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macro H2 CHEMISTRY

Kinetics

ORDERS OF REACTION

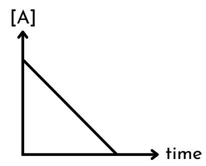
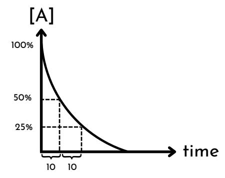
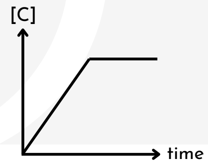
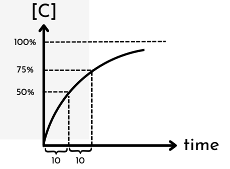
OBSERVATIONS	ORDER OF REACTION
When [A] is doubled, the rate of reaction doubles	Rate ∝ [A] Reaction is **first order** with respect to [A]
When [A] is doubled, the rate of reaction quadruples	Rate ∝ $[A]^2$ Reaction is **second order** with respect to [A]
When [A] is doubled, the rate of reaction does not change	Rate ∝ $[A]^0$ Reaction is **zero order** with respect to [A]

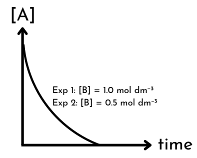
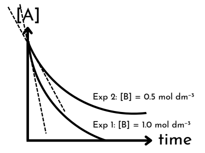
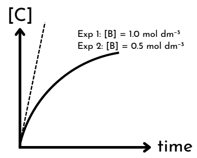
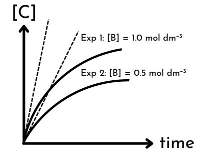
RATE EQUATION DEFINITIONS

TERM	DEFINITION
Rate equation	An experimentally-determined equation that relates the rate of reaction to the concentrations of the reactants raised to the appropriate orders.
Order of Reaction	The power on a reactant's concentration term in the rate equation. This power is determined experimentally.
Overall Order of Reaction	The sum of the individual orders.
k	The proportionality constant in the experimentally-determined rate equation.

CONTINUOUS METHOD QUESTIONS

Question: Consider the reaction 2A + B → C. A couple of experiments were conducted to study the reaction kinetics. B is kept in excess for all experiments. Find the order of reaction with respect to A and B.

If order of reaction w.r.t A is...	Zero Order	First Order
The [reactant]-time graph would look like...		
Answering technique	The [A] decreases **linearly** over time. This suggests that the decrease in [A] has no effect on the rate of reaction.	***find two half-lives**: 100% → 50% and 50% → 25%* Since, half-life is constant at 10 min, reaction is first order w.r.t. [A].
The [product]-time graph would look like...		
Answering technique	The [C] increases **linearly** over time. This suggests that the decrease in [A] has no effect on the rate of reaction.	*find final [C] (100%) + two half-lives: **0% → 50%** and **50% → 75%*** Since, half-life is constant at 10 min, reaction is first order w.r.t. [A].

If order of reaction w.r.t B is...	Zero Order	First Order
The [reactant]-time graph would look like...		
The [product]-time graph would look like...		
Answering technique	When the [B] halves, the initial rate of the reaction did not change. This suggests that the decrease in [B] has no effect on the rate of reaction.	*draw a **tangent at t=0** for each graph and calculate gradient* When [B] halves, the initial rate halves. Reaction is first order with respect to [B].

INITIAL RATE METHOD QUESTIONS

Consider the reaction 2A + B → C.
A couple of experiments were conducted to find the order of reaction with respect to A and B.

Exp	V of A /cm^3	V of B /cm^3	V of H_2O/cm^3	Initial rate
1	5	5	10	1.0
2	5	10	5	2.0
3	10	10	0	8.0

Why must water be added to experiments 1 and 2?

This is to ensure that **total volume remains constant.** When total volume is constant, the concentration of reagents is proportional to volume (**[A] ∝ V of A**. When volume doubles, concentration doubles).

What is the rate equation?

Comparing experiments 1 and 2, where [A] is constant, when [B] doubles, the initial rate doubles. Therefore, reaction is first order with respect to [B].

Comparing experiments 2 and 3, where [B] is constant, when [A] doubles, the initial rate increases by 4 times. Therefore, reaction is second order with respect to [A].

Therefore, rate = $k[A]^2[B]$

HALF-LIFE

is the time taken for the concentration of a reactant to decrease to half its initial value.

For an overall first - order reaction, half-life is

$t_{1/2}$ = ln 2 / k, where k is the rate constant

% remaining = $(1/2)^n$, where n is the number of half-lives

When 25 mg dm^{-3} melphalan is dissolved in blood, the decrease in its concentration has a constant half-life of 90 minutes. What is the concentration of melphalan in the blood six hours later?

n = 360 / 9 = 4

amount remaining = initial amount $(1/2)^n$

= 25 $(1/2)^4$

= 1.5625 mg dm^{-3}

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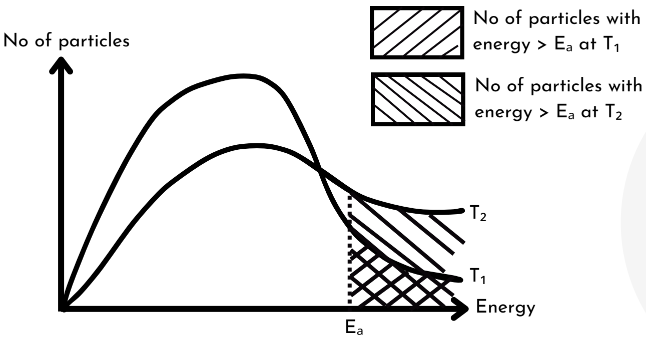
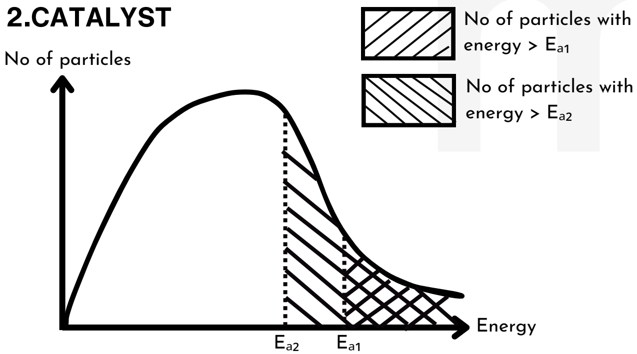
FACTORS AFFECTING RATE OF REACTION

1. TEMPERATURE



- Average kinetic energy of reactant particles increases when temperature increases T_1 to T_2
- More reactant particles possess energies greater than or equal to activation energy
- Frequency of effective collisions increases
- Rate of reaction increases

2.CATALYST



- In the presence of a catalyst, activation energy of the reaction lowers E_{a1} to E_{a2}
- More reactant particles possess energies greater than or equal to E_{a2}
- Frequency of effective collisions increases
- Rate of reaction increases

A. HOMOGENEOUS CATALYSIS

Explain the catalytic role of Fe^{2+} in the $I^-/S_2O_8^{2-}$ reaction

Step 1: $2Fe^{2+}(aq) + S_2O_8^{2-}(aq) \rightarrow 2Fe^{3+}(aq) + 2SO_4^{2-}(aq)$

Step 2: $2Fe^{3+}(aq) + 2I^-(aq) \rightarrow 2Fe^{2+}(aq) + I_2(aq)$

Overall equation: $2I^-(aq) + S_2O_8^{2-}(aq) \rightarrow I_2(aq) + 2SO_4^{2-}(aq)$

Explain how a catalytic converter removes harmful exhaust gases

$C_xH_y(g) + (x + y/4)\,O_2(g) \rightarrow xCO_2(g) + H_2O(g)$

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$

$2NO(g) + 2CO(g) \rightarrow N_2(g) + 2CO_2(g)$

Explain the role of oxides of nitrogen in the formation of acid rain

Step 1: $SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$

Step 2: $NO(g) + 1/2O_2(g) \rightarrow NO_2(g)$

Overall equation: $SO_2(g) + 1/2O_2(g) \rightarrow SO_3(g)$

Step 3: $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

B. HETEROGENEOUS CATALYSIS

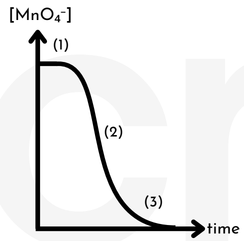
Explain the mode of action of Fe in catalysing the Haber Process.

PROCESS	EXPLANATION
Adsorption	N_2 and H_2 **diffuse** towards the surface and **adsorbs** onto the active sites of the catalyst by formation of weak attraction forces
At the active site	**BOWAF**: • Molecules are **brought closer(B)** together, and in the right **orientation (O)**. • N≡N and H-H covalent bonds within the molecules are **weakened (W)**. • **Activation energy(A)** of the reaction decreases • **Frequency(F)** of effective collision increases
Desorption	• NH_3 **desorbs** and **diffuses** away from the surface • The active sites are available for further reaction

C. AUTOCATALYSIS

Given that Mn^{2+} behaves as a catalyst, explain how the $[MnO_4^-]$ changes over time.

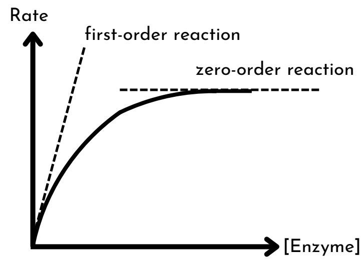
$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$



POINTS	EXPLANATION
(1)	Rate of reaction is slow as there are limited amounts of catalyst Mn^{2+} at the start.
(2)	Rate of reaction increases sharply as more catalyst Mn^{2+} is produced as reaction proceeds
(3)	Rate of reaction slows down as there are less reactants

D. BIOLOGICAL CATALYSTS

Explain how to concentration of enzyme affects the rate of a biologic reaction.



POINTS	EXPLANATION
At low [substrate]	• There are still many active sites available for substrate to bind to. • Rate of reaction increases proportionally with increasing substrate concentration. • Hence reaction is first order w.r.t the substrate.
At high [substrate]	• All active sites are filled. Substrates molecules have to wait to bind to the active sites. • Any further increase in substrate concentration will have no effect on the rate of reaction. • Hence reaction is zero order w.r.t the substrate.