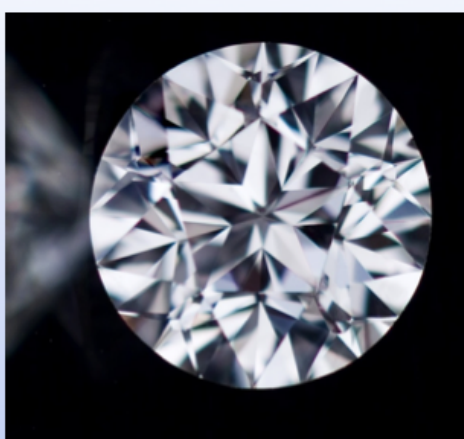


Today
Kinetics

How fast are reactions?
What are the rates?

Interconversion of two forms of carbon



Diamond



$$\Delta_{\text{R}}G^{\circ} = -3 \text{ kJ mol}^{-1}$$

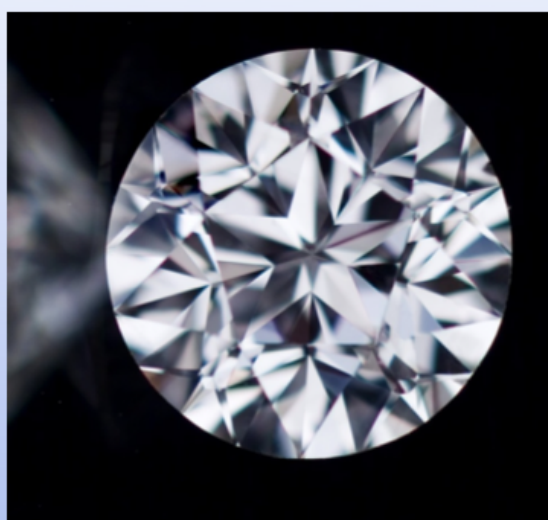


Graphite

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

- A. we know diamond is more stable from $\Delta_{\text{R}}G^{\circ}$
- B. the reaction is extremely slow
- C. the reaction will only happen if we add energy

Thermodynamics vs. Kinetics



Diamond



Graphite

$$\Delta_{\text{R}}G^{\circ} = -3 \text{ kJ mol}^{-1}$$

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

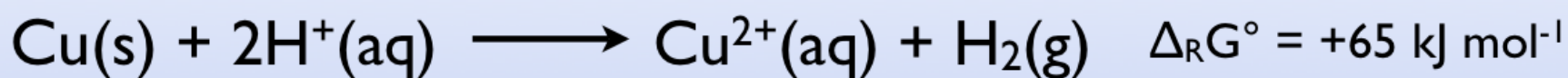
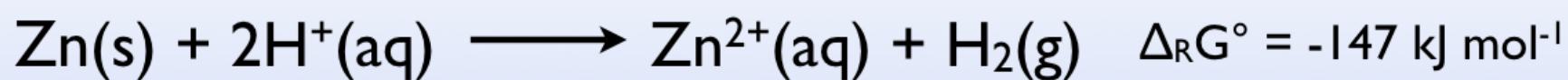
To understand how fast a reaction proceeds we need to think about what is actually happening during the reaction



What actually happens?

Presumably somehow the reactants have to physically interact before there can be any chemistry
(assuming we are not doing this in an electrochemical cell)

Let's look at some reactions



which will be faster to react?

A. Zn

B. Cu This reaction doesn't happen at all

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

Let's look at some reactions



which will be faster to react?

A. Zn dust

B. Zn chunks

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

more surface \rightarrow more collisions
w/ H^+
 \rightarrow faster
RXN

Let's look at some reactions



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)

More H^+ = more collisions
↳ FASTER

What can affect the rate of reactions?

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

Physical

Chemical

First you have to get the reactants together

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

First you have to get the reactants together

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

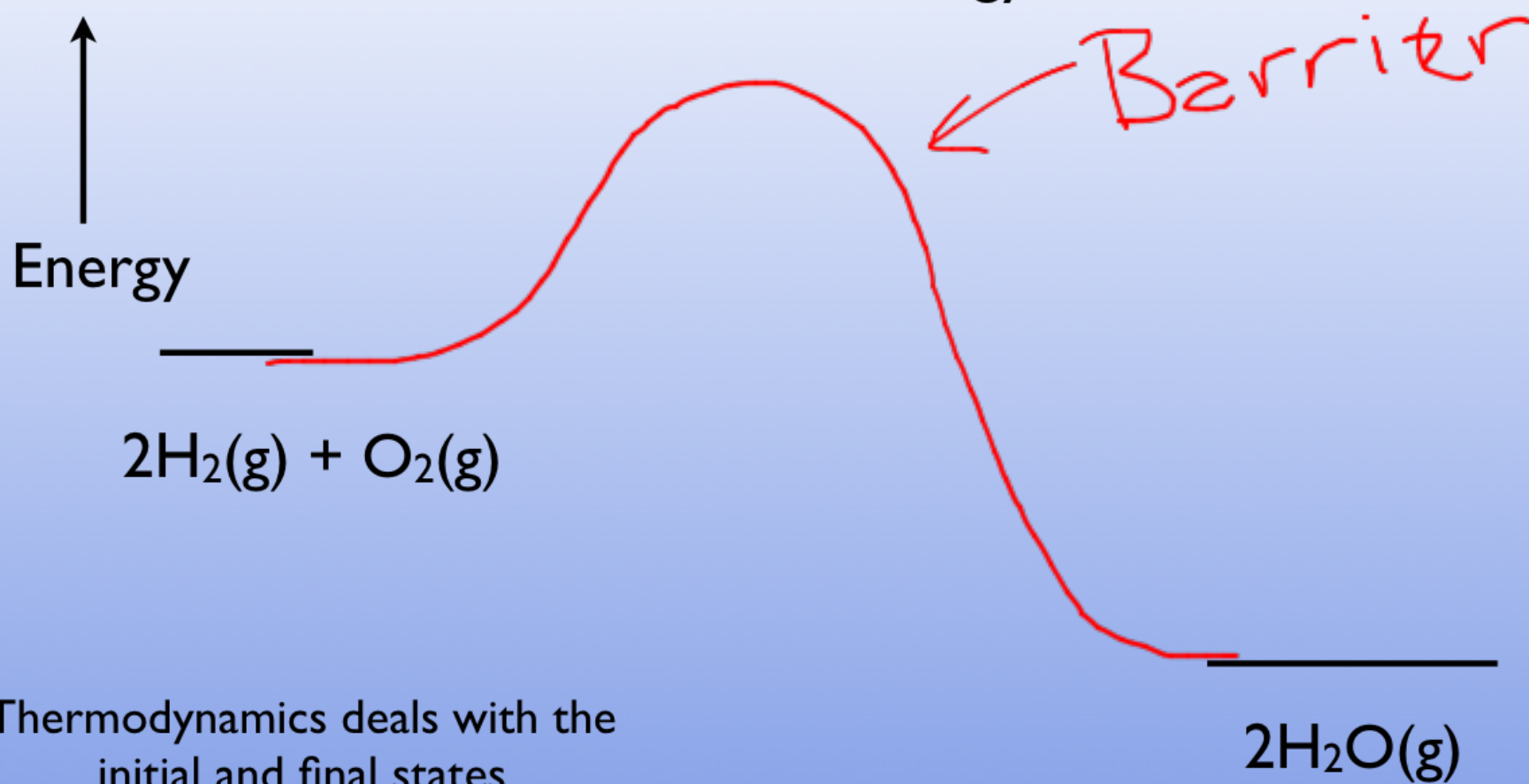
How do you speed up a reaction?

More interactions

“Nature” of the reactant
(more surface area for solids)

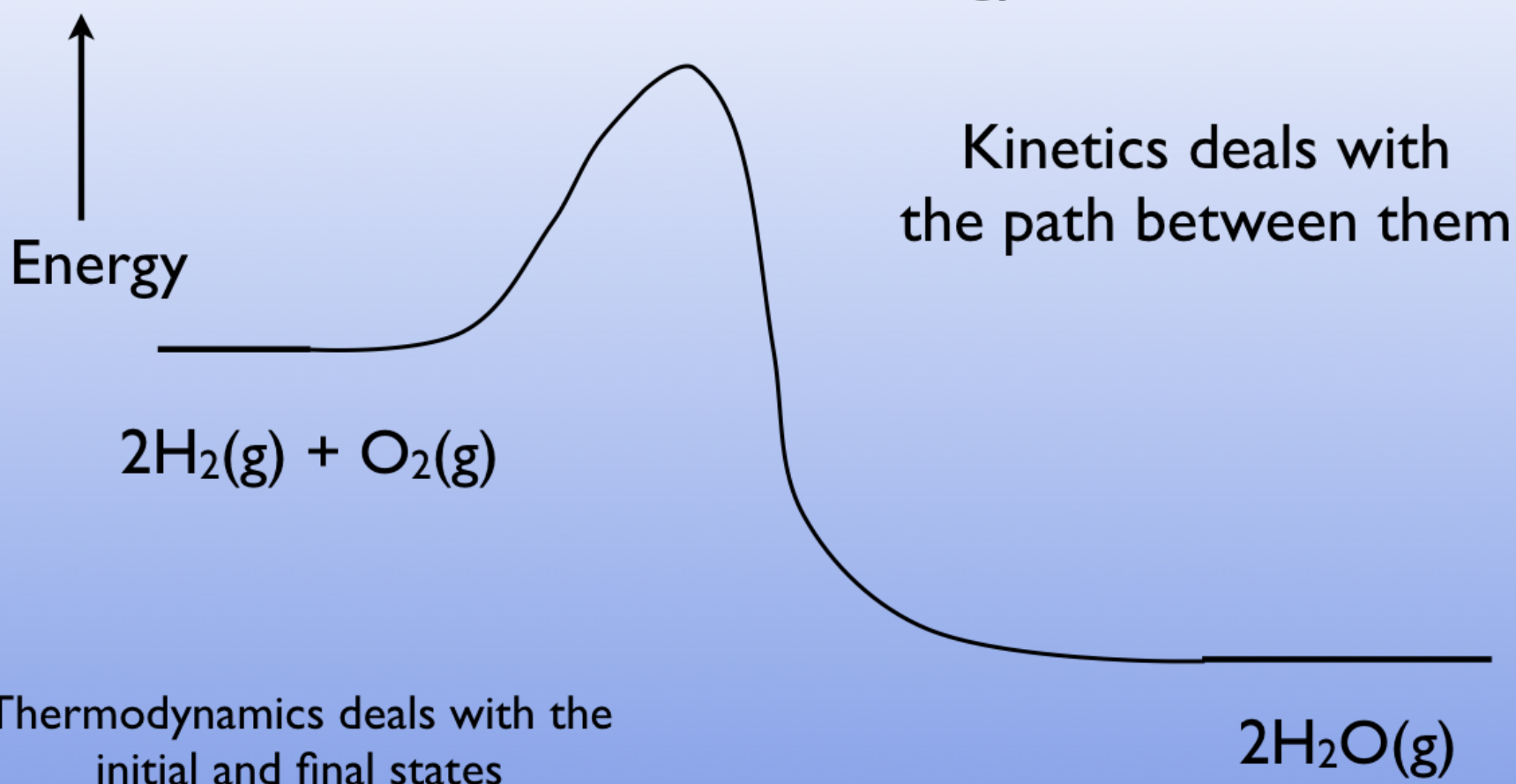
Higher concentrations
(more collisions for species in solution)

What prevents reactions from going "downhill" in energy?



Thermodynamics deals with the initial and final states

What prevents reactions from going "downhill" in energy?



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)

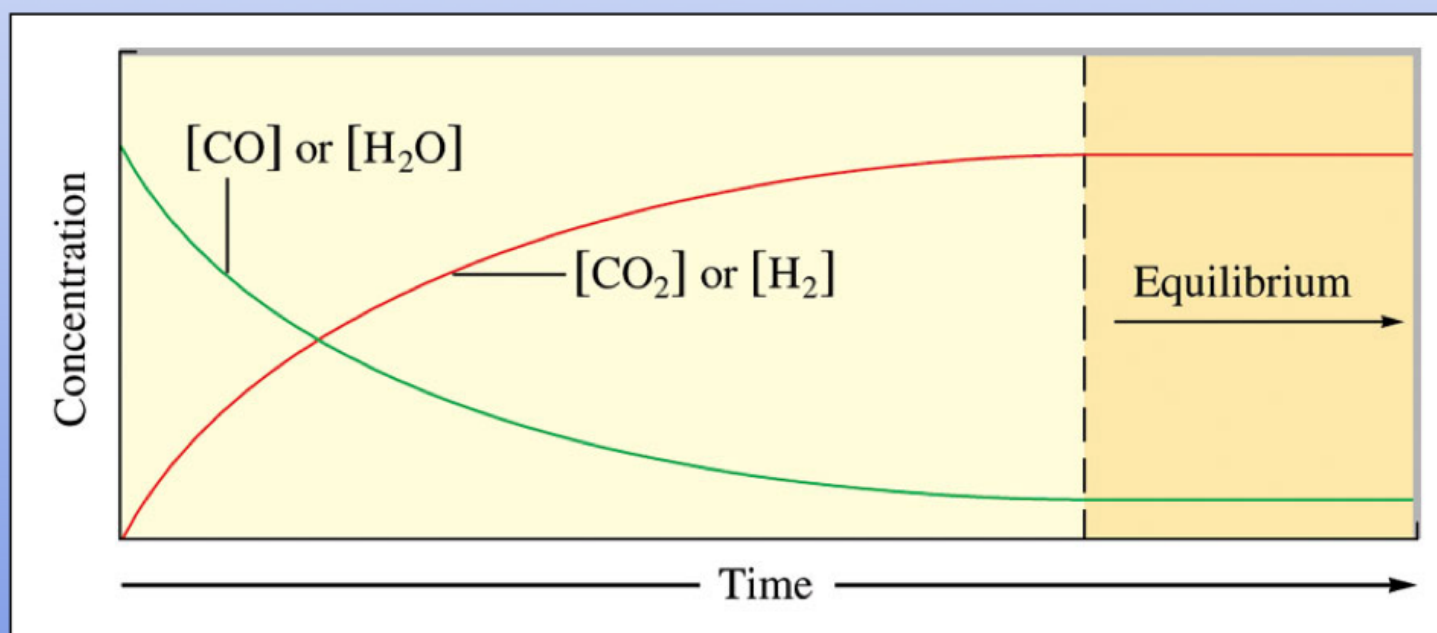
How do we know how fast a reaction is?

We look at the rate $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2$

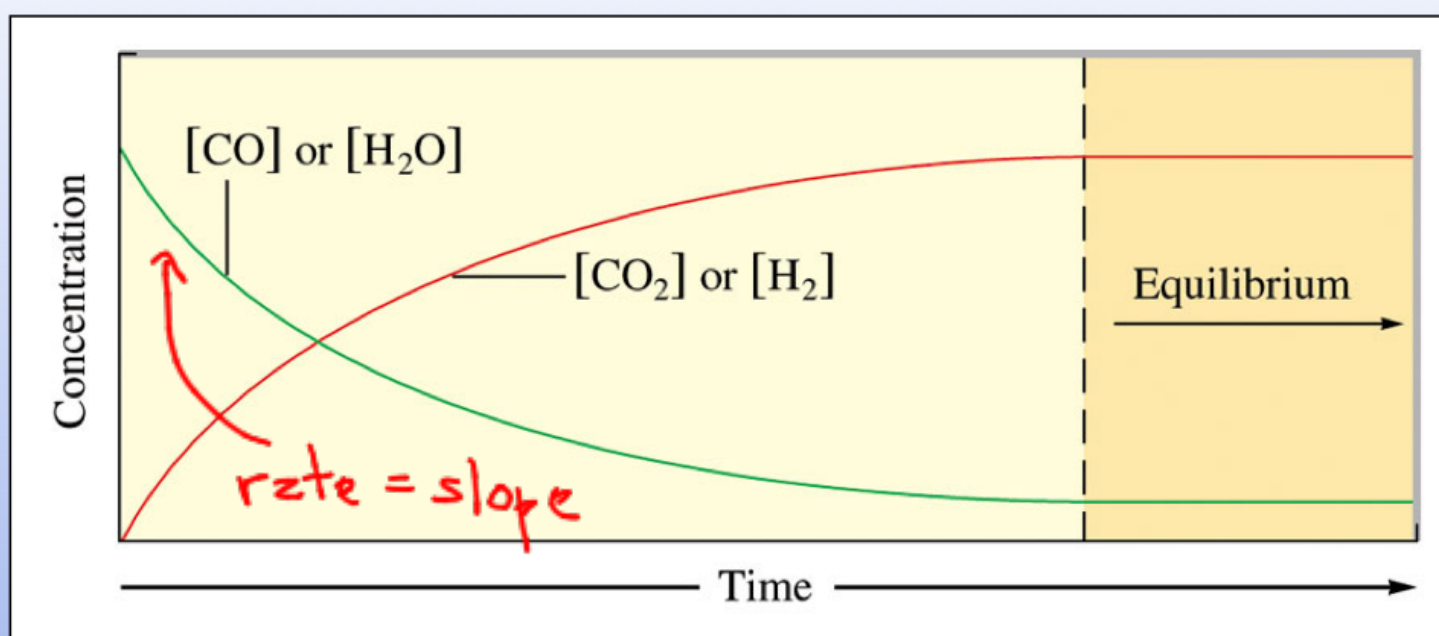
Rate is change per time

Reaction rate is change in concentration per time

+ H_2



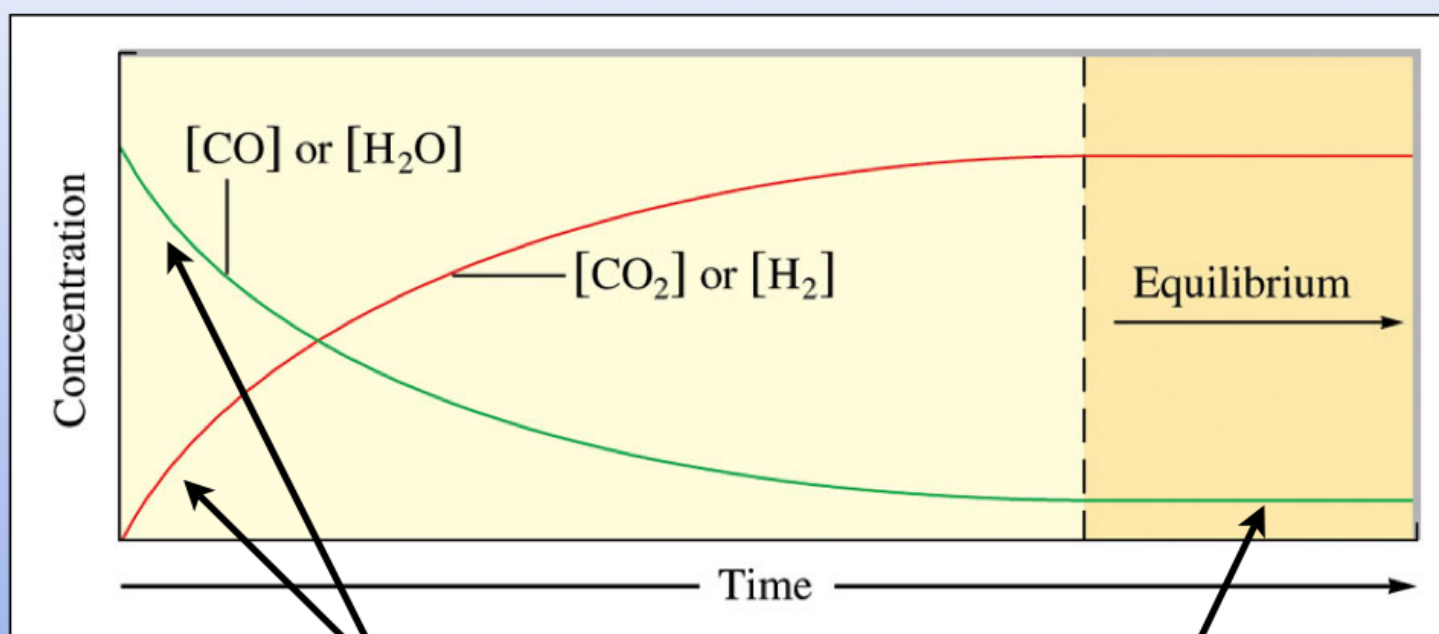
For this reaction



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

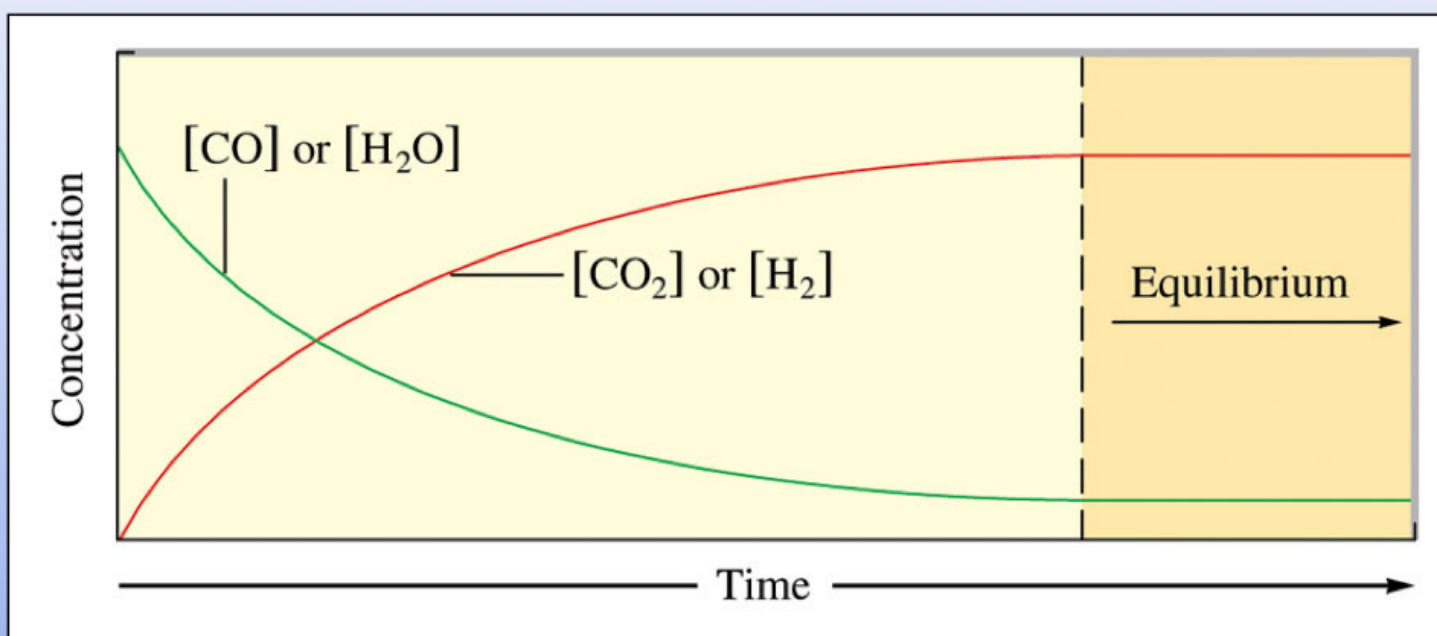
Rate is change in concentration per unit time

Rate is the slope of the graph of concentration vs time

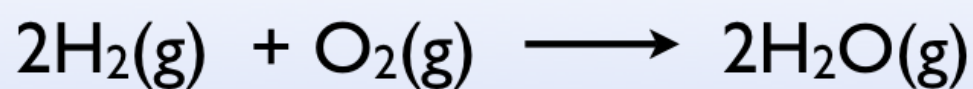


Steepest slope at the start

at equilibrium rate = 0 (reaction has “stopped”)



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



Rate of consumption
of H_2

reactant decrease

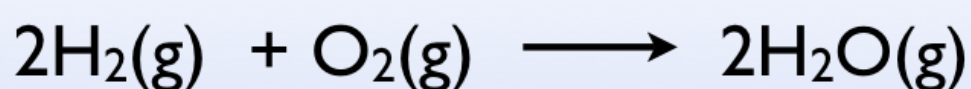
$$= - \frac{\Delta[\text{H}_2]}{\Delta t} = - \frac{d[\text{H}_2]}{dt}$$

Change

Rate of formation
of H_2O

products increase

$$= + \frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = + \frac{d[\text{H}_2\text{O}]}{dt}$$



Rate of
consumption
of H_2

=

2 x the Rate of
consumption
of O_2

=

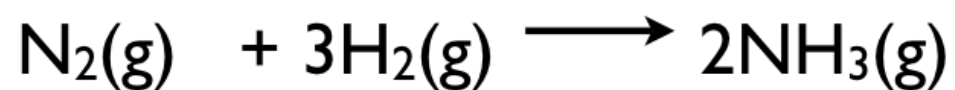
Rate of
formation
of H_2O

Faster

Slower

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

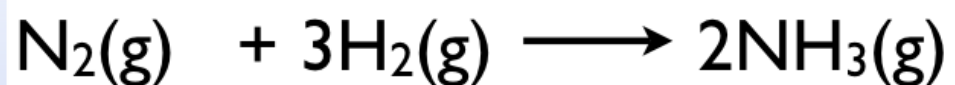
For this reactions



the rate of production of NH_3 is

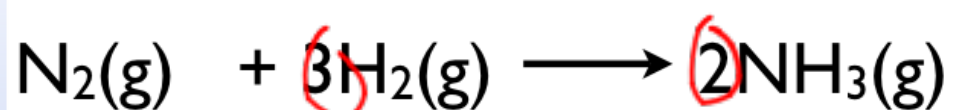
- A. 2 times the rates of consumption of H_2
- B. 1.5 times the rate of consumption of H_2
- C. $\frac{2}{3}$ times the rate of consumption of H_2

For this reactions



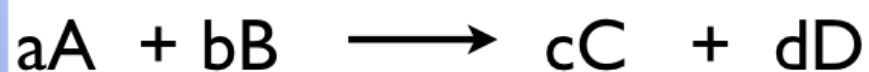
$$\text{Rate of Reaction} = -\frac{1}{1} \frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

For this reactions



$$\text{Rate of Reaction} = -\frac{1}{1} \frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt} = +\frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

Generic Reaction



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

How to get the rate? Do the experiment!

TABLE 15.1 Concentrations of Reactant and Products as a Function of Time for the Reaction
 $2\text{NO}_2(g) \longrightarrow 2\text{NO}(g) + \text{O}_2(g)$ (at 300°C)

Time (± 1 s)	Concentration (mol/L)		
	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

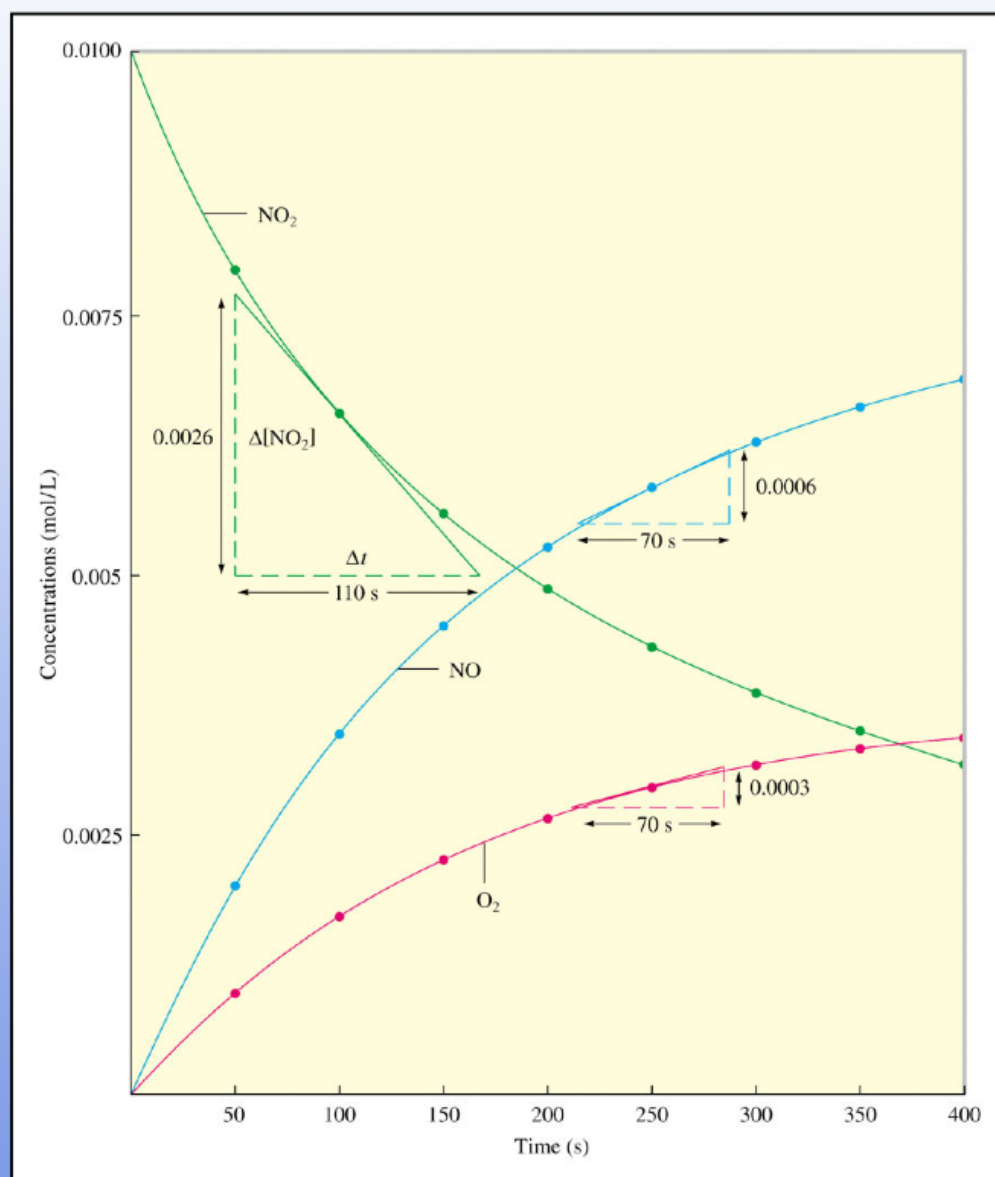
Characterizing rates

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?

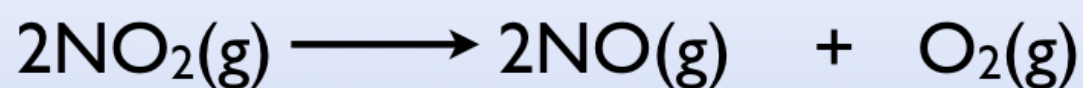
Rate is some function of the concentration
of the reactant molecules

What is the function?

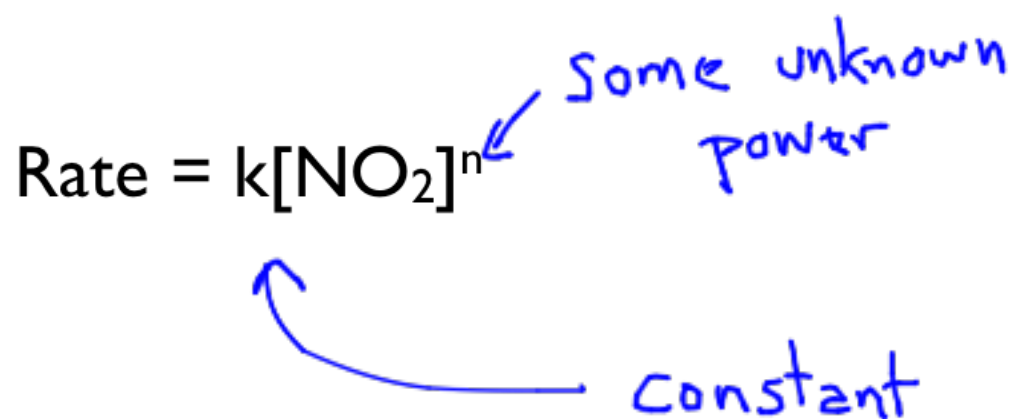
To **predict** the function we need to know
the **mechanism** (the individual step in the reaction)

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



We write the rate as a function of the **Reactant concentrations**



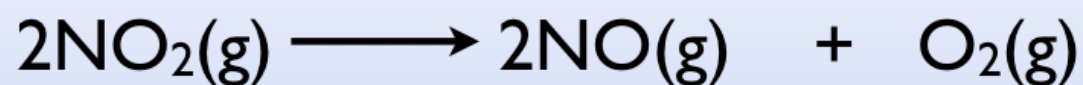
Rate = $k[\text{NO}_2]^n$

Some unknown power

constant

The image shows the rate equation $\text{Rate} = k[\text{NO}_2]^n$ with two handwritten blue annotations. One arrow points from the text "Some unknown power" to the exponent n . Another arrow points from the text "constant" to the rate constant k .

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



unknown constant

Rate = $k[\text{NO}_2]^n$

n typically 0, 1, or 2

unknown exponent

k is the "rate constant"

n is the "reaction order" with respect to NO_2

The grand overview of all of the kinetics



measure in experiment

figure out from data

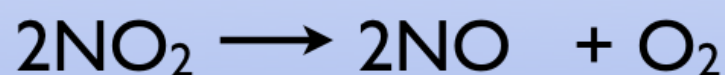
$$\frac{-\Delta[A]}{a\Delta t} = \frac{\Delta[C]}{c\Delta t} = \text{rate} = k[A]^x[B]^y$$

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 I looked at the data for this reaction and found

$$\text{rate} = k[\text{NO}_2]^2$$

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



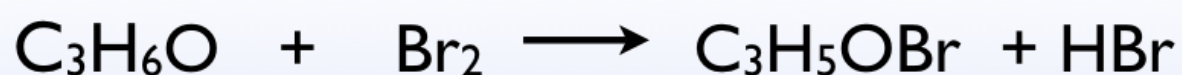
Experiment	$[\text{C}_3\text{H}_6\text{O}]_0$	$[\text{Br}_2]_0$	initial rate (M s^{-1})
1	0.1M	0.1M	1.64×10^{-5}
2	0.1M	0.2M	1.65×10^{-5}
3	0.2M	0.1M	3.29×10^{-5}



Experiment	$[\text{C}_3\text{H}_6\text{O}]_0$	$[\text{Br}_2]_0$	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}

- 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

Double $\text{Br}_2 \rightarrow$ Rate unchanged



Experiment	$[\text{C}_3\text{H}_6\text{O}]_0$	$[\text{Br}_2]_0$	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}

- 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

Double Acetone \rightarrow Rate Doubles



Experiment	$[\text{C}_3\text{H}_6\text{O}]_0$	$[\text{Br}_2]_0$	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}

A. $k = [\text{C}_3\text{H}_6\text{O}][\text{Br}_2]$

B. $k = [\text{C}_3\text{H}_6\text{O}]^2[\text{Br}_2]$

C. $k = [\text{C}_3\text{H}_6\text{O}]$

D. $k = [\text{Br}_2]$

E. $k = \text{constant}$

rate = $k [\text{C}_3\text{H}_6\text{O}]^1 [\text{Br}_2]^0$



Experiment	$[\text{C}_3\text{H}_6\text{O}]_0$	$[\text{Br}_2]_0$	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}

- 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

