Today

Kinetic Mechanisms
Why does a reaciton follow a particular rate law?
What is actually happening in the reaction?
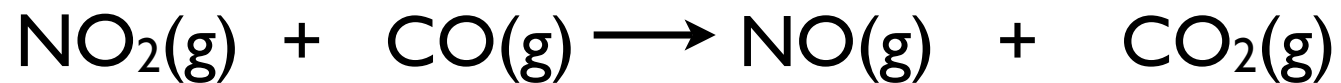
Transition State Theory
Arrhenius Theory

What is the rate law for the following reaction?

$$NO_2 + CO \longrightarrow NO + CO_2$$

A.   rate = $k[NO_2][CO]$

B.   rate = $k[NO][CO_2]$

C.   rate = $k[NO_2]^2[CO]$

D.   rate = $k[NO_2]^2$

E.   there is no way to know with our more information

What are the actual steps of the reaction?

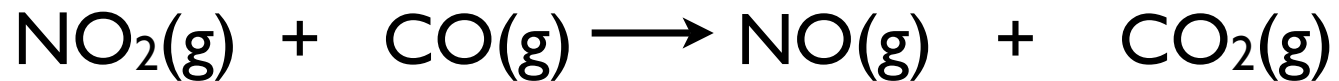$$NO_2(g) \;+\; CO(g) \longrightarrow NO(g) \;+\; CO_2(g)$$

One possibility

Step 1

NO$_2$ collides with CO and an oxygen atoms switches molecules to form NO and CO$_2$

What are the actual steps of the reaction?

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$
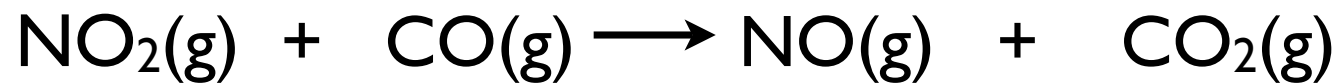
One possibility

Step 1

NO_2 collides with CO and an oxygen atoms switches molecules to form NO and CO_2

Step 1 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Overall $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

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What are the actual steps of the reaction?

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Another possibility

Step 1   Two NO_2 collide to form NO and NO_3

Step 2 NO_3 collides with CO to form NO_2 and CO_2

Step 1

Step 2

Overall $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

What are the actual steps of the reaction?

$$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$$

Another possibility

Step 1   Two NO_2 collide to form NO and NO_3

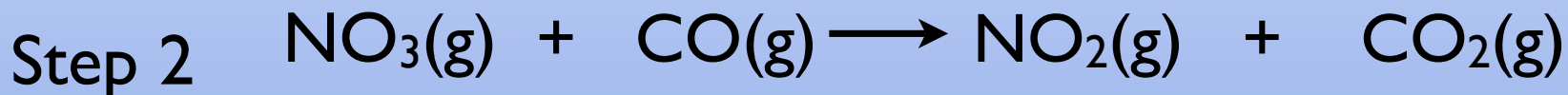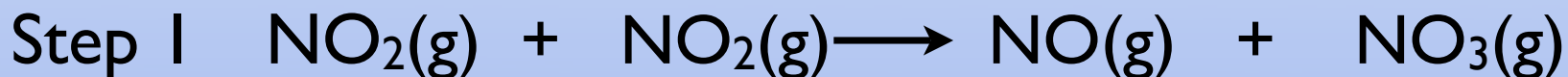Step 2 NO_3 collides with CO to form NO_2 and CO_2

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$

Overall $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

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Two mechanisms

Step 1 $NO_2(g)$ + $CO(g) \longrightarrow NO(g)$ + $CO_2(g)$

OR

Step 1 $NO_2(g)$ + $NO_2(g) \longrightarrow NO(g)$ + $NO_3(g)$

Step 2 $NO_3(g)$ + $CO(g) \longrightarrow NO_2(g)$ + $CO_2(g)$
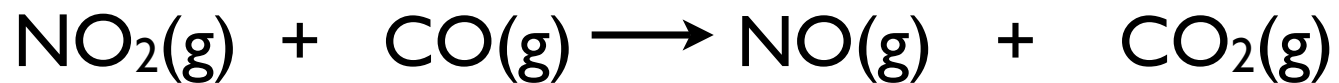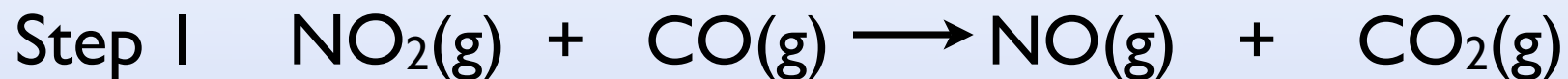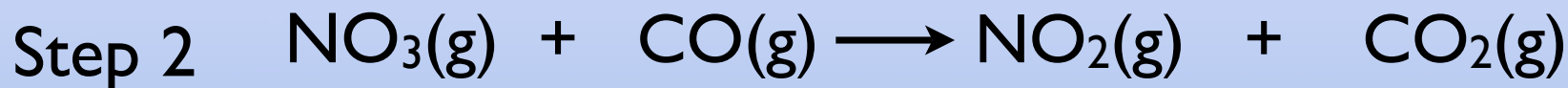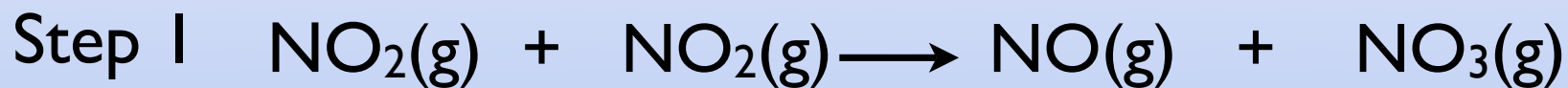
What do these two predict?

How do we predict the rate law from a mechanism?

First we need the rate laws for the elementary reactions (the steps in the reaction)

Second we need to know relative to each other which steps are fast and which steps are slow

We need to look at the individual steps
(elementary reactions)

Unimolecular Reaction

One reactant in the step
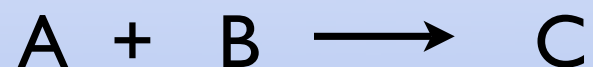
$$A \longrightarrow B$$

For this step, the rate will be first order in A

$$\text{rate} = k[A]$$

We need to look at the individual steps
(elementary reactions)

Bimolecular Reaction

Two reactants in the step

$$A + B \longrightarrow C$$

For this step, the rate will be first order in A
and first order in B

$$rate = k[A][B]$$

What is the rate for the following individual step?

$$NO_2 + NO_2 \longrightarrow NO + NO_3$$

A.   rate = $k[NO_2]$

B.   rate = $k[NO_2]^2$

C.   rate = $k[NO_2]^2[NO]$

D.   rate = $k[NO_2]^2/[NO][NO_3]$

E.   there is no way to know with our more information

What is the rate for the following individual step?

$$NO_2 + CO \longrightarrow NO + CO_2$$

A.   rate = $k[NO_2]$

B.   rate = $k[NO_2]^2$

C.   rate = $k[NO_2][CO]$

D.   rate = $k[CO]$

E.   rate = $k[CO_2][NO]$

What steps determine the overall rate or a reaction?

What determines the rate of people exiting a plane?

A. the rate at which people stand up

B. the rate at which people go through the door of the plane

C. the rate at which people walk up the jetway
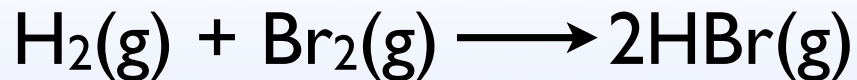
D. they all matter

Nonsense "real world" example

student + quiz + TA $\longrightarrow$ happy student with quiz turned in

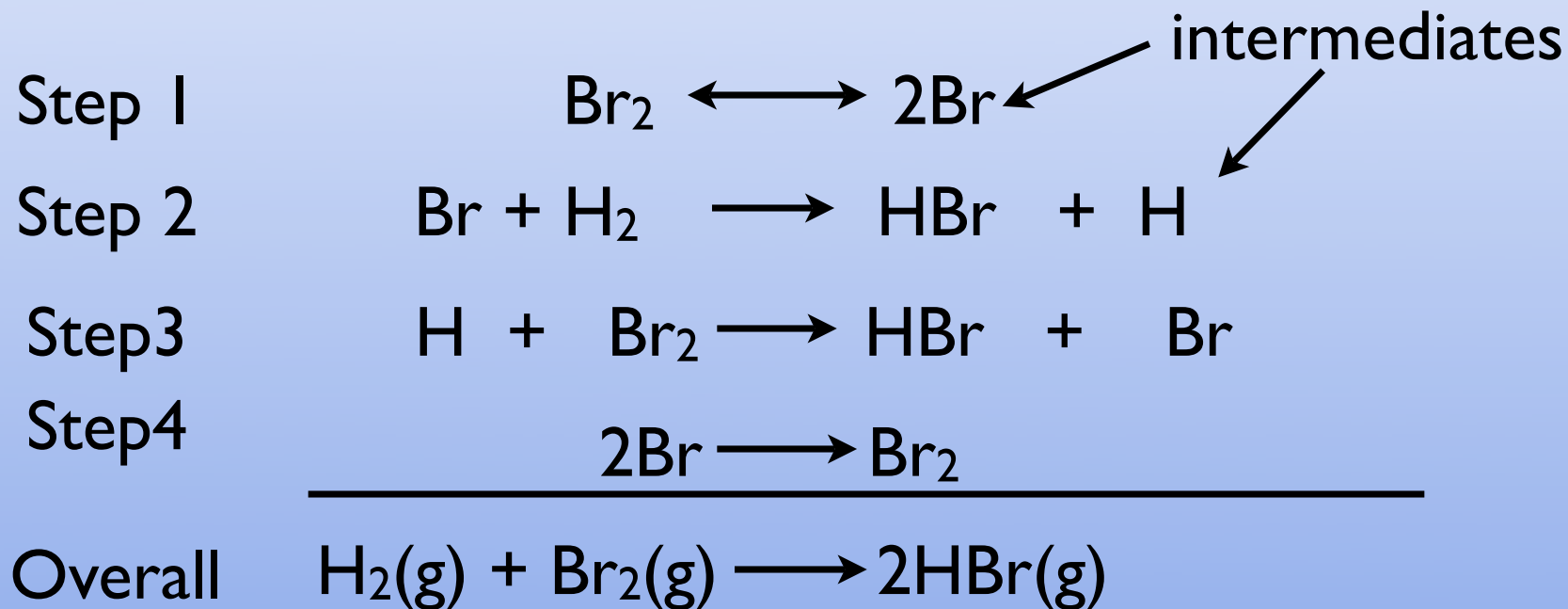student + TA + quiz $\longrightarrow$ student with quiz + TA

student with quiz $\longrightarrow$ student with completed quiz

student with completed quiz + TA $\longrightarrow$ happy student with quiz turned in

What controls the rate of this reaction?

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$$

What actually happens?
Does a H_2 and a Br_2 molecule collide and react?
Does something else happen?

intermediates

Step 1 $Br_2 \longleftrightarrow 2Br$

Step 2 $Br + H_2 \longrightarrow HBr + H$

Step3 $H + Br_2 \longrightarrow HBr + Br$

Step4 $2Br \longrightarrow Br_2$

Overall $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$

Which Step Matters?

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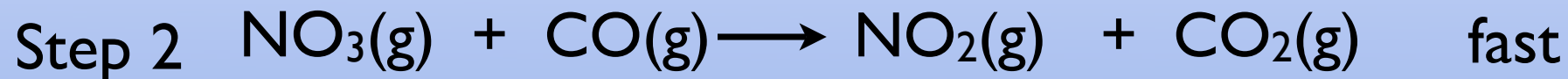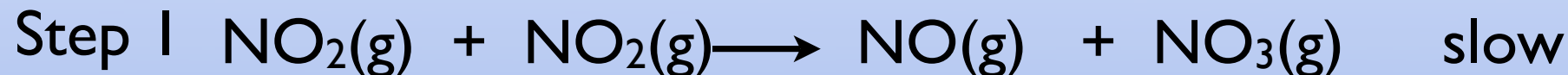
We can simplify things by taking an extreme view.

The only things that matters is the slowest step
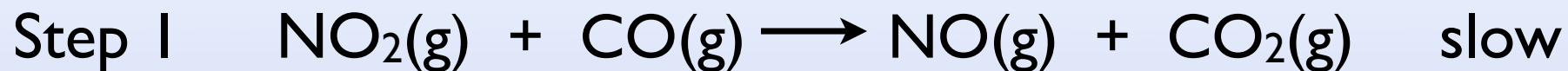
This is called the rate determining step

Two mechanisms

Step 1 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ slow

OR

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ slow

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ fast

Two mechanisms

Step 1 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ slow

$$rate = k[NO_2][CO]$$

OR

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ slow

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ fast
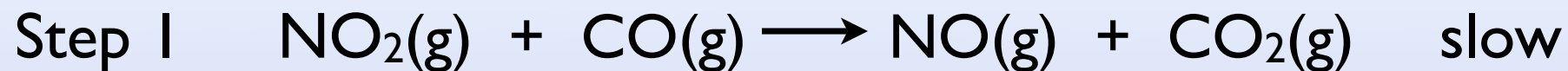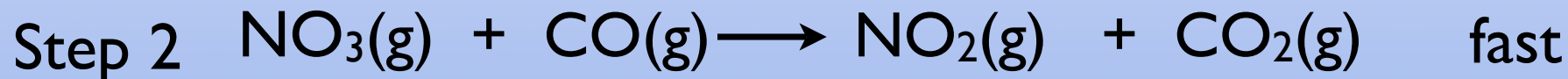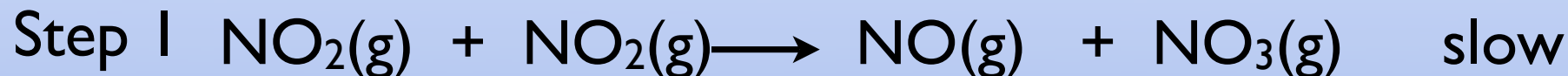
$$rate = k[NO_2]^2$$

Two mechanisms

Step 1 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ slow

$$rate = k[NO_2][CO]$$

OR

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ slow

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ fast
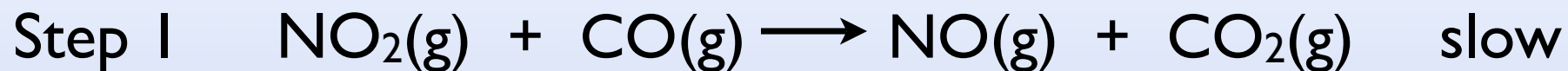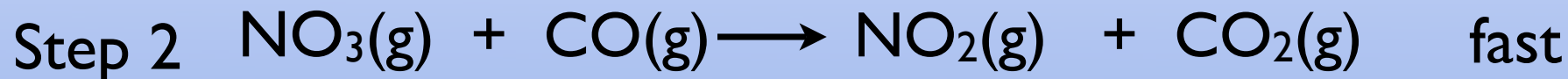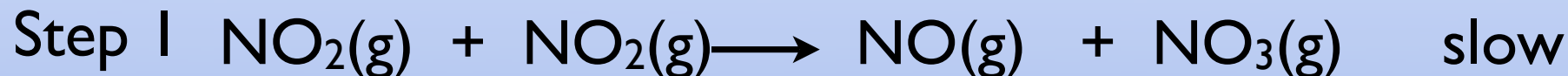
$$rate = k[NO_2]^2$$

What is the rate for the following mechanism?

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ fast

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ slow

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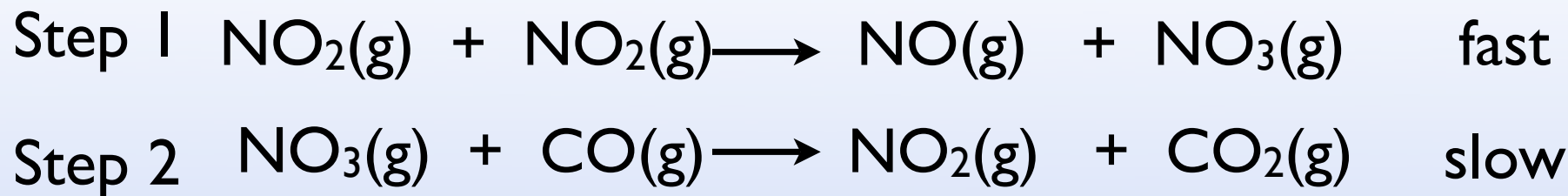
A.   rate = $k_1[NO_2]$

B.   rate = $k_1[NO_2]^2$

C.   rate = $k_2[NO_3][CO]$

D.   rate = $k_1 k_2[NO_2]^2[NO_3][CO]$

E.   rate = $k_1[NO_2]^2 + k_2[NO_3][CO]$

Typically our rate law does not have anything chemical species that are not found in the overall reaction

Step 1 $NO_2(g) + NO_2(g) \longleftrightarrow NO(g) + NO_3(g)$ fast

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ slow
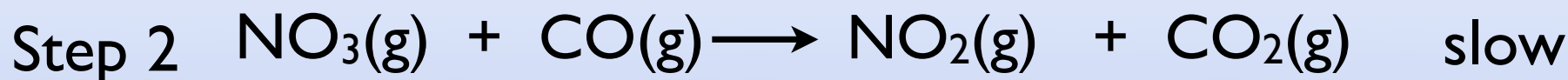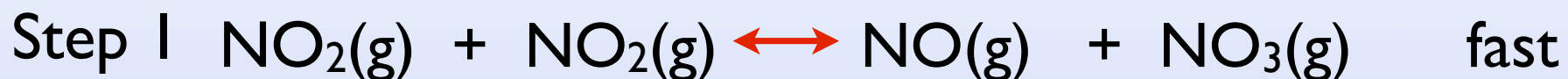
$$\text{rate} = k_2[NO_3][CO]$$

$$K = \frac{[NO_3][NO]}{[NO_2]^2} \qquad [NO_3] = \frac{K[NO_2]^2}{[NO]}$$

$$\text{rate} = k_2 \frac{K[NO_2]^2}{[NO]}[CO] = k\frac{[NO_2]^2[CO]}{[NO]}$$

What are the intermediates in this reaction?

$$Cl_2 \longleftrightarrow Cl + Cl \qquad \text{fast}$$

$$Cl + H_2S \longleftrightarrow HCl + HS \qquad \text{fast}$$

$$Cl + HS \longrightarrow HCl + S \qquad \text{slow}$$

$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

A.   Cl

B. H_2S

C.   HS

D.   A and B

E.   A,B, and C

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What is the predicted rate law for this reaction?

$$Cl_2 \longleftrightarrow Cl + Cl \qquad \text{fast}$$

$$Cl + H_2S \longleftrightarrow HCl + HS \qquad \text{fast}$$

$$Cl + HS \longrightarrow HCl + S \qquad \text{slow}$$

_____

$$Cl_2 + H_2S \longrightarrow 2HCl + S$$

A. rate = $k[Cl_2] + k[Cl][H_2S] + k[Cl][HS]$

B. rate = $k[Cl][HS]$

C. rate = $k[Cl_2][H_2S]/[HCl]$

D. rate = $k[Cl_2][H_2S]/[HCl]^2$

E. rate = $k[Cl_2][H_2S]/[HCl]^2[S]$

Connecting kinetics and equilibria
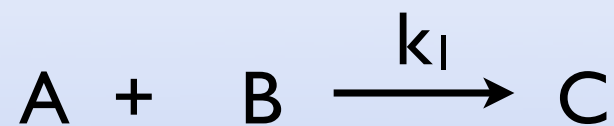
Elementary Reaction at Equilibrium

$$A \; + \; B \; \xrightarrow{\;k_1\;} \; C$$

$$A \; + \; B \; \xleftarrow{\;k_{-1}\;} \; C$$

Connecting kinetics and equilibria

Elementary Reaction at Equilibrium
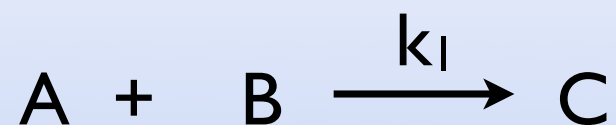
$$A \; + \; B \; \xrightarrow{\; k_1 \;} \; C$$
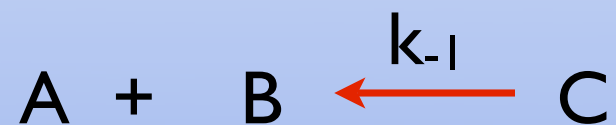
$$rate = k_1[A][B]$$

$$A \; + \; B \; \xleftarrow{\; k_{-1} \;} \; C$$

$$rate = k_{-1}[C]$$

At Equilibrium
forward rate = backward rate
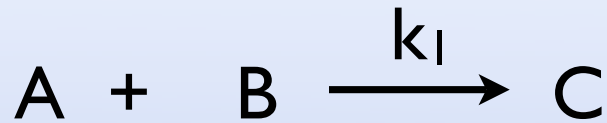
$$A + B \xrightarrow{k_1} C \qquad\qquad A + B \xleftarrow{k_{-1}} C$$
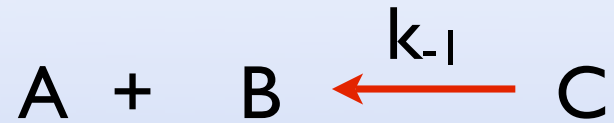
$$\text{rate} = k_1[A][B] \qquad\qquad \text{rate} = k_{-1}[C]$$

$$k_1[A][B] = k_{-1}[C]$$

$$K = \frac{[C]}{[A][B]} \qquad K = \frac{k_1}{k_{-1}}$$