Reactions Mechanisms

17. **$2\,NO_2\,(g) \;+\; F_2\,(g) \;\rightarrow\; 2\,FNO_2\,(g)$** **rate = k $[NO_2][F_2]$**

a. Describe the collisions that would need to occur for this reaction to occur in a single step. How many molecules must collide? Explain why it is unlikely.

Three molecules would need collide simultaneously. Not likely.

b. What would the rate law be if the reaction occurred in one step? How does the experimentally determined rate law eliminates this possibility.

rate = k $[NO_2]^2[F_2]$ – in elementary steps the rate law is determined by the stoichiometry of the reaction as opposed to the overall rate law that MUST be determined experimentally.

c. The proposed mechanism includes two steps. Identify the rate limiting step. Justify your reasoning.

Elementary Step 1: $NO_2\,(g) + F_2\,(g) \rightarrow FNO_2\,(g) + F\,(g)$ (slow , higher E_a smaller k_1)

Elementary Step 2: $NO_2\,(g) + F\,(g) \rightarrow FNO_2\,(g)$ (fast , lower E_a larger k_2)

The rate limiting step is the slow step, since the reaction can only go as fast as the slowest step.

b. Explain how the proposed mechanism is consistent with the experimental rate law.

Elementary Step 1: $NO_2\,(g) + F_2\,(g) \rightarrow FNO_2\,(g) + F\,(g)$ rate = k $[NO_2][F_2]$

(slow , E_a smaller - k_1) NO_2 must collide with F_2 in a single collision

Elementary Step 2: $NO_2\,(g) + F\,(g) \rightarrow FNO_2\,(g)$ rate = k $[NO_2][F]$

(fast , E_a larger - k_2) NO_2 must collide with F in a single collision

The steps add up to the overall reaction since the F cancels out as an intermediate.

The rate limiting step shows a rate law that is consistent with the experimental determined rate law

e. Explain why the rate limiting step has a greater activation energy, E_a and lower rate constant, k.

Higher activation energy – will require more energy in order for a collision to be effective thus a smaller fraction of collisions will be effective

18. The Raschig reaction produces the industrially important reducing agent hydrazine (N_2H_4), from NH_3 and OCl^- in a basic aqueous solution

Step 1:	Fast	$NH_3\,(aq) + OCl^-\,(aq) \rightarrow \cancel{NH_2Cl}\,(aq) + \cancel{OH^-}\,(aq)$
Step 2:	Slow	$\cancel{NH_2Cl}\,(aq) + NH_3\,(aq) \rightarrow \cancel{N_2H_5^+}\,(aq) + Cl^-(aq)$
Step 3:	Fast	$\cancel{N_2H_5^+}(aq) + \cancel{OH^-}\,(aq) \rightarrow N_2H_4\,(aq) + H_2O\,(l)$

a. What is the overall stoichiometric equation? Hint: combine the reactions and cross out intermediates.

$2\,NH_3\,(aq) + OCl^-\,(aq) \rightarrow N_2H_4\,(aq) + H_2O\,(l)$

b. Which step is the rate-limiting step? How did you pick this step from among the three?

Step 2 is the rate limiting step since it is the slow step
and reaction can only go as fast as the slowest step

c. Write the rate equation for the rate-limiting step.

Rate = k $[NH_2Cl][NH_3]$ for step 2

d. What reaction intermediates is included in the rate law for the slow step?

NH_2Cl created in step 1 and reacts in step 2

e. The overall rate law may not include an intermediate. Adjust the rate law for the slow step to replace the intermediate. This is the rate law for the overall reaction.

Rate law for step 1 = Rate = k $[NH_3][OCl^-]$ this must be substituted into the rate law for step 2 to get the overall NOT in terms of an intermediate

Rate = k $[NH_2Cl][NH_3]$ for step 2

Rate = k $[NH_3][OCl^-]$ for step 1 that creates intermediate

Put rate law for step 1 into rate law for step 2 putting in place of the NH_2Cl intermediate

Rate = k $[NH_3][OCl^-][NH_3]$

19. Hypochlorite ion undergoes self-oxidation to give chlorate and chloride ions.

$3\ ClO^-$ (aq) $\rightarrow$ ClO_3^- (aq) + $2\ Cl^-$ (aq)

It is thought the reaction occurs in two steps.

Step 1 ClO^- (aq) + ClO^- (aq) $\rightarrow$ ClO_2^- (aq) + Cl^- (aq) bim

Step 2 ClO_2^- (aq) + ClO^- (aq) $\rightarrow$ ClO_3^- (aq) + Cl^- (aq)

a. What is molecularity of each step? What is the rate equation for each step?

Step 1 ClO^- (aq) + ClO^- (aq) $\rightarrow$ ClO_2^- (aq) + Cl^- (aq) bimolecular – two molecules must collide

Rate = k $[ClO^-][ClO^-]$ or Rate = k $[ClO^-]^2$

Step 2 ClO_2^- (aq) + ClO^- (aq) $\rightarrow$ ClO_3^- (aq) + Cl^- (aq) bimolecular – two molecules must collide

Rate = k $[ClO_2^-][ClO^-]$ or Rate = k $[ClO^-]^2$

b. The rate law for the overall reaction is **rate = k $[ClO^-]^2$**. Identify the rate limiting step and justify your selection.

Since the overall rate law is consistent with the first step – the rate limiting step must be the first step. The reaction rate and therefore the rate law depends upon the slowest step since the reaction can no faster than the slowest step.

20. Nitric oxide is reduced by hydrogen to give water and nitrogen

2 NO (g) + $2\ H_2$ (g) $\rightarrow$ N_2 (g) + $2\ H_2O$(g)

It is thought the reaction occurs in three steps.

Step 1 2 NO (g) $\leftrightarrows$ N_2O_2 (g)

Step 2 N_2O_2 (g) + H_2 (g) $\rightarrow$ N_2O (g) + H_2O(g)

Step 3 N_2O (g) + H_2 (g) $\rightarrow$ N_2 (g) + H_2O(g)

a. Copy the equations for the three steps. Write the rate law for each elementary step next to the equation.

Step 1 2 NO (g) $\leftrightarrows$ N_2O_2 (g) rate = k$[NO]^2$

Step 2 N_2O_2 (g) + H_2 (g) $\rightarrow$ N_2O (g) + H_2O(g) rate = k$[N_2O_2][H_2]$

Step 3 N_2O (g) + H_2 (g) $\rightarrow$ N_2 (g) + H_2O(g) rate = k$[N_2O][H_2]$

b. Show how the three steps add up to the overall reaction.

Step 1 2 NO (g) $\leftrightarrows$ $\cancel{N_2O_2}$ (g)

Step 2 $\cancel{N_2O_2}$ (g) + H_2 (g) $\rightarrow$ $\cancel{N_2O}$ (g) + H_2O(g)

Step 3 $\cancel{N_2O}$ (g) + H_2 (g) $\rightarrow$ N_2 (g) + H_2O(g)

c. The rate law for the reaction is **rate = k $[NO]^2$**. Identify the rate limiting step and justify your selection.

rate = k $[NO]^2$ experimentally determined rate law

reaction can go only the slowest step – rate of reaction rate of slowest step

first step must be slowest since its rate law is consistent with the overall rate law

21. **NO_2 (g) + CO (g) $\rightarrow$ NO (g) + CO_2 (g)** **rate = k $[NO_2]^2$**

If the reaction were to occur in a single bimolecular step- what would the rate equation be?

Elementary Step 1: NO_2 (g) + NO_2 (g) $\rightarrow$ NO_3 (g) + NO (g)

Elementary Step 2: NO_3 (g) + CO (g) $\rightarrow$ NO_2 (g) + CO_2 (g)

a. Copy the steps to show how they add up to the overall reaction.

The NO3 is an intermediate – on both sides – that cancels out. Plus one of the NO2 cancels out leaving the overall reaction

Elementary Step 1: NO_2 (g) + $\cancel{NO_2}$ (g) $\rightarrow$ $\cancel{NO_3}$ (g) + NO (g)

Elementary Step 2: $\cancel{NO_3}$ (g) + CO (g) $\rightarrow$ $\cancel{NO_2}$ (g) + CO_2 (g)

b. Identify the rate limiting step. Justify your selection.
The rate law of an elementary step is consistent with stoichiometry, since elementary steps represent the actual collision of the molecules their concentrations directly impact the rate in the manner shown in the equation.

Rate law for elementary step 1 rate = $k[NO_2]^2$
$NO_2\ (g) + NO_2\ (g) \rightarrow NO_3\ (g) + NO\ (g)$

c. Use the reaction mechanism to explain why this reaction is zero order with respect to [CO].

Since CO does not appear in the reaction mechanism until after the rate determining step – the slow step, changing the concentration of the CO has no effect on the rate. The rate can only be as fast as the slowest step. The rate is not influenced by steps after that slowest step.

22. Nitrogen monoxide from jet engines reacts with ozone in the air to produce nitrogen dioxide and oxygen.
The experimental rate law is rate = $k\,[NO][O_3]$

a. Write the balanced equation for this reaction. $NO\ (g) + O_3\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$

b. Which of the following mechanisms is consistent with this rate law? Explain why you eliminated each of the others.

NO **(1)** $NO\ (g) + NO\ (g) \rightarrow N_2O_2\ (g)$ (slow) rate = $k\,[NO]^2$ This would not be consistent with experimental overall rate law, since the the rate would be second order for NO and zero order for O_3
$O_3\ (g) + N_2O_2\ (g) \rightarrow N_2O_3\ (g) + O_2\ (g)$ (fast)
$N_2O_3\ (g) \rightarrow NO\ (g) + NO_2\ (g)$ (fast)
The steps do actually add up and cancel out to yield the overall reaction.

NO **(2)** $NO\ (g) + NO_2\ (g) \rightarrow N\ (g) + O\ (g)$ (slow)
$O_3\ (g) + O\ (g) \rightarrow 2\ O_2(g)$ (fast)
$N\ (g) + O_2\ (g) \rightarrow NO_2\ (g)$ (fast)
The steps do NOT actually add up and cancel out to yield the overall reaction.

YES **(3)** $NO\ (g) + O_3\ (g) \rightarrow NO_3\ (g) + O\ (g)$ (slow) rate = $k[NO][O_3]$
Ozone must collide with NO in bimolecular collisions. The rate law for this elementary step is first order for both reactants and consistent with the overall experimentally determined rate.
$NO_3\ (g) + O\ (g) \rightarrow NO_2\ (g) + O_2\ (g)$ (fast)
The steps do actually add up and cancel out to yield the overall reaction. The NO3 and O are both reactive intermediates – produced and consumed within the reaction.

23. $2N_2O\ (g) \rightarrow 2\ N_2\ (g) + O_2\ (g)$ rate = $k\,[N_2O]$
A proposed mechanism
$N_2O\ (g) \rightarrow N_2\ (g) + O\ (g)$
$N_2O\ (g) + O\ (g) \rightarrow N_2\ (g) + O_2\ (g)$
Which of the two steps is the rate determining step? Since the experimentally determined overall rate law is first order for N2O the first step must be the rate limiting step.
What is the molecularity of the rate determining step? Unimolecular

24. $H_2O_2\ (aq) + 3I^-\ (aq) + 2H^+(aq) \rightarrow 2\ H_2O\ (l) + I_3^-\ (aq)$
A proposed mechanism
$H_2O_2\ (aq) + I^-\ (aq) + H^+(aq) \rightarrow H_2O\ (l) + HOI\ (aq)$ (slow)
$HOI\ (aq) + I^-\ (aq) + H^+(aq) \rightarrow H_2O\ (l) + I_2\ (aq)$ (fast)
$I^-\ (aq) + I_2\ (aq) \rightarrow I_3^-\ (aq)$ (fast)

If this mechanism is correct, what is the rate law for the overall reaction? rate = $k[H_2O_2][I^-][H^+]$
What is the molecularity of the rate determining step? Trimolecular - unusual

25. The iodine catalyzed decomposition of hydrogen peroxide.

A proposed mechanism

H_2O_2 (aq) + I^- (aq) → H_2O (l) + OI^- (aq) (slow)
H_2O_2 (aq) + OI^- (aq) → H_2O (l) + O_2 (g) + I^- (aq) (fast)

Write an equation for the overall reaction. I- is a catalyst – present as a reactant in the first step and reformed in the second step. OI- is an intermediate.

H_2O_2 (aq) → H_2O (l) + O_2 (g)

What is the rate law for the overall reaction?

Rate = $k[H_2O_2][I^-]$ I- the catalyst does appear in the rate law since the rate of catalyzed reaction will depend upon the concentration of catalyst.

26. The rate law for the reactions 2 NO (g) + Cl_2 (g) → 2 NOCl (g) is rate = $k[NO]^2[Cl_2]$

Show that the following mechanism is consistent with this rate law:

2 NO (g) ⇆ N_2O_2 (g) (fast) rate = $[NO]^2$
N_2O_2 (g) + Cl_2 (g) → 2 NOCl (g) (slow) rate = $k[N_2O_2][Cl_2]$

The rate determining step is the second step – the slow step limits the rate of the reaction. The rate law for the overall will be consistent with this slow step (rate = $k[N_2O_2][Cl_2]$) However an interemediate appears in ths rate law and must be replaced with the rate law that forms that intermediate (rate = $[NO]^2$). When $[N_2O_2]$ is replaced with rate = $[NO]^2$, we get an overall rate law of rate = $k[NO]^2[Cl_2]$

27. The following mechanism has been proposed for the reaction of NO and O_2 gases:

2 NO (g) ⇆ N_2O_2 (g) (fast)
N_2O_2 (g) + O_2 (g) → $2NO_2$ (g) (slow)

Write the overall equation and identify any intermediates that are present.

2 NO (g) + O_2 (g) → 2 NO_2 (g)
N_2O_2 – an intermediate prodcued in first step and consumed in second step.

Write the rate law for the overall reaction.

rate = $k[NO]^2[O_2]$ similar to question above