16.1 Rate expression and reaction mechanism

Rate law: an equation that expresses the mathematical relationship between the initial rate of a chemical reaction and the concentration of the reactants.

Example:

For the reaction: A + B ---> product(s)
the rate law expression would be:

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

(where k is the rate constant)

Note: exponents x and y <u>must</u> be determined experimentally or derived from given data.

Example:

For the reaction: $A + B \dashrightarrow$ product(s)
the rate law expression would be:

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

(where k is the rate constant)

The order of reaction is said to be "x" with respect to substance A,
and "y" with respect to substance B.
The overall order of reaction is their sum, x+y.

Sample Problem **1**:

i. Determine the rate law for A + 3B---> products

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

Trial	Initial [A]	Initial [B]	Initial Rate (mol/L·s)	exponents	
				X	Y
1	0.10 M	0.10 M	0.040	2	1
2	0.20 M	0.10 M	0.160		
3	0.30 M	0.10 M	0.360		
4	0.20 M	0.20 M	0.320		

$$\text{rate} = k[A]^2[B]^1$$

ii. What is the order of the reaction with respect to… A? __ B? __

iii. What is the overall order of the reaction?

iv. Calculate the value for the rate constant, k (including correct units).

Sample Problem 2:
Determine the rate law for

$2I^- + S_4O_8^{2-} \longrightarrow$ Products $\quad$ rate = $k[I^-]^x[S_4O_8^{2-}]^y$

Trial	Initial $[I^-]$	Initial $[S_4O_8^{2-}]$	Initial Rate (mol/L·s)	exponents	
				X	Y
1	0.080 M	0.040 M	0.125	1	1
2	0.040 M	0.040 M	0.0625		
3	0.080 M	0.020 M	0.0625		

$$rate = k[I^-]^1[S_4O_8^{2-}]^1$$

ii. What is the order of the reaction with respect to… I^-? __ $S_4O_8^{2-}$? __

iii. What is the overall order of the reaction?

iv. Calculate the value for the rate constant, k (including correct units).

Practice:

1. Determine the units of k in each of the rate expressions below:

a. rate $=k[A]^2$

b. rate $=k[A]$

c. rate $=k[A]^0$

d. rate $=k[A][B]^2$

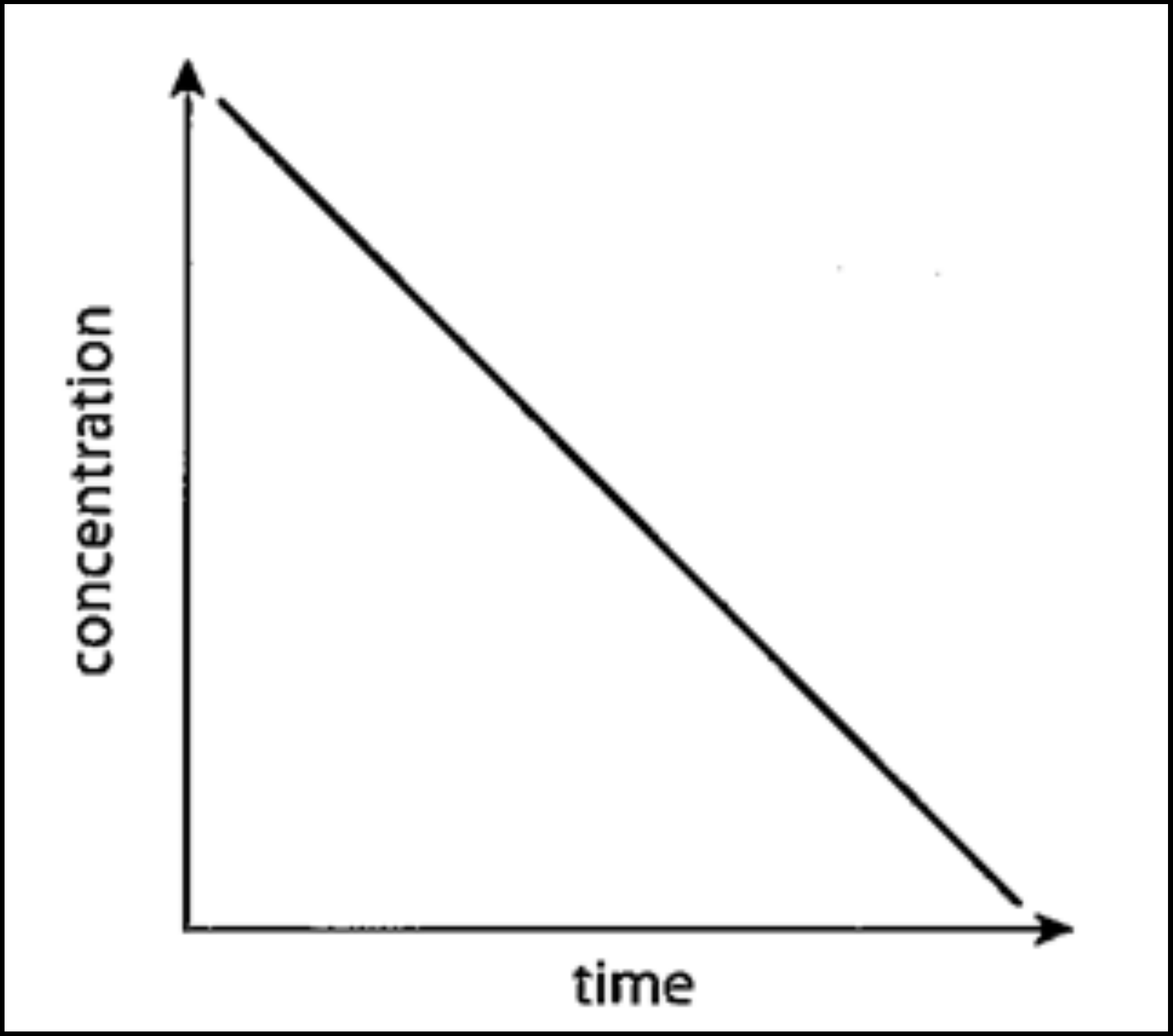
e. rate $=k[A][B]$

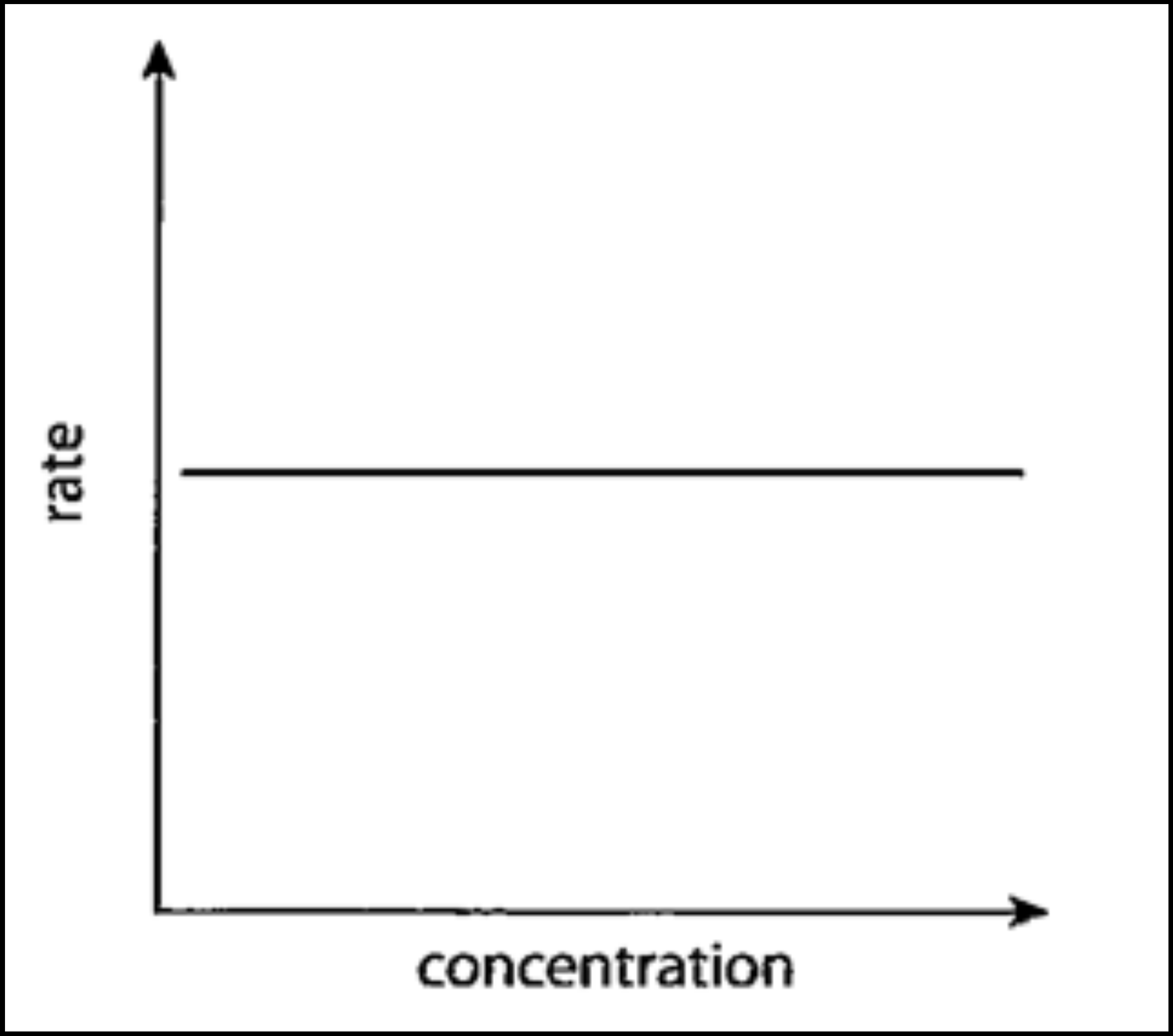
2. The reaction $2N_2O_5(g) \dashrightarrow 4NO_2(g) + O_2(g)$ has a value of $k=6.9\times10^{-4}\ s^{-1}$. Deduce the rate expression for this reaction.

Graphical representations for zero, first, and second-order reactions.

Zero-order Reactions (concentration has no affect on rate)

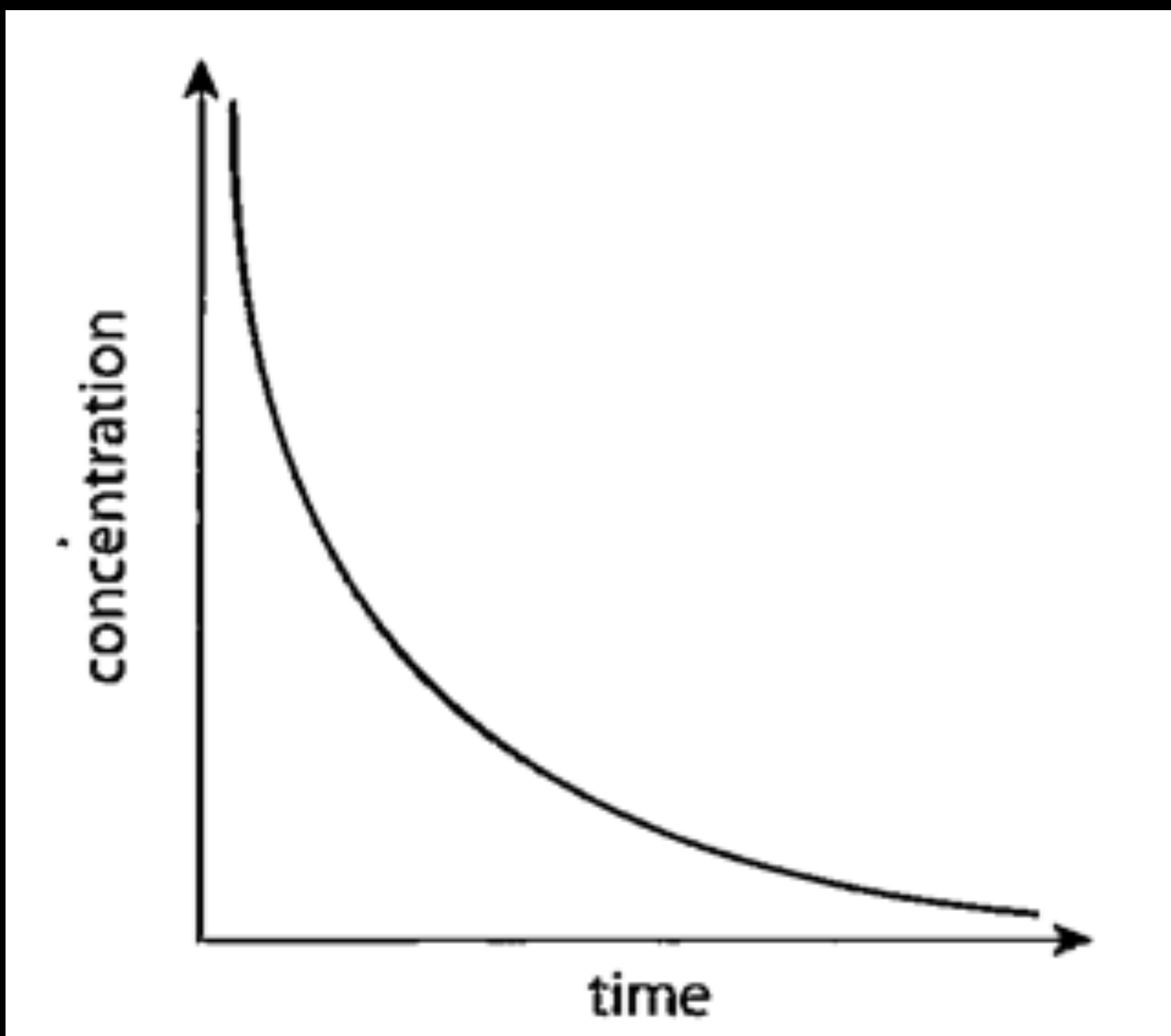
$$Rate = k[A]^{\circ} = k$$

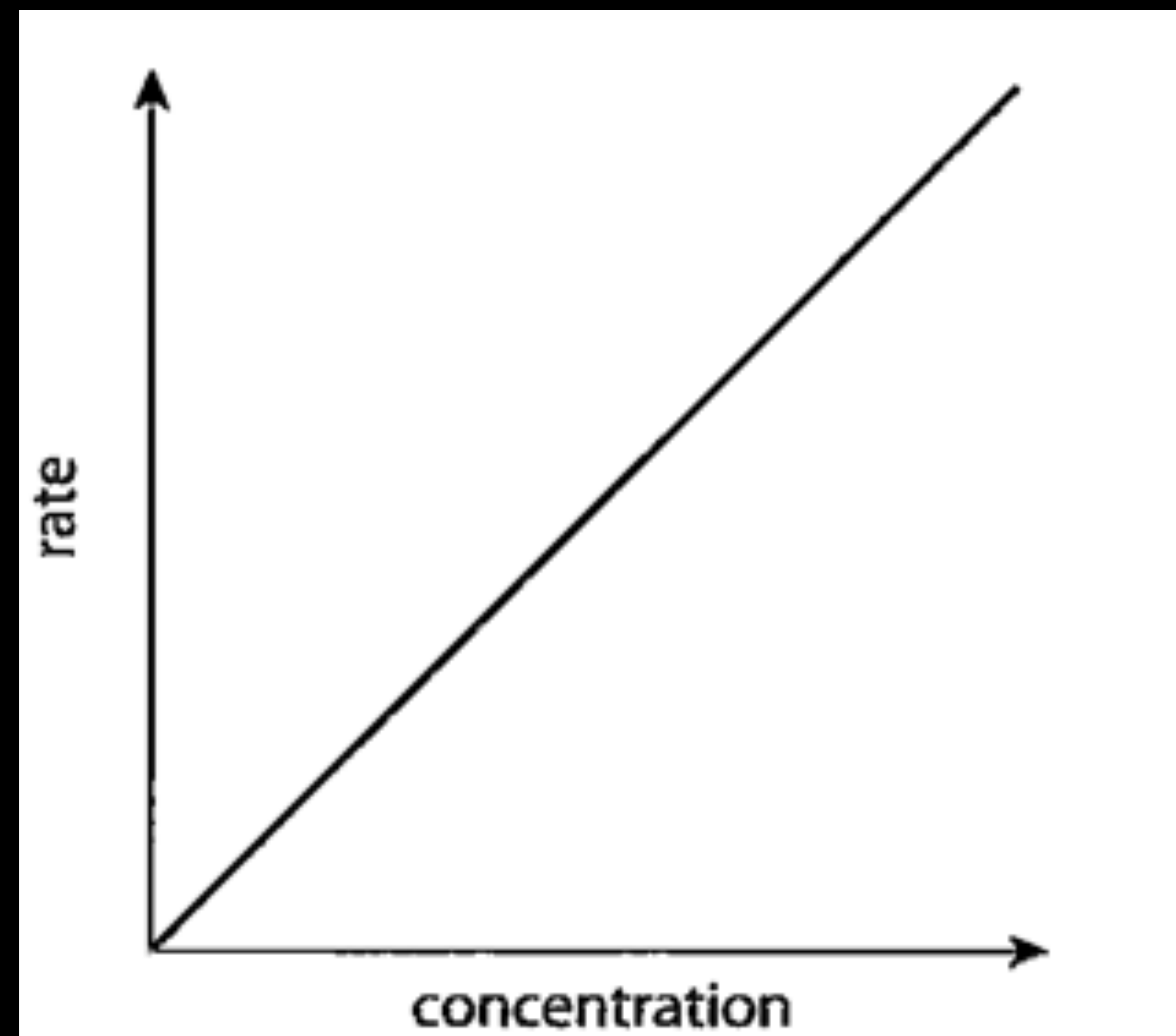




First-order Reactions
(concentration and rate are directly proportional)

Rate = k[A]

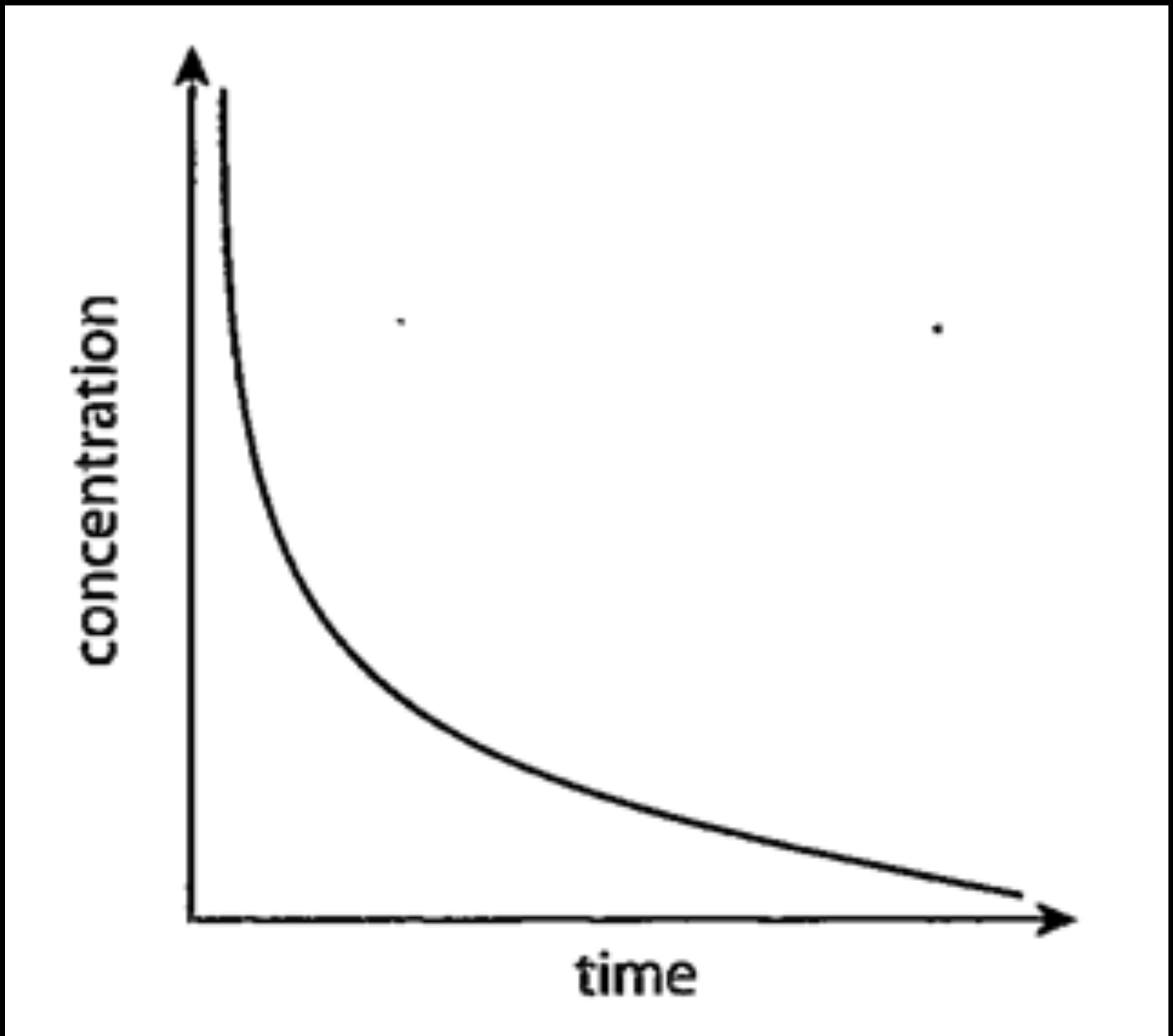


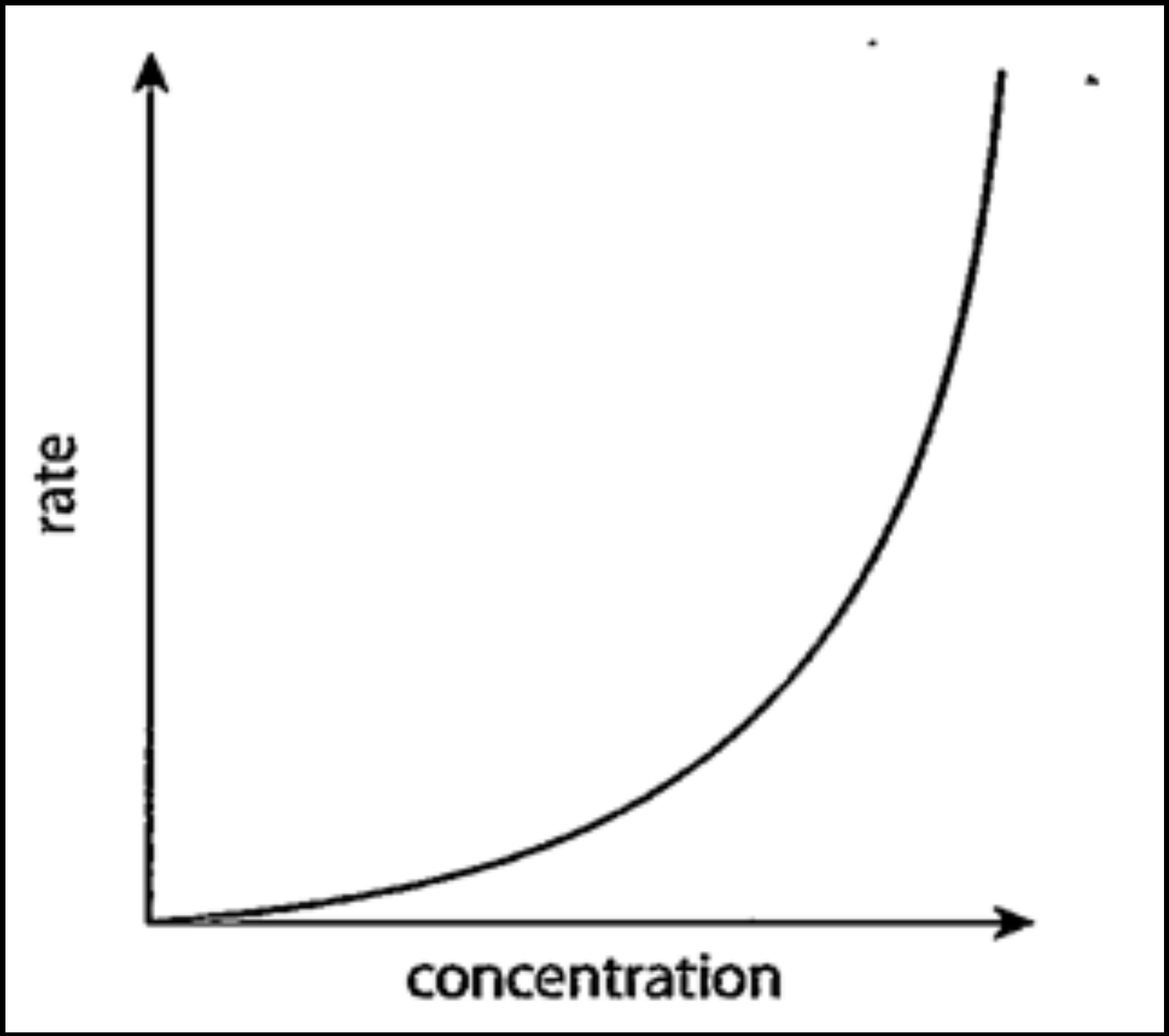


Second-order Reactions

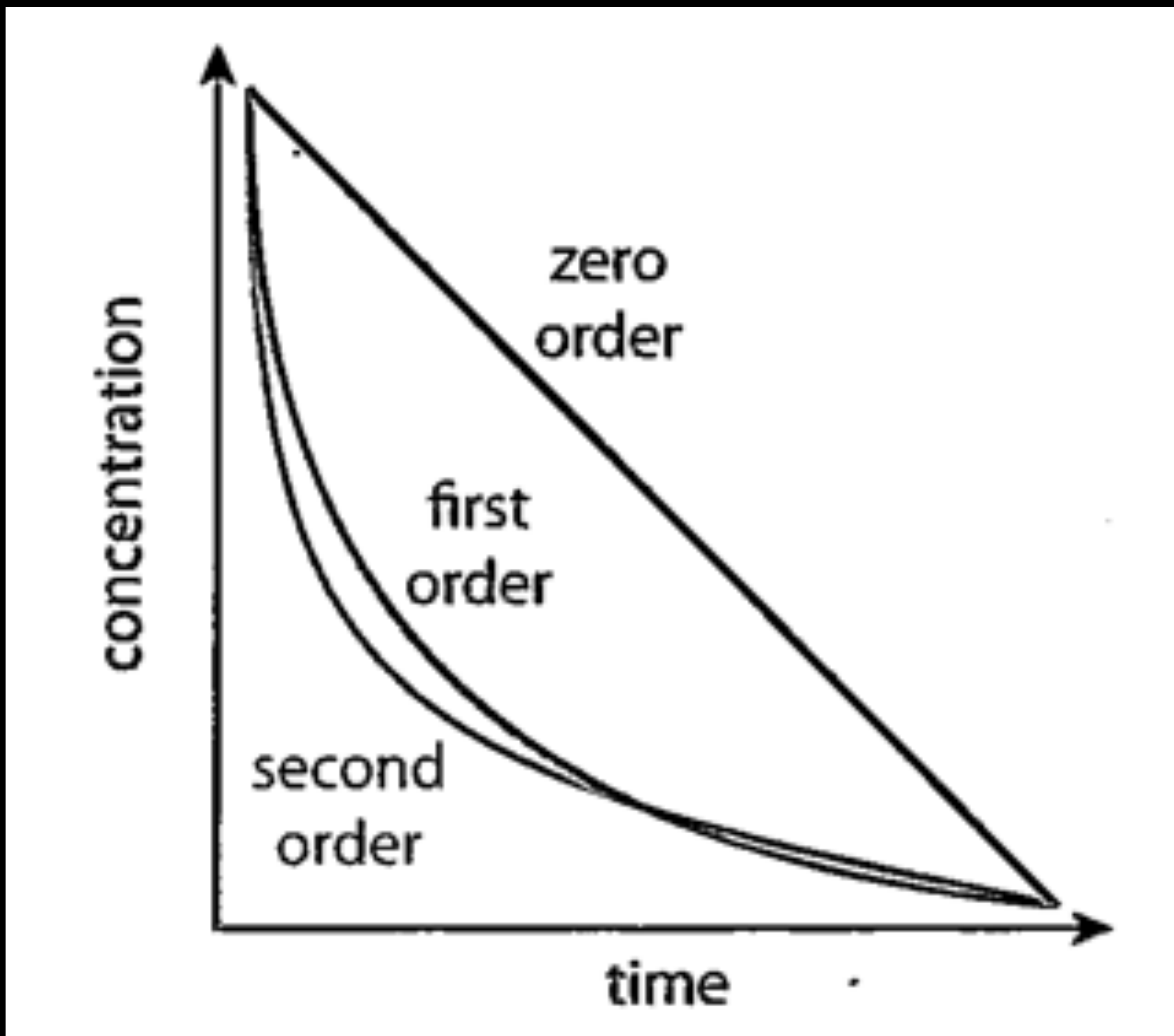
(rate is proportional to the square of the concentration)

$$\text{Rate} = k[A]^2$$

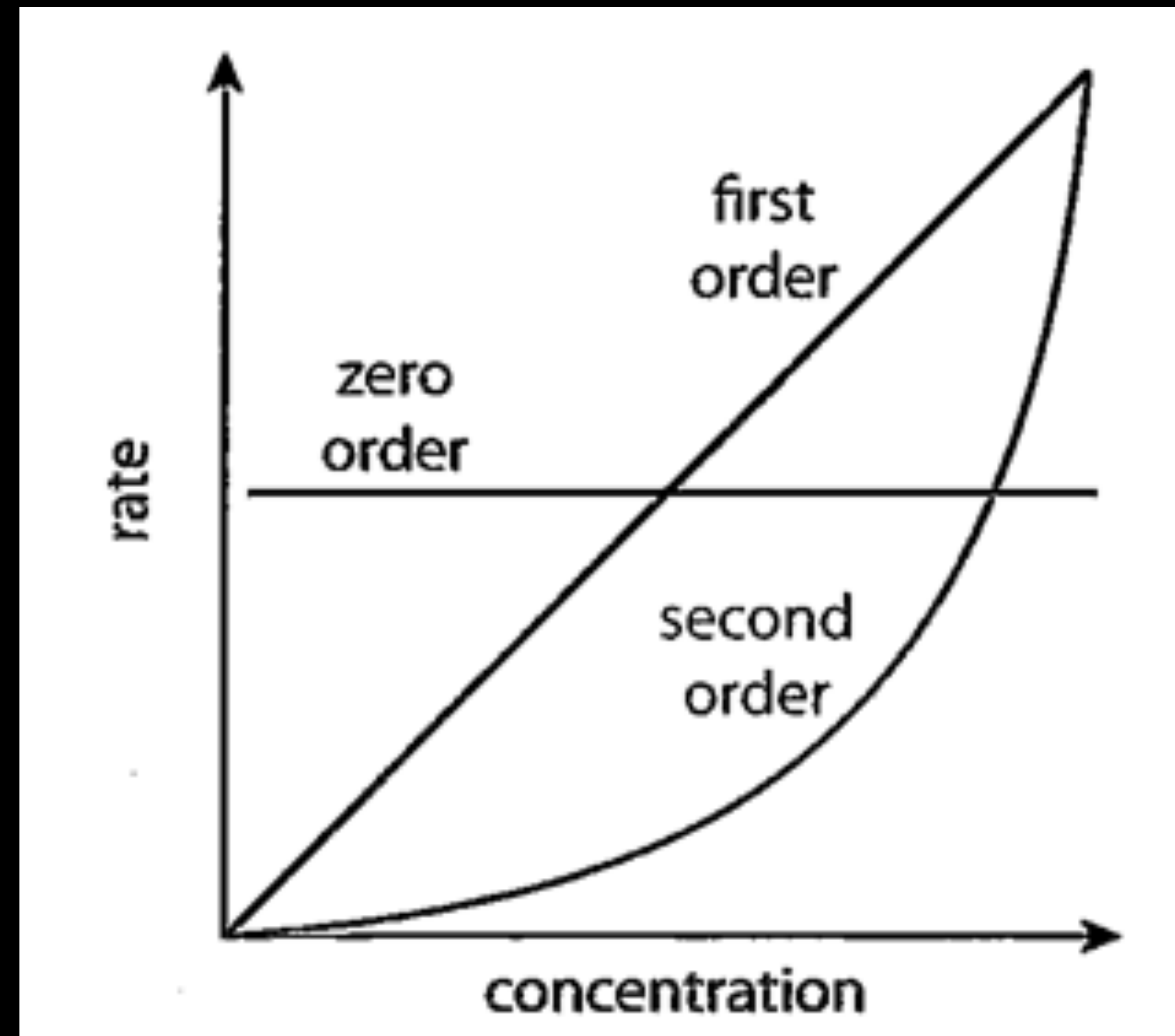




Summary



concentration
zero
order
first
order
second
order
time



rate
first
order
zero
order
second
order
concentration

Reaction Mechanism

Reaction mechanism:
The sequence of elementary steps which show how reactants are converted into products.

Elementary step:
A single step in a reaction usually involving a small number of particles that collide.

Example: the catalytic decomposition of ozone in the upper atmosphere, $2O_3 \text{--->} 3O_2$

This reaction is called a "complex" reaction, in that it actually takes place in three "elementary" steps:

Elementary step:	$Cl + O_3 \rightarrow O_2 + ClO$
Elementary step:	$O_3 \rightarrow O_2 + O$
Elementary step:	$ClO + O \rightarrow Cl + O_2$
Complex reaction	$2O_3 \rightarrow 3O_2$

Elementary step:	$Cl + O_3 \rightarrow O_2 + \cancel{ClO}$
Elementary step:	$O_3 \rightarrow O_2 + \cancel{O}$
Elementary step:	$\cancel{ClO} + \cancel{O} \rightarrow Cl + O_2$
Complex reaction	$2O_3 \rightarrow 3O_2$

ClO and O are intermediates.

whereas, Cl is a... catalyst!

Molecularity:
The number of reactant particles taking part in an elementary step.

1. Unimolecular: An elementary step that involves a single reactant particle.

2. Bimolecular: An elementary step that involves two reactant particles.

Elementary step:	$Cl + O_3 \rightarrow O_2 + ClO$
Elementary step:	$O_3 \rightarrow O_2 + O$
Elementary step:	$ClO + O \rightarrow Cl + O_2$
Complex reaction	$2O_3 \rightarrow 3O_2$

Step 2: unimolecular

Steps 1 and 3: bimolecular

Since no other reaction is involved for an elementary step, its rate law can be immediately determined from the coefficients:

Equation for rate-determining step	Molecularity	Rate law
$A \rightarrow$ products	unimolecular	rate = $k[A]$
$2A \rightarrow$ products	bimolecular	rate = $k[A]^2$
$A + B \rightarrow$ products	bimolecular	rate = $k[A][B]$

Example:

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

Step 1	$2NO \longrightarrow N_2O_2$	(fast)
Step 2	$N_2O_2 + H_2 \longrightarrow N_2O + H_2O$	(slow)
Step 3	$N_2O + H_2 \longrightarrow N_2 + H_2O$	(fast)

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

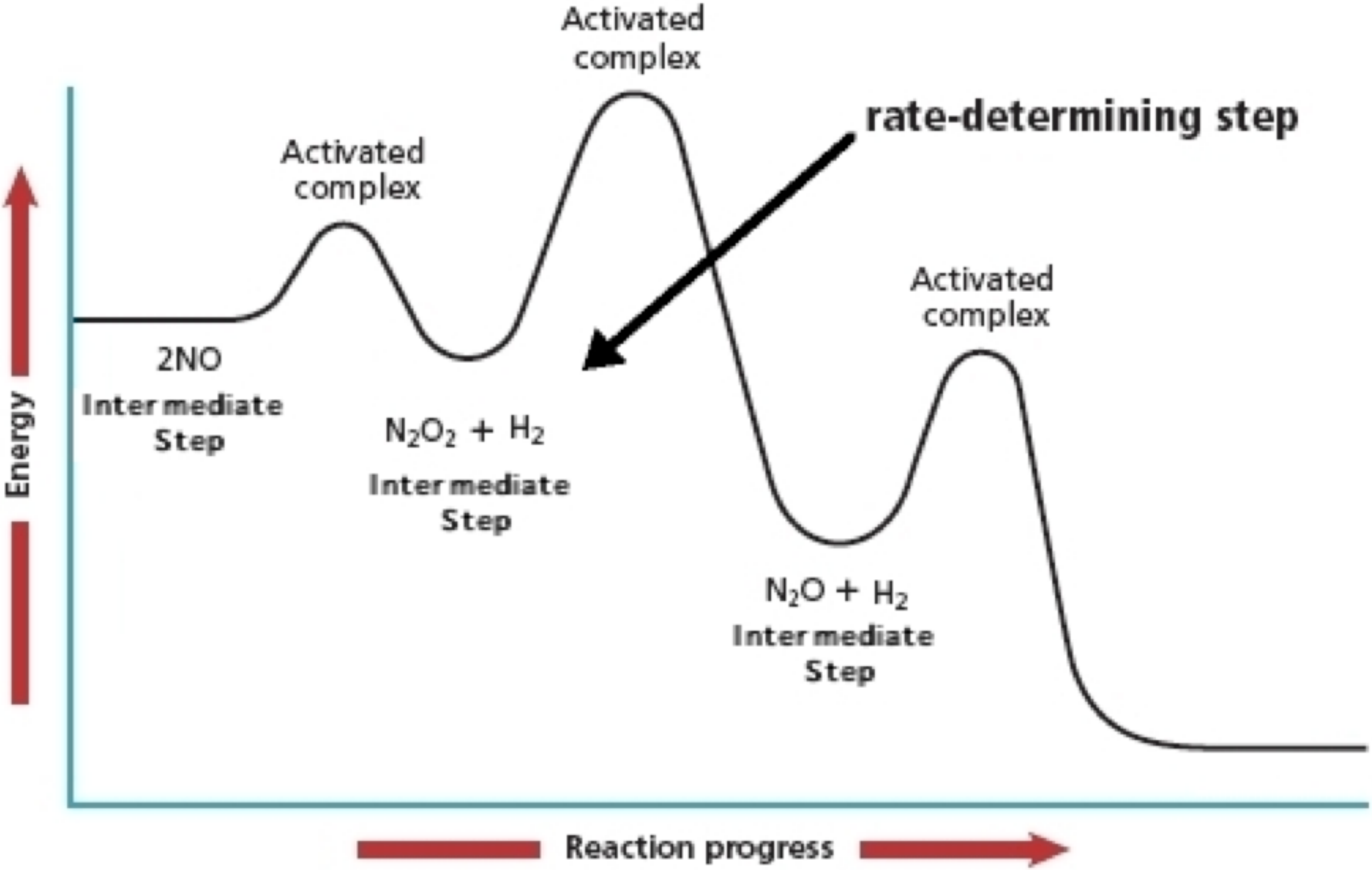
$$2NO \rightarrow N_2O_2 \quad \text{(fast)}$$

$$\boxed{N_2O_2 + H_2 \rightarrow N_2O + H_2O \quad \text{(slow)}}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O \quad \text{(fast)}$$

The slowest step is the "rate-determining step."

IB CHEMISTRY VIDEO REVIEW COMPLETE



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

Once the rate determining step is known, the rate expression can be found…

$$2NO \longrightarrow N_2O_2 \qquad \text{(fast)}$$
$$\boxed{N_2O_2 + H_2 \longrightarrow N_2O + H_2O \qquad \text{(slow)}}$$
$$N_2O + H_2 \longrightarrow N_2 + H_2O \qquad \text{(fast)}$$

for step 2: rate = $k[N_2O_2][H_2]$

But N_2O_2 is an intermediate from step 1…

therefore, the overall rate of the reaction is determined by only [NO] and $[H_2]$

The rate expression for the overall reaction is: rate = $k[NO]^2[H_2]$