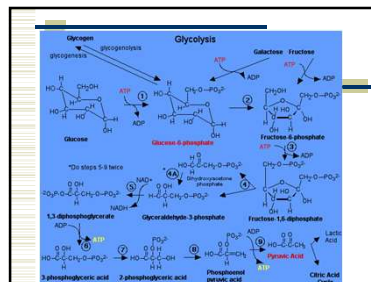


Reaction Mechanisms

Chemical Reactions

- Glycolysis
- $C_6H_{12}O_6 + 2 NAD^+ + 2 ADP + 2 P \rightarrow 2 CH_3COCO_2H + 2 ATP + 2 NADH + 2 H^+$
- This is the way we normally express the chemical reaction, however it ignores everything that happens in the reaction. It only gives your starting and end points.



Reaction Mechanism.

- A **reaction mechanism** is a series of simpler reactions that add up to the overall reaction.
- Mechanisms are influenced by elementary steps, molecularity, and reaction rate.

Elementary Reactions and Molecularity.

- Elementary reactions (steps)** are simple reactions that describe a single molecular event in a proposed reaction mechanism.
- Elementary steps are characterized by **molecularity**, the number of reactant particles involved in a proposed reaction mechanism.

Molecularity

- A **unimolecular reaction** is an elementary reaction that involves just one reactant species. This is a decomposition or rearrangement of that molecule.
- $A \rightarrow \text{products}$
- $N_2O_4 \rightarrow 2NO_2$

Molecularity

- A **bimolecular reaction** is an elementary reaction involving two reactant species.
- $A + A \rightarrow \text{products}$
- $A + B \rightarrow \text{products}$
- $H_2O + H_2O \rightarrow H_3O^+ + OH^-$
- $NO_2 + NO_2 \rightarrow NO_3 + NO$
- $H^+ + H_2O \rightarrow H_3O^+$
- $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

Molecularity

- Some **termolecular reactions** exist, but are rare because it is difficult for three things to collide at once with a proper orientation.
- $2 NO + O_2 \rightarrow 2 NO_2$

Rate Law Order

- The rate law of an **overall reaction** is **never** determined from the balanced equation, but through **experimentation**.
- The rate law for an **elementary step**, however, **can** be determined from the reaction stoichiometry.
- The reaction order equals the molecularity.

Molecularity	Elementary Step	Rate Law
Unimolecular	$A \rightarrow \text{products}$	Rate = $k[A]$
Bimolecular	$A + A \rightarrow \text{products}$	Rate = $k[A]^2$
	$A + B \rightarrow \text{products}$	Rate = $k[A][B]$

The Rate Limiting Step of a Reaction Mechanism.

- A reaction can only move as fast as its **slowest step**.
- A **rate-limiting (rate-determining) step** is the slowest step in a reaction mechanism and therefore is the step that limits the overall rate of the reaction.

Intermediates

- A **reaction intermediate** is a substance that is formed and used up during the overall reaction and therefore does not appear in the overall reaction.
- They are usually **unstable** relative to the reactants and products.
- They are molecules with normal bonds and are sometimes stable enough to be isolated.

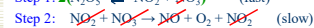
Constructing the Mechanism from the Rate Law.

- We can never fully prove that a particular mechanism is the way the chemical change actually occurs.
- We can only look for evidence that supports the idea.
- Regardless of the elementary steps that are proposed for the mechanism, they must obey three criteria.

3 criteria

1. The elementary steps must add up to the overall equation.
2. The mechanism must be consistent with the rate law.
3. The elementary steps must be physically reasonable (unimolecular or bimolecular).

Decomposition of N_2O_5



Now compare what is left to your initial equation

Mechanisms with a slow initial step.

- The overall rate law includes only species up to and including those in the rate-determining step.
- Each step in the mechanism has its own *transition state*.

Mechanisms with a fast initial step.

- Some mechanisms have a fast equilibrium step first that must be consumed by the slow step.
- In writing the rate law for the rate-determining step, keep in mind that an overall rate law must include only those substances in the overall equation.
- Write rate laws for both directions of the fast equilibrium step and for the slow step.

- Show that the slow step's rate law is equivalent to the overall rate law by expressing the intermediate concentration in terms reactant concentration; set the forward rate law of the fast, reversible step equal to the reverse rate law

- Solve for the concentration of the intermediate.
- Substitute the concentration of the intermediate into the rate law for the slow step to obtain the overall rate law.

The gas-phase reaction between H_2 and I_2

- $H_2(g) + I_2(g) \rightarrow 2HI(g)$
- $rate = k [H_2][I_2]$
- The accepted mechanism is
 1. $I_2(g) \rightleftharpoons 2I(g)$ [fast, reversible]
 2. $H_2(g) + I(g) \rightleftharpoons H_2I(g)$ [fast, reversible]
 3. $H_2I(g) + I(g) \rightarrow 2HI(g)$ [slow; rate limiting]
- Show that the mechanism is consistent with the rate law.

Answer

- First check the steps are reasonable (start and end with the same products)
- The experimentally determined rate law
- $rate = k [H_2][I_2]$
- Will have to be in agreement with the rate law proposed by these mechanisms.
- The orders are determined by the stoichiometry for steps ONLY, not for a reaction.

Cont.

- Step 3 is the rate determining step so it must be equivalent to the overall rate law
- $Rate_3 = k_3 [H_2][I]$
- Set 1 and 2 are reversible. Therefore at equilibrium their rate of forward and backwards reaction are equal.
- $Rate_{f1} = rate_{r1}$
- $k_{f1}[I_2] = k_{r1}[I]^2$
- $k_{f2}/k_{r2} [H_2][I] = [H_2I]$

Cont.

- $Rate_{f1} = rate_{r1}$
- $k_{f1} [I_2] = k_{r1} [I]^2$
- $k_{f1} [I_2] / k_{r1} = [I]^2$
- Substituting
- $Rate_3 = k_3 [H_2][I]$
- $Rate_3 = k_3 k_{f2} / k_{r2} [H_2][I]$
- $Rate_3 = k_3 k_{f2} / k_{r2} [H_2][I]^2$
- $Rate_3 = k_3 k_{f1} k_{f2} / k_{r1} k_{r2} [H_2][I_2]$

Finishing

- So assuming $k = k_3 k_{f1} k_{f2} / k_{r1} k_{r2}$
- $Rate_3 = k [H_2][I_2] = Rate$

formation of carbon tetrachloride from chloroform

- $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$
- $rate = k [CHCl_3][Cl_2]^{1/2}$
- The accepted mechanism is
 - $Cl_2(g) \rightleftharpoons 2Cl(g)$ [fast, reversible]
 - $CHCl_3(g) + Cl(g) \rightarrow HCl(g) + CCl_3(g)$ [slow]
 - $CCl_3(g) + Cl(g) \rightarrow CCl_4(g)$ [fast]
- Show that the mechanism is consistent with the rate law.

Nitrogen Dioxide and Fluorine

- $2NO_2 + F_2 \rightarrow 2NO_2F$
- Rate law = $k [NO_2][F_2]$
- Mechanism
 - $NO_2 + F_2 \rightarrow NO_2F + F$
 - $F + NO_2 \rightarrow NO_2F$
- Which step must be the rate determining step?

Questions 42-44 refer to the following information.

When free $Cl(g)$ atoms encounter $O_3(g)$ molecules in the upper atmosphere, the following reaction mechanism is proposed to occur.

$Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$	slow step
$ClO(g) + O_3(g) \rightarrow Cl(g) + 2O_2(g)$	fast step
$2O_3(g) \rightarrow 3O_2(g)$	overall reaction $\Delta H = -218 \text{ kJ/mol}_{rxn}$

42. Which of the following rate laws for the overall reaction corresponds to the proposed mechanism?

(A) $Rate = k[O_3]^2$
 (B) $Rate = k[Cl][O_3]$
 (C) $Rate = k[ClO][O_3]^2$
 (D) $Rate = k \frac{[O_3]^2}{[O_2]^2}$