Chemical Kinetics

DPP-3: Complex Reactions - Solutions

"One question. Full focus. No distraction. Repeat till victory."

TYPE-1: Complex Reactions – Mechanism & Rate Determining Step

Question 1

For an elementary process 2X + Y → Z + W, the molecularity is:

Explanation

Molecularity is defined as the number of reacting species (atoms, ions, or molecules) that participate in an elementary reaction.
For the elementary process: 2X + Y → Z + W
Count the total number of reactant molecules/species involved:

- 2 molecules of X
- 1 molecule of Y

Total = 2 + 1 = 3
Therefore, molecularity = 3

Approach

Molecularity is just counting heads! How many reactant species are bumping into each other in this single step? 2 X's and 1 Y = 3 total. It's like asking "how many people are needed for this dance?" – the answer is 3!

Answer

Answer: (3) 3

Question 2

The rate law for the single step reaction 2A + B → 2C, is given by:

Explanation

For an **elementary reaction** (single step), the rate law can be written directly from the stoichiometric coefficients.
Given: 2A + B → 2C (elementary/single step)
The rate law is:

$$\text{Rate} = K[A]^2[B]^1 = K[A]^2[B]$$

Key point: This rule ONLY applies to elementary reactions. For complex multi-step reactions, you cannot write the rate law from stoichiometry alone.

Approach

For elementary reactions, the exponents in the rate law match the coefficients in the balanced equation. It's a direct translation: 2A becomes $[A]^2$, and 1B becomes $[B]^1$. Think of it as "what you see is what you get" – but only for single-step reactions!

Answer

Answer: (2) Rate = $\mathbf{K[A]^2[B]}$

Question 3

Following mechanism has been proposed for a reaction 2A + B → D + E:

A + B → C + D (slow)

A + C → E (fast)

The rate law expression for the reaction is:

Explanation

For a multi-step reaction, the **rate-determining step (slowest step)** controls the overall rate.
Mechanism:

$$\text{Step 1 (slow):} \quad A + B \rightarrow C + D$$
$$\text{Step 2 (fast):} \quad A + C \rightarrow E$$

The slowest step is Step 1, so the overall rate is determined by this step.
For the slow step (elementary): A + B → C + D
Rate law from slow step:

$$r = K[A]^1[B]^1 = K[A][B]$$

This is the rate law for the overall reaction.

Approach

The slowest step is the bottleneck – like the narrowest part of a highway that controls traffic flow. Everything else might be fast, but you can only go as fast as the slowest step allows. Write the rate law using only the slow step's reactants!

Answer

Answer: (2) $r = K[\mathbf{A}][\mathbf{B}]$

Question 4

The chemical reaction $2O_3 \rightarrow 3O_2$ proceeds as follows:

$O_3 \rightleftharpoons O_2 + O$ (fast)

$O + O_3 \rightarrow 2O_2$ (slow)

The rate law expression should be:

Explanation

Step 1: Identify the slow step
The slow step is: $O + O_3 \rightarrow 2O_2$
Rate from slow step: $r = K_{slow}[O][O_3]$
Step 2: Eliminate intermediates
O (oxygen atom) is an intermediate – it doesn't appear in the overall reaction, so we must eliminate it using the fast equilibrium.
From the fast equilibrium: $O_3 \rightleftharpoons O_2 + O$
Equilibrium constant:

$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$

Solving for [O]:

$$[O] = \frac{K_{eq}[O_3]}{[O_2]}$$

Step 3: Substitute into rate law

$$r = K_{slow}[O][O_3]$$

$$r = K_{slow} \times \frac{K_{eq}[O_3]}{[O_2]} \times [O_3]$$

$$r = K_{slow} \times K_{eq} \times \frac{[O_3]^2}{[O_2]}$$

Let $K = K_{slow} \times K_{eq}$:

$$r = K\frac{[O_3]^2}{[O_2]} = K[O_3]^2[O_2]^{-1}$$

Approach

When the slow step contains an intermediate (like O atom here), you can't leave it in your final rate law. Use the fast equilibrium to "replace" the intermediate with actual reactants/products. It's like substitution in algebra – replace the unknown with something you know!

Answer

Answer: (2) $r = K[\mathbf{O}_3]^2[\mathbf{O}_2]^{-1}$

Question 5

The hypothetical reaction $A_2 + B_2 \rightarrow 2AB$ follows the mechanism:
$A_2 \rightleftharpoons A + A$ (fast)
$A + B_2 \rightarrow AB + B$ (slow)
$A + B \rightarrow AB$ (fast)
The order of the overall reaction is:

Explanation

Step 1: Write rate law from slow step
Slow step: $A + B_2 \rightarrow AB + B$
Rate $= K_{slow}[A][B_2]$
Step 2: Eliminate intermediate A
A is an intermediate (not in overall reaction). Use the fast equilibrium:
$A_2 \rightleftharpoons A + A$

$$K_{eq} = \frac{[A]^2}{[A_2]}$$

$$[A] = \sqrt{K_{eq}[A_2]} = K_{eq}^{1/2}[A_2]^{1/2}$$

Step 3: Substitute

$$r = K_{slow}[A][B_2]$$

$$r = K_{slow} \times K_{eq}^{1/2}[A_2]^{1/2} \times [B_2]$$

Let $K = K_{slow} \times K_{eq}^{1/2}$:

$$r = K[A_2]^{1/2}[B_2]^1$$

Overall order $= \frac{1}{2} + 1 = \frac{3}{2} = 1.5 = 1\frac{1}{2}$

Approach

The intermediate A comes from breaking A_2 into two A atoms (equilibrium), but the slow step only uses one A atom. So A has a "half relationship" with A_2 – hence the 1/2 power. Total order: 1/2 from A_2 + 1 from B_2 = 1.5!

Answer

Answer: (3) $1\frac{1}{2}$

Question 6

The reaction $2A + B \rightarrow P$, follows the mechanism:

$2A \rightleftharpoons A_2$ (fast)
$A_2 + B \rightarrow P$ (slow)
The order of the reaction is:

Explanation

Step 1: Write rate law from slow step
Slow step: $A_2 + B \rightarrow P$
Rate $= K_{slow}[A_2][B]$
Step 2: Eliminate intermediate A_2
A_2 is an intermediate. Use the fast equilibrium:
$2A \rightleftharpoons A_2$

$$K_{eq} = \frac{[A_2]}{[A]^2}$$

$$[A_2] = K_{eq}[A]^2$$

Step 3: Substitute

$$r = K_{slow}[A_2][B]$$
$$r = K_{slow} \times K_{eq}[A]^2 \times [B]$$

Let $K = K_{slow} \times K_{eq}$:

$$r = K[A]^2[B]^1$$

Overall order $= 2 + 1 = 3$

Approach

Two A's combine to form A_2 in equilibrium, so $[A_2]$ depends on $[A]^2$. When you substitute this into the rate law from the slow step, you get $[A]^2[B]$, giving total order = 3.

Answer

Answer: (2) 3

Question 7

For the reaction $2NO + Cl_2 \rightarrow 2NOCl$, the following mechanism has been proposed:
$NO + Cl_2 \rightarrow NOCl_2$ (fast)
$NOCl_2 + NO \rightarrow 2NOCl$ (slow)
The rate law for the reaction is:

Explanation

Step 1: Write rate law from slow step
Slow step: $NOCl_2 + NO \rightarrow 2NOCl$
Rate $= K_{slow}[NOCl_2][NO]$
Step 2: Eliminate intermediate $NOCl_2$
$NOCl_2$ is an intermediate. From the fast step:
$NO + Cl_2 \rightarrow NOCl_2$ (fast, but not at equilibrium)
Wait – this is NOT shown as an equilibrium ($\rightleftharpoons$), it's shown as a one-way arrow. However, since it's labeled "fast," we typically treat fast steps before the slow step as being at quasi-equilibrium.
Assuming equilibrium: $NO + Cl_2 \rightleftharpoons NOCl_2$

$$K_{eq} = \frac{[NOCl_2]}{[NO][Cl_2]}$$

$$[NOCl_2] = K_{eq}[NO][Cl_2]$$

Step 3: Substitute

$$r = K_{slow}[NOCl_2][NO]$$
$$r = K_{slow} \times K_{eq}[NO][Cl_2] \times [NO]$$
$$r = K_{slow} \times K_{eq} \times [NO]^2[Cl_2]$$

Let $K = K_{slow} \times K_{eq}$:

$$r = K[NO]^2[Cl_2]$$

Approach

$NOCl_2$ is formed from NO and Cl_2 in the fast step. When you substitute this intermediate out, you end up with $[NO]^2[Cl_2]$ – two NO's because one comes from the fast step and one from the slow step!

Answer

Answer: (1) Rate = $K[NO]^2[Cl_2]$

Question 8

In the sequence of reaction $A \xrightarrow{K_1} B \xrightarrow{K_2} C \xrightarrow{K_3} D$; where $K_3 > K_2 > K_1$, the rate determining step is:

Explanation

In a sequence of reactions, the **rate-determining step** is the **slowest step**.
The rate constant K is inversely related to the time taken for the reaction:

- **Large K** → fast reaction (small activation energy)
- **Small K** → slow reaction (large activation energy)

Given: $K_3 > K_2 > K_1$
This means:

- A → B has the smallest rate constant → SLOWEST
- B → C has medium rate constant → medium speed
- C → D has largest rate constant → FASTEST

Therefore, the rate-determining step is: **A → B**

Approach

Smallest rate constant = slowest step = bottleneck! Think of K as "how fast you can go" – the smallest K is like the slowest car in a convoy. Everyone has to wait for it, so it determines the overall speed.

Answer

Answer: (1) A → B

Question 9

The reaction mechanism for the reaction P → R is:

$P \xrightarrow{K_1} 2Q$ (fast); $2Q + P \xrightarrow{K_2} R$ (slow)

The rate law for the main reaction (P → R) is [where K_1 is an equilibrium constant]:

Explanation

Step 1: Write rate law from slow step
Slow step: 2Q + P → R
Rate = $K_2[Q]^2[P]$
Step 2: Eliminate intermediate Q
Q is an intermediate. From the fast equilibrium:
$P \rightleftharpoons 2Q$

$$K_1 = \frac{[Q]^2}{[P]}$$

$$[Q]^2 = K_1[P]$$

Step 3: Substitute

$$r = K_2[Q]^2[P]$$

$$r = K_2 \times K_1[P] \times [P]$$

$$r = K_1K_2[P]^2$$

Approach

P breaks into 2Q in equilibrium, so $[Q]^2$ is proportional to [P]. The slow step needs 2Q + P, so when you substitute, you get [P] × [P] = $[P]^2$. The overall rate depends on $[P]^2$!

Answer

Answer: (3) $K_1K_2[\mathbf{P}]^2$

Question 10

The reaction of ozone with oxygen atoms in the presence of chlorine atoms can occur by a two step process:

$O_3(g) + Cl\cdot(g) \rightarrow O_2(g) + ClO\cdot(g)$ $k_I = 5.2 \times 10^9$ L mol^{-1}s^{-1}

$ClO\cdot(g) + O\cdot(g) \rightarrow O_2(g) + Cl\cdot(g)$ $k_{II} = 2.6 \times 10^{10}$ L mol^{-1}s^{-1}

Find the closest rate constant for the overall reaction $O_3(g) + O\cdot(g) \rightarrow 2O_2(g)$:

Explanation

Let's analyze this mechanism:
Step 1: $O_3 + Cl\cdot \rightarrow O_2 + ClO\cdot$ ($k_I = 5.2 \times 10^9$)
Step 2: $ClO\cdot + O\cdot \rightarrow O_2 + Cl\cdot$ ($k_{II} = 2.6 \times 10^{10}$)
Overall: $O_3 + O\cdot \rightarrow 2O_2$ ($Cl\cdot$ is a catalyst)
Note that:

- $Cl\cdot$ appears as a reactant in Step 1 but is regenerated in Step 2 (catalyst)
- $ClO\cdot$ is an intermediate (formed in Step 1, consumed in Step 2)

Determining the rate-determining step:
Compare rate constants:

- $k_I = 5.2 \times 10^9$ L mol^{-1}s^{-1} (smaller)
- $k_{II} = 2.6 \times 10^{10}$ L mol^{-1}s^{-1} (larger, about 5 times bigger)

Since $k_I < k_{II}$, Step 1 is the slower step (rate-determining).
For a two-step mechanism where the first step is rate-determining, the overall rate constant is approximately equal to k_I.
Therefore: $k_{\text{overall}} \approx k_I = 5.2 \times 10^9$ L mol^{-1}s^{-1}

Approach

In a series of steps, the slowest step (smallest k) is the bottleneck. Since k_I is about 5 times smaller than k_{II}, Step 1 is slower. The overall reaction can only go as fast as the slowest step, so $k_{\text{overall}} \approx k_I$.

Answer

Answer: (2) 5.2×10^9 **L mol^{-1}s^{-1}**