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BIG PICTURE IDEAS

#1. A rate of a chemical reaction is measured as the change in amount of substances over time.

#2. Reaction rates are affected by four factors: temperature, concentration, catalyst and particle size.

#3. A rate law shows the relationship between the concentration of reactant species raised to some power and the rate.

#4. The graph of concentration versus time of reacting species is used to determine whether the order of a reaction is zeroth, first or second order.

#5. The rate law of a chemical reaction is inferred from the stoichiometry of the collision of particles for an elementary reaction.

#6. Collision theory states the rate of an elementary reaction is dependent on the energy and orientation of collisions.

#7. A reaction energy profile illustrates the energy involved in a reaction as it progresses over time.

#8. A series of steps for a chemical reaction is represented as a reaction mechanism.

KEY VOCAB

Reaction Rate	Concentration	First Order	Catalyst	Reaction Mechanisms
Rate Law	Surface Area	Second Order	Collision Theory	Slow Step
Order of Reaction	Temperature	Zeroth Order	Elementary Reaction	Integrated Rate Law

TOPIC 5.1- REACTION RATES

1. Use the chemical equation and the given scenarios below to complete the table. Place a ✔ in the box of the correct response.

$$2\,N_2O_5(g) \rightarrow 2\,N_2(g) + 5\,O_2(g) \qquad \Delta H_{rxn} > 0$$

Scenario	Increase in Rate of Reaction	Decrease in Rate of Reaction	Reaction Rate Unchanged
Increase in [N_2O_5]	✔		
Increase in pressure	✔		
Use of a catalyst	✔		
Lower the temperature		✔	
Increase the volume of the container		✔	
Decrease the pressure of N_2O_5		✔	
Add inert He gas			✔

For the same reaction above, it took 80. seconds for 1.00 M of N_2O_5 to decompose to 0.050 M. Calculate the following:

2. The rate of the consumption of N_2O_5? (1.00 M – 0.050 M) / (80. s) = 0.011875 M/s ≈ 0.012 M/s

3. The rate of production of O_2? 0.011875 M/s x (5 O_2 / 2 N_2O_5) = 0.02969 M/s ≈ 0.030 M/s

4. How does the rate of production of O_2 compare to the rate of consumption of N_2O_5? Explain. The rate of production of O_2 is 5/2 (or 2.5 times) as fast as the rate of consumption of N_2O_5. This is because of the stoichiometry of the reaction; 5 moles N_2 to 2 moles of N_2O_5.

TOPIC 5.2- INTRODUCTION TO RATE LAW

The initial rates of the reaction represented by the equation below were measured for different initial concentrations of BrO(g) and I_2(g).

$$\mathbf{2\,BrO(g) + I_2(g) \rightarrow 2\,IO(g) + Br_2(g)}$$

Experiment	[BrO] (*M*)	[I_2] (*M*)	Rate of Reaction (M/s)
1	0.01	0.01	5.0×10^{-4}
2	0.02	0.01	2.0×10^{-3}
3	0.01	0.02	1.0×10^{-3}
4	0.02	0.02	?

5. What is the order of the reaction with respect to BrO? Exp 1 & 2, Doubles BrO, Rate Quadruples. Second Order.

6. What is the order of the reaction with respect to I_2? Exp 1 and 3, Doubles I_2, Rate Doubles. First Order

7. Write the rate law for this reaction. Rate = $k[BrO]^2[I_2]$

8. What is the value of the rate constant, k, for this reaction? Include units. Rate = $k[BrO]^2[I_2]$, 5.0×10^{-4} M/s = $k\,(0.01)^2(0.01)$ k = 500 $M^{-2}s^{-1}$

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TOPIC 5.2- INTRODUCTION TO RATE LAW (continued)

9. What is the rate of the reaction for Experiment 4? Plug into Rate = $k[BrO]^2[I_2]$, Rate = $(500\ M^{-2}s^{-1})(0.02\ M)^2(0.02M) = 4.0 \times 10^{-3}$ M/s

An experiment was conducted to determine the rate law for the reaction $X_2 + Y_2 \longrightarrow 2\ XY$. The table below shows the data collected. Based on the data in the table, determine the following.

Experiment	$[X_2]$	$[Y_2]$	Initial Rate of Appearance of XY
1	1.5 *M*	1.5 *M*	5.0×10^2 *M/s*
2	3.0 *M*	1.5 *M*	1.0×10^3 *M/s*
3	1.5 *M*	6.0 *M*	2.0×10^3 *M/s*

10. The rate law for the reaction. Rate = $k[X_2][Y_2]$ See Exp 1 & 2, Double X_2...Rate Doubles...first order. See Exp 1 & 3, Quadrupled Y_2, Rate Quadruples...first order.
11. The overall order for this reaction. Overall order is the sum of the individual orders. Overall 2nd order.
12. The value of the rate constant, k. Plug into the rate law using data from any reaction. Using Rate of Reaction = 5.0×10^2 M/s from 1st trial. 5.0×10^2 M/s = k [1.5 M] [1.5 M] .... k = 222.2 $M^{-1}s^{-1} \approx 220\ M^{-1}/s^{-1}$

TOPIC 5.3- CONCENTRATION CHANGES OVER TIME

A chemist wanted to collect rate law data on the following chemical reaction: $A \longrightarrow B + C + D$. The chemist started with 2.0 M of A and allowed it to decompose over time. After collecting and analyzing the data, the following linear graph was created by plotting 1/[A] versus time.

13. What is the order of the reaction with respect to A? Explain. 2nd Order. The graph of 1/[A] vs time is a straight line.
14. Write the rate law expression. Rate = $k[A]^2$
15. What is the value of the rate constant, k? Include units. Slope of graph = +k. Using ordered pairs (25, 3) and (0, 0.5): $(3\ M^{-1} - 0.5\ M^{-1}) / (25\ s - 0\ s) = 0.10\ M^{-1}s^{-1}$
16. If this experiment were repeated at a higher temperature, what would happen to the value of k? Explain. Increase. Rate of reaction increases.

Another chemist wanted to study the product, B, from the previous reaction. As he isolated 1.5 M initially of B, he studied the decomposition over time. $B \longrightarrow A$. Answer the following questions from the graph of ln[B] v. time below.

17. Explain why the order of the reaction is not 2nd order. It is not second order because the graph of ln[B] versus time is a straight line - that implies a first order process.
18. What is the value of the rate constant? Include units. Slope = –k. Using the ordered pairs (0, 0.42 and (10, –0.17), the slope is *approximately* –0.059. k=0.059 s^{-1}
19. Write the Rate law for the decomposition of B. Rate = k[B]
20. How long will it take 1.0 M to decompose to 0.50 M? For a first-order process, $t_{1/2} = 0.693/k$ ...$0.693/0.059 s^{-1}$ = 12 seconds

TOPIC 5.4- ELEMENTARY REACTIONS

Each equation is from the elementary step in a chemical reaction. Write the rate laws for each elementary step and then identify the overall order of the step.

21. $\mathbf{2\ POBr \longrightarrow 2PO + Br_2}$ Rate = $k[POBr]^2$, overall order = 2
22. $\mathbf{Cl_2 + 2\ O_3 \longrightarrow 2\ ClO_3^-}$ Rate = $k[Cl_2][O_3]^2$, overall order = 3
23. $\mathbf{CH_3CH_2Cl \longrightarrow CH_3CH_2^+ + Cl^-}$ Rate = $k[CH_3CH_2Cl]$, overall order = 1
24. Of the three elementary steps in the three previous questions, which would you expect to be the slowest? Explain your answer. The reaction in Question 22 would be expected to be the slowest, since it is a termolecular step. Termolecular steps require three molecules to collide in the right orientation and with sufficient energy. These are quite rare, and when they occur, they are usually very slow.

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TOPIC 5.5- COLLISION MODEL

The rate-determining step for a reaction is $SO_3(g) \rightarrow SO(g) + O_2(g)$. The graph shows the distribution of energies for $SO_3(g)$ molecules at two temperatures. Answer the following questions regarding this reaction.

25. Explain the observation that much less product is formed at Temperature 1 than at Temperature 2. Temperature 2 is higher and represents a higher energy - so more particles will meet the threshold of the activation energy and undergo a reaction.

26. Identify two factors that affect the success of a chemical reaction. Energy of the reactant particles. Orientation of the particles.

27. Another reaction was conducted in which the partial pressure of $SO_3(g)$ was increased. This increase in partial pressure resulted in more products being formed. Explain this result using Collision Theory. Increasing the pressure decreases the distances between the particles. This increases the frequency of collisions of $SO_3(g)$ particles - allowing them to react and form products more often.

TOPIC 5.6- REACTION ENERGY PROFILE

$$CH_3Cl + OH^- \rightarrow CH_3OH + Cl^-$$

Use the labeled energy profile for the reaction given above to identify the letter(s) that represent each of the following:.

28. Enthalpy of reaction, $\Delta H_{rxn.}$ *B*
29. Activation Energy of the Reaction, $E_{a,}$ *C*
30. Activation Energy of the Reverse Reaction, $E_{a,\ reverse}$ *B + C*
31. The letter(s) affected by the use of a catalyst. A & C.
32. What is the value of $\Delta H_{rxn.}$? 314 – 406 = –92 kJ/mol
33. Is this reaction exothermic or endothermic? Explain. Exothermic; products are lower in energy than the reactants. ΔH_{rxn} <0
34. What is the value of the E_a of the forward reaction? 454 - 406 = +48 kJ/mol
35. What is the value of the E_a of the reverse reaction? B + C; 92 kJ/mol + 48 kJ/mol = 140 kJ/mol
36. Would the reverse of this reaction happen faster or slower than the forward? Explain. Slower. The activation energy for the reverse is higher, so it would take more energy and be slower to reverse.

TOPIC 5.7- INTRODUCTION TO REACTION MECHANISMS

A similar three step experiment was studied for the oxidation of iodide ion by hydrogen peroxide:

$H_2O_2 + I^- \rightarrow HOI + OH^-$	**Step 1 (*fast*)**
$HOI + I^- \rightarrow I_2 + OH^-$	**Step 2 (*fast*)**
$2\ OH^- + 2\ H_3O^+ \rightarrow 4\ H_2O$	**Step 3 (*slow*)**

37. What is the overall balanced equation? $H_2O_2 + 2\ I^- + 2\ H_3O^+ \rightarrow I_2 + 4\ H_2O$
38. Identify all reaction intermediates. HOI, OH^-
39. Referencing the overall reaction for the oxidation of iodide ions, explain why it is not likely that this reaction occurs in one step. There are too many particles required to collide (five total), so it is highly unlikely the reaction will happen in one step.

A two-step reaction mechanism is proposed for a chemical reaction, represented below.

Step 1	$2\ PS_2 \rightarrow PS + PS_3$	**(*slow*)**
Step 2	$PS_3 + SiS \rightarrow PS_2 + SiS_2$	**(*fast*)**

40. What is the chemical equation for the overall reaction? $PS_2 + SiS \rightarrow PS + SiS_2$
41. Identify the reaction intermediate in this mechanism. PS_3

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TOPIC 5.8- REACTION MECHANISM AND RATE LAW

Following is a representation of a proposed mechanism for the reaction involving the reaction of cyclohexane, $C_6H_{12}(g)$ with bromine, $Br_2(g)$.

Step 1: $Br_2 \rightarrow 2Br$ **(slow)**

Step 2: $Br + C_6H_{12} \rightarrow HBr + C_6H_{11}$ **(fast)**

Step 3: $C_6H_{11} + Br \rightarrow C_6H_{11}Br$ **(fast)**

42. What is the overall balanced equation? $C_6H_{12}(g) + Br_2(g) \rightarrow C_6H_{11}Br(g) + HBr(g)$

43. Write a rate law for the reaction that is consistent with the mechanism. Explain how this rate law is consistent. Rate = $k[Br_2]$ ...the slow step is the rate-determining step, so the rate law for the slow step will be the rate law for the whole reaction.

44. Explain the observation that increasing or decreasing the concentration of $C_6H_{12}(g)$ does not affect the rate of the reaction. The rate law only includes Br_2 ...which means the rate is zeroth order with respect to $C_6H_{12}(g)$...it does not affect the rate.

45. A student claims that $Br_2(g)$ is a catalyst in the reaction. Explain why the student's claim is false. Br_2 is a reactant involved in the chemical reaction - it cannot be a catalyst.

Below is a mechanism proposed for the reaction of ozone in the upper atmosphere with nitrogen dioxide gas:

Step 1: $O_3 + NO_2 \rightarrow NO_3 + O_2$ **(slow)**

Step 2: $NO_3 + NO_2 \rightarrow N_2O_5$ **(fast)**

46. Identify the reaction intermediate. NO_3

47. What is the overall balanced equation for this process? $O_3 + 2\,NO_2 \rightarrow O_2 + N_2O_5$

48. Write a rate law for this reaction based on the mechanism. Rate = $k\,[O_3]\,[NO_2]$

49. State the order of the reaction with respect to each of the reactants, as well as the overall order of the reaction.
The reaction is 1st order with respect to O_3, 1st order with respect to NO_2, and overall 2nd order.

TOPIC 5.9- STEADY STATE APPROXIMATION

A two step-mechanism for the synthesis of $POI(g)$ is shown below. Answer the questions that follow.

Step 1: $PO(g) + I_2(g) \rightleftarrows POI_2(g)$ ***(fast, equilibrium)***

Step 2: $PO(g) + POI_2(g) \rightarrow 2\,POI(g)$ ***(slow)***

50. What is the overall chemical reaction? $2\,PO(g) + I_2(g) \rightarrow 2\,POI(g)$

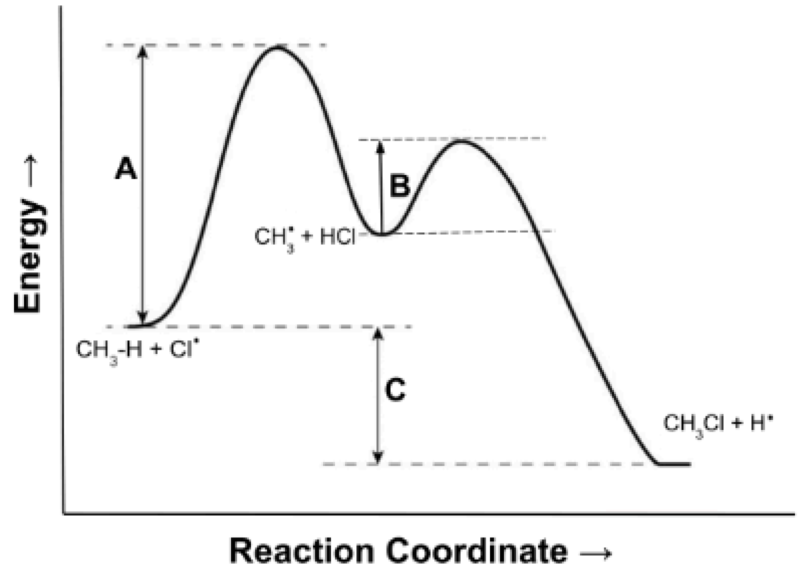
51. Identify any intermediates or catalysts involved in the mechanism. POI_2 is an intermediate

52. In this mechanism, the rate determining step contains an intermediate. Explain why we cannot use a rate law that contains a reaction intermediate. According to the Steady-State Approximation - a reaction intermediate in a mechanism is consumed as quickly as it is generated and its concentration remains constant; this would make predicting rates difficult. Furthermore, an intermediate is not part of the balanced chemical equation and its quantity would be difficult to determine.

53. Identify a rate law that would be consistent with this mechanism. Rate = $k\,[PO]^2[I_2]$

TOPIC 5.10- MULTISTEP REACTION ENERGY PROFILE

The energy profile shown below represents the multistep mechanism for the substitution reaction of chlorine and methane to produce methyl chloride: **$2\,CH_4(g) + Cl_2(g) \rightarrow 2\,CH_3Cl + H_2(g)$**



54. Is this reaction exothermic or endothermic? Explain. Exothermic; the final products are lower in energy than the initial reactants.

55. How many steps are involved in this mechanism? 2

56. Which step is the rate determining step in the mechanism? Explain. Step 1 (Arrow A). The activation energy of the first step is higher than the second step (represented by Arrow B) — which means it would require more energy and take more time to occur.

57. If this reaction was catalyzed, which letters would be affected? Explain. A & B. Catalysts affect the speed of a reaction by lowering the activation energy. A & B are the activation energies for the 1st and 2nd step.

TOPIC 5.11- CATALYSIS

A kinetics experiment studied the single replacement of halogens with the following three step mechanism:

Step 1: $ClO^- + H_2O \rightarrow HOCl + OH^-$ (*slow*)

Step 2: $Br^- + HOCl \rightarrow HOBr + Cl^-$ (*fast*)

Step 3: $OH^- + HOBr \rightarrow H_2O + BrO^-$ (*fast*)

58. What is the chemical equation for the overall reaction? $ClO^- + Br^- \rightarrow Cl^- + BrO^-$

59. What reaction intermediates are involved in this mechanism? HOCl, HOBr and OH^-

60. What is the catalyst involved in this mechanism? H_2O

A reaction mechanism for the decomposition of hydrogen peroxide is shown below:

Step 1: $H_2O_2 + I^- \rightarrow OI^- + H_2O$ (*slow*)

Step 2: $H_2O_2 + OI^- \rightarrow I^- + H_2O + O_2$ (*fast*)

61. What is the overall balanced equation for the reaction represented by the mechanism? $2\,H_2O_2 \rightarrow 2\,H_2O + O_2$

62. Identify the reaction intermediate and the catalyst in this process. Intermediate is OI^-, catalyst is I^-