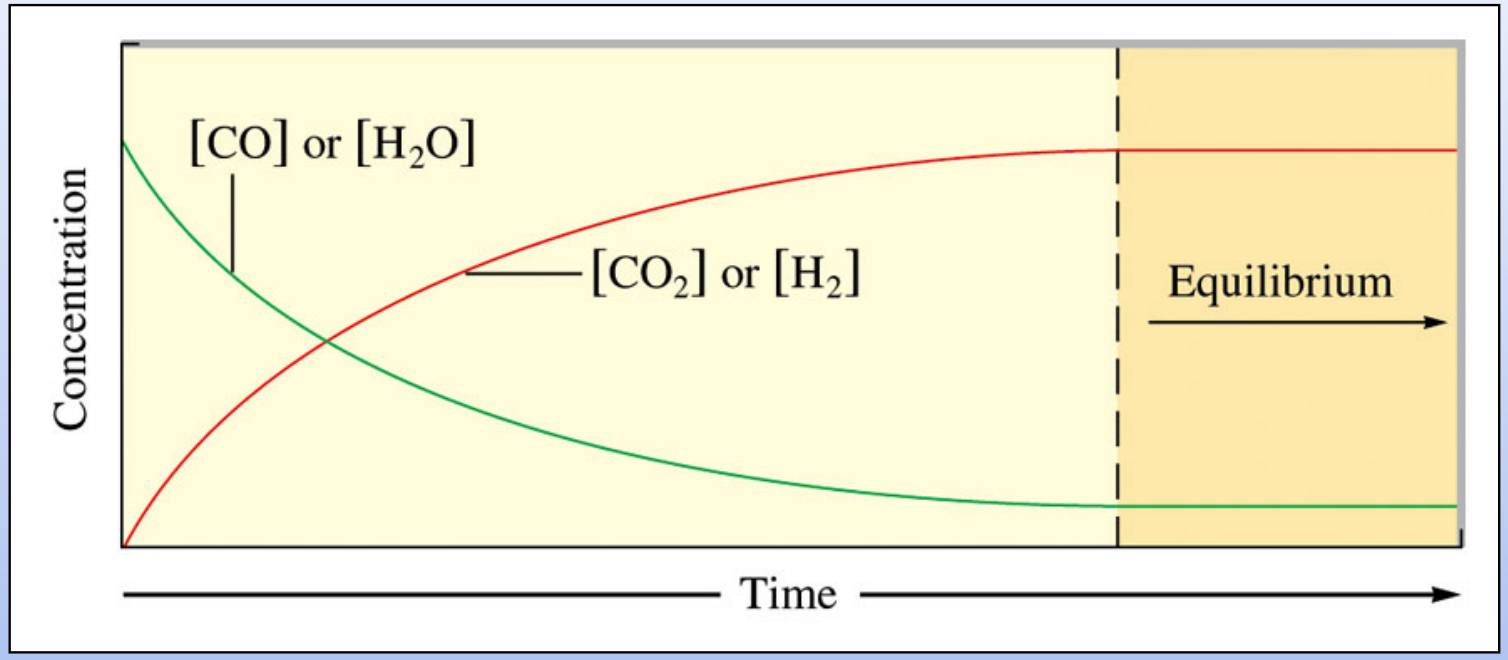
Rate is the slope of the graph of concentration vs time



Steepest slope 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 have 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

For this reactions

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

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

For this reactions

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Generic Reaction

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

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

How to get the rate? Do the experiment!

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

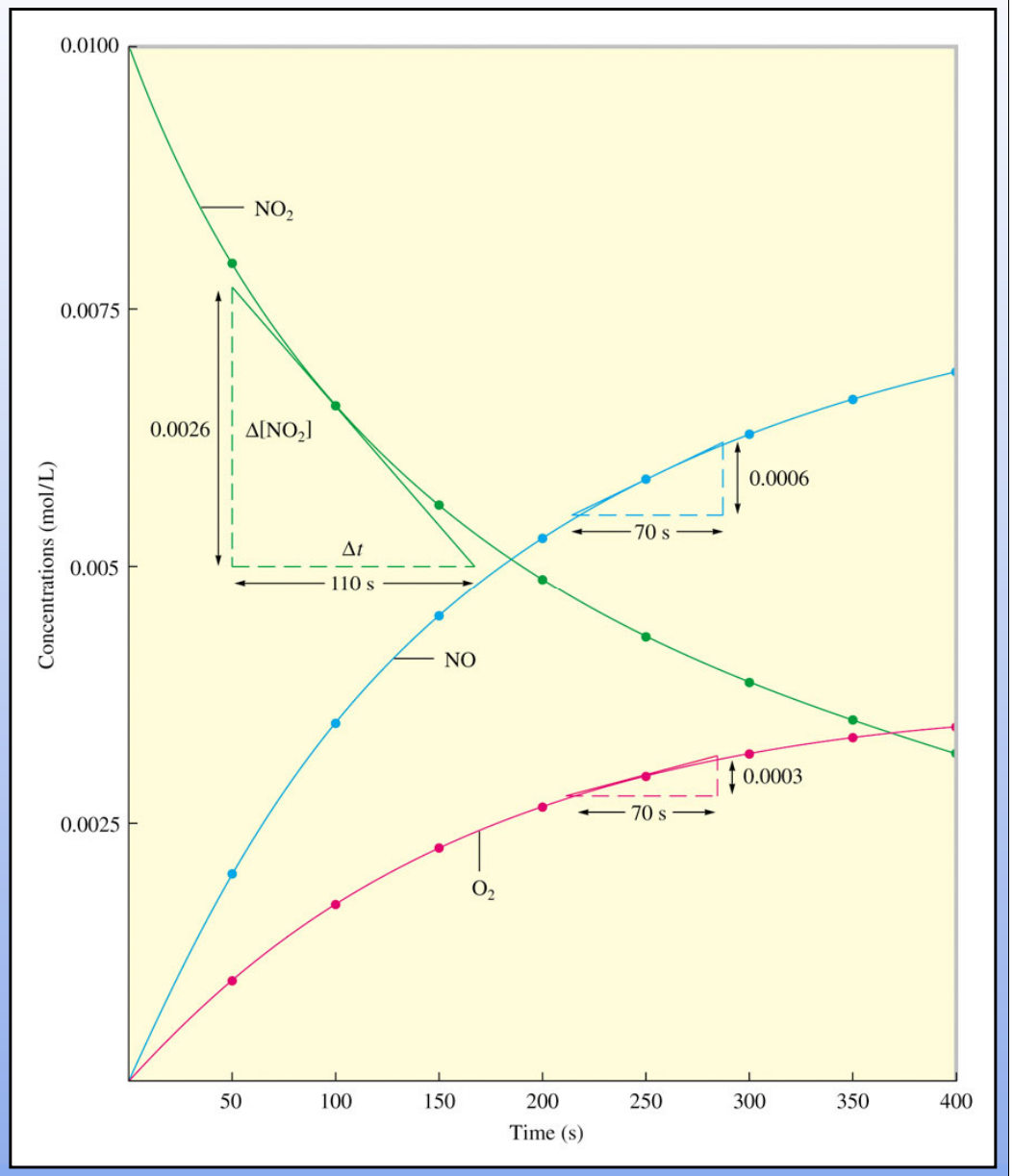
Characterizing rates

Change in concentration
divided by
Change in time

We want the slope

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

Note
Rate is changing with
concentration



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?

To predict the function we need to know the mechanism (the individual step in the reaction)

Or we can do an experiment to directly measure how the rate varies with concentration

For the reaction rate we typically are looking at the forward reaction

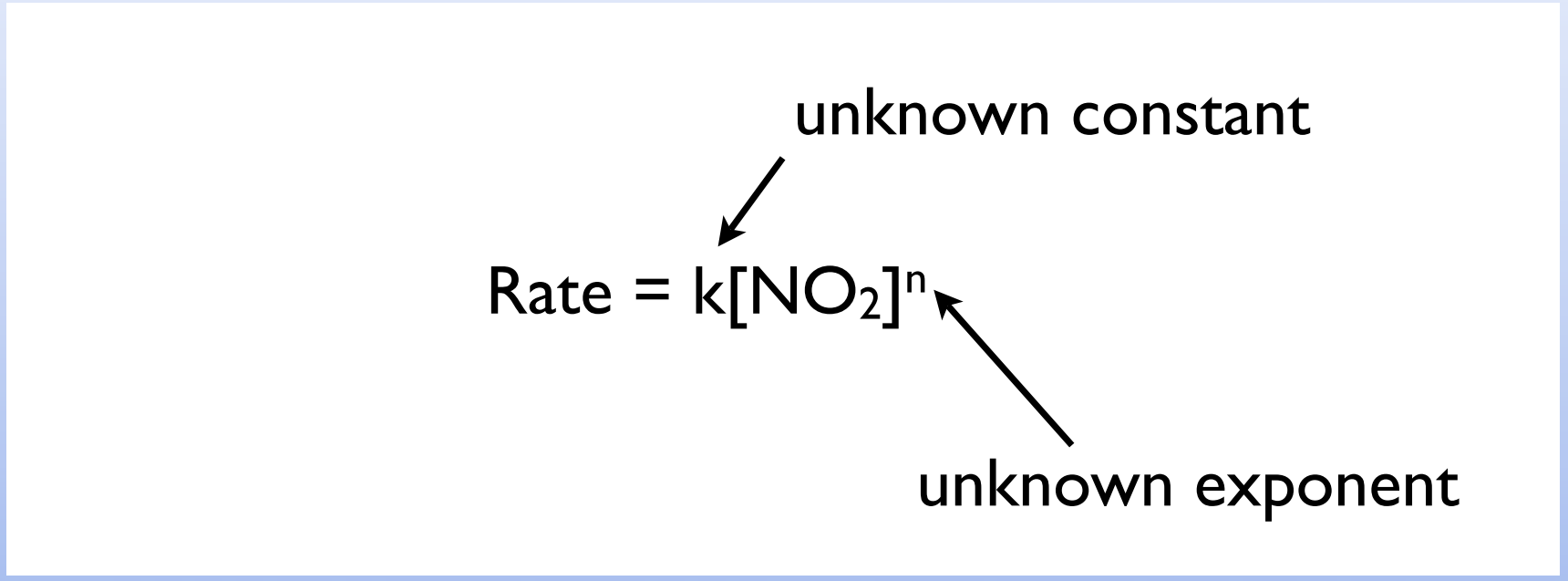
$$2NO_2(g) \longrightarrow 2NO(g) + O_2(g)$$

We write the rate as a function of the Reactant concentrations

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

For the reaction rate we typically are looking at the forward reaction

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



k is the "rate constant"

n is the "reaction order" with respect to NO_2

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 I looked at the data for this reaction and found

$$\text{rate} = k[NO_2]^2$$

this reaction is 2nd order in NO_2

Method of initial rates

Since the rate can change as the reaction proceeds, one way to determine the affect of concentration on a rate is to perform many experiments at different starting concentrations and measure the initial rate

Experiment	$[C_3H_6O]_o$	$[Br]_o$	initial rate ($M\ s^{-1}$)
1	0.1M	0.1M	1.64×10^{-5}
2	0.1M	0.2M	1.65×10^{-5}
3	0.2M	0.1M	3.29×10^{-5}

$$C_3H_6O + Br_2 \longrightarrow C_3H_5OBr + HBr$$

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A. the rate is independent on Br_2 concentration

B. the rate is linear dependent on Br_2 concentration

C. the rate depends on the concentration of Br_2 squared

$$C_3H_6O + Br_2 \longrightarrow C_3H_5OBr + HBr$$

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A. the rate is independent on acetone concentration

B. the rate is linear dependent on acetone concentration

C. the rate depends on the concentration of acetone squared

$$C_3H_6O + Br_2 \longrightarrow C_3H_5OBr + HBr$$

Experiment	$[C_3H_6O]_o$	$[Br]_o$	initial rate ($M\ s^{-1}$)
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A. $k = [C_3H_6O][Br_2]$

B. $k = [C_3H_6O]^2[Br_2]$

C. $k = [C_3H_6O]$

D. $k = [Br_2]$

E. k = constant

$$C_3H_6O + Br_2 \longrightarrow C_3H_5OBr + HBr$$

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A. the rate is first order in acetone and first order in Br_2

B. the rate is first order in acetone and zeroth order in Br_2

C. the rate is second order overall

D. A & C