Today

Kinetic Mechanisms

Why does a reaction follow a particular rate law?
What is actually happening in the reaction?

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

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

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

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

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

SLOWEST

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

Bimolec

rate = $k[NO_2][CO]$

OR

Step 1 $NO_2(g) + NO_2(g) \longrightarrow NO(g) + NO_3(g)$ k_1 slow

Step 2 $NO_3(g) + CO(g) \longrightarrow NO_2(g) + CO_2(g)$ k_2 fast

Bimolecular

rate = $k[NO_2]^2$

$k_2 >> k_1$

Two mechanisms

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

$$\text{rate} = k[NO_2][CO]$$

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

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

This is what is seen in experiment

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

A. rate = $k_1[NO_2]$

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

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

D. rate = $k_1k_2[NO_2]^2[NO_3][CO]$

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

Equil

Step 1 $NO_2(g) + NO_2(g) \leftrightarrow NO(g) + NO_3(g)$ 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?

$$Cl_2 \leftrightarrow Cl + Cl \quad \text{fast}$$

$$Cl + H_2S \leftrightarrow HCl + HS \quad \text{fast}$$

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

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

A. Cl

B. H_2S

C. HS

D. A and B

E. A,B, and C

What is the predicted rate law for this reaction?

$$Cl_2 \leftrightarrow Cl + Cl \quad \text{fast}$$

$$Cl + H_2S \leftrightarrow HCl + HS \quad \text{fast}$$

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

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

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

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

$$rate = k_1[A][B]$$

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

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

Connecting kinetics and equilibria

Elementary Reaction at Equilibrium

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

$$\text{rate} = k_1[A][B]$$

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

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

At Equilibrium

forward rate = backward rate

$$A + B \xrightarrow{k_1} C \qquad\qquad A + B \xleftarrow{k_{-1}} C$$

$$\text{rate} = k_1[A][B] \qquad = \qquad \text{rate} = k_{-1}[C]$$

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

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

$$\frac{\text{forward const.}}{\text{back const.}}$$

$$\text{rate} = k_3 [Cl][HS]$$

$$K_2 = \frac{[HS][HCl]}{[Cl][H_2S]} \qquad [HS] = \frac{K_2 [Cl][H_2S]}{[HCl]}$$

$$\text{rate} = \frac{k_3 [Cl] K_2 [Cl][H_2S]}{[HCl]}$$

$$K_1 = \frac{[Cl]^2}{[Cl_2]} \qquad [Cl]^2 = K_1 [Cl_2]$$

$$\text{rate} = \frac{k_3 K_2 [H_2S]}{[HCl]} K_1 [Cl_2]$$

$$= k \frac{[H_2S][Cl_2]}{[HCl]}$$

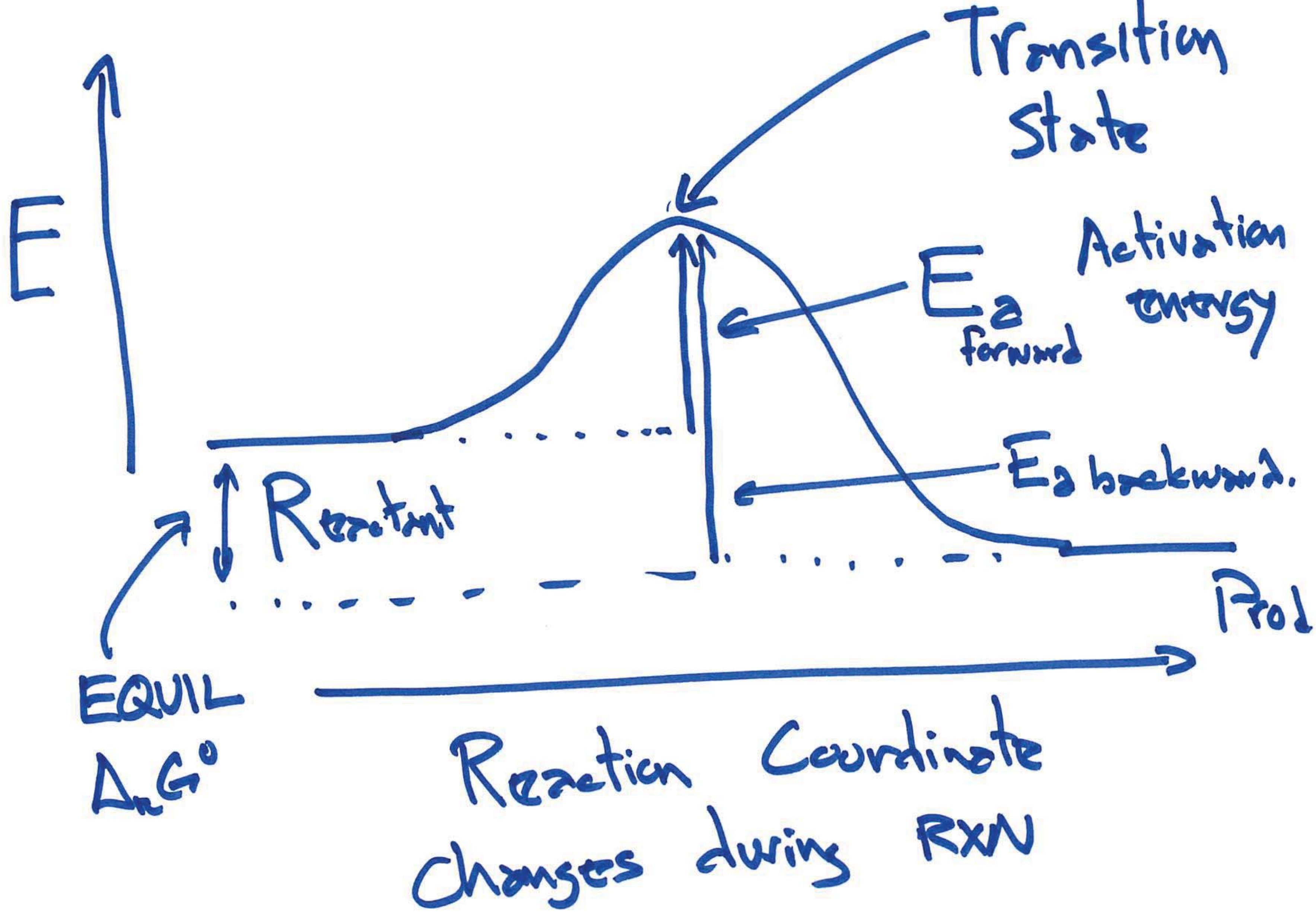
$$\text{rate} = k\,\frac{\cancel{[Cl]}\cancel{[HS]}\cancel{[Cl]}[H_2S][Cl_2]}{\cancel{[Cl]^2}[HCl]\cancel{[HS]}}$$

$$= k\,\frac{[H_2S][Cl_2]}{[HCl]}$$

K related to E_a

& T.

at higher T
molecules have more
K.E.


Transition State
E
Activation energy
Ea forward
Ea backward.
Reactant
Prod
EQUIL
ΔrG°
Reaction Coordinate
Changes during RXN