Big Idea #4 Kinetics

Rates of chemical reactions are determined by the details of the molecular collisions.

Enduring Understanding Standards

4.A: Reaction rates that depend on temperature and other environmental factors are determined by measuring changes in concentrations of reactants or products over time.

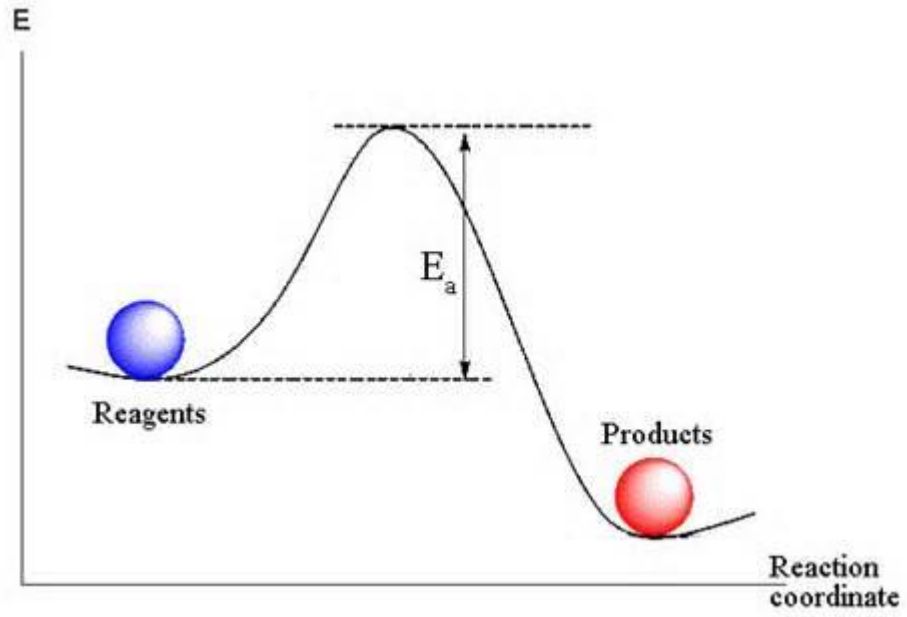
4.B: Elementary reactions are mediated by collisions between molecules. Only collisions having sufficient energy and proper relative orientation of reactants lead to products.

4.C: Many reactions proceed via a series of elementary reactions.

4.D: Reaction rates may be increased by the presence of a catalyst.

Collision theory

- A reaction requires a collisions:
  - Collisions must require a minimum amount of energy. (Energy $_{activation}$)
  - Collisions require a specific geometry during the collision.



Factors affecting the speed of a reactions

Relate to collision theory:

<u>Increased number of collisions</u>

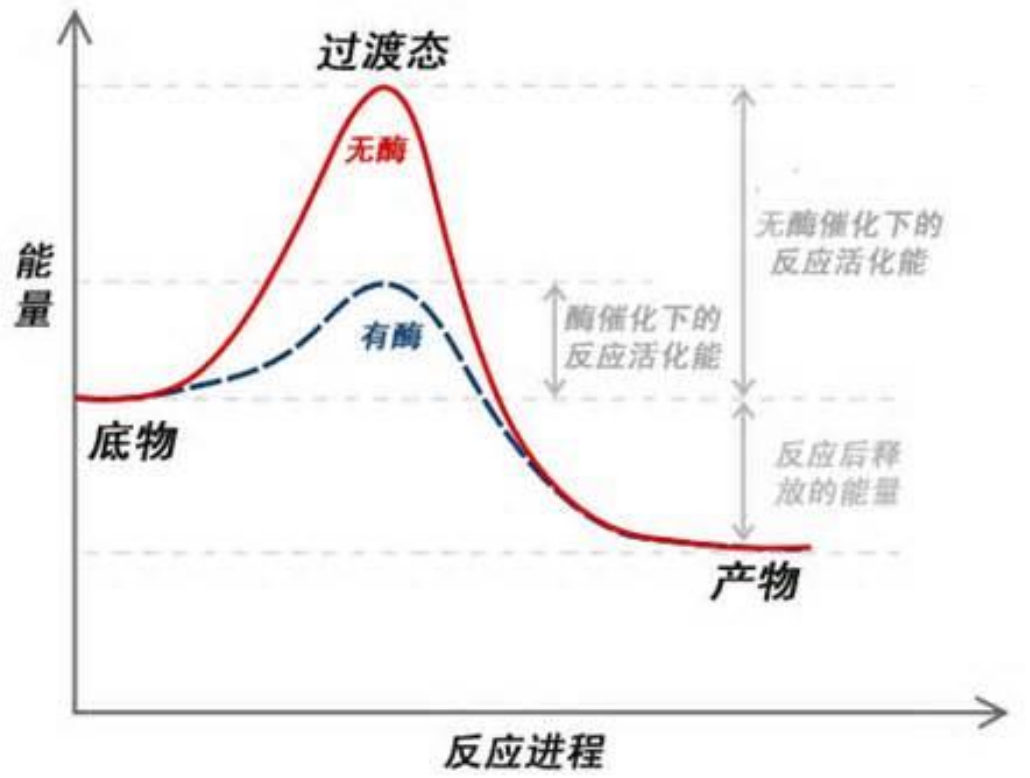
- Increase temperature
- Concentration
  - Surface area
  - Concentration
  - pressure

<u>More energetic Collisions</u>

-Increase temperature

Add a catalyst

- Creates a different pathway which has a lower activation energy.



Note:
-- Lower activation energies mean faster reactions!
-- Actually a different mechanism!
-- Same start…
-- Same end…
-- Same Enthalpy ΔH

-- Not consumed in the reaction
-- Can not make impossible possible

Rate with in the reaction

- $1X + 2Y \Rightarrow 3Z$

- If Z is being produced at 1.5moles/hour
- Then Y is being consumed at -1.0 moles/hour
- Then X is being consumed at -.5 moles/hour

- Simply stoichiometric ratio

Initial rate and the Rate law

- Objective: Create a mathematical formula to predict initial rate

$$X + 2Y \Rightarrow 3Z$$

$$\text{Initial Rate} = K[X]^m[Y]^n$$

Order of reaction (m & n)

- These orders must be determined from
  - Experimental data
  - A confirmed reaction mechanism

Example

$$X + 2Y \Rightarrow 3Z$$

$$\text{Rate} = K[X]^1[Y]^1$$

- If you double the concentration of X what happens to the rate?
- What is the order overall?
- What is the order with respect to the X?

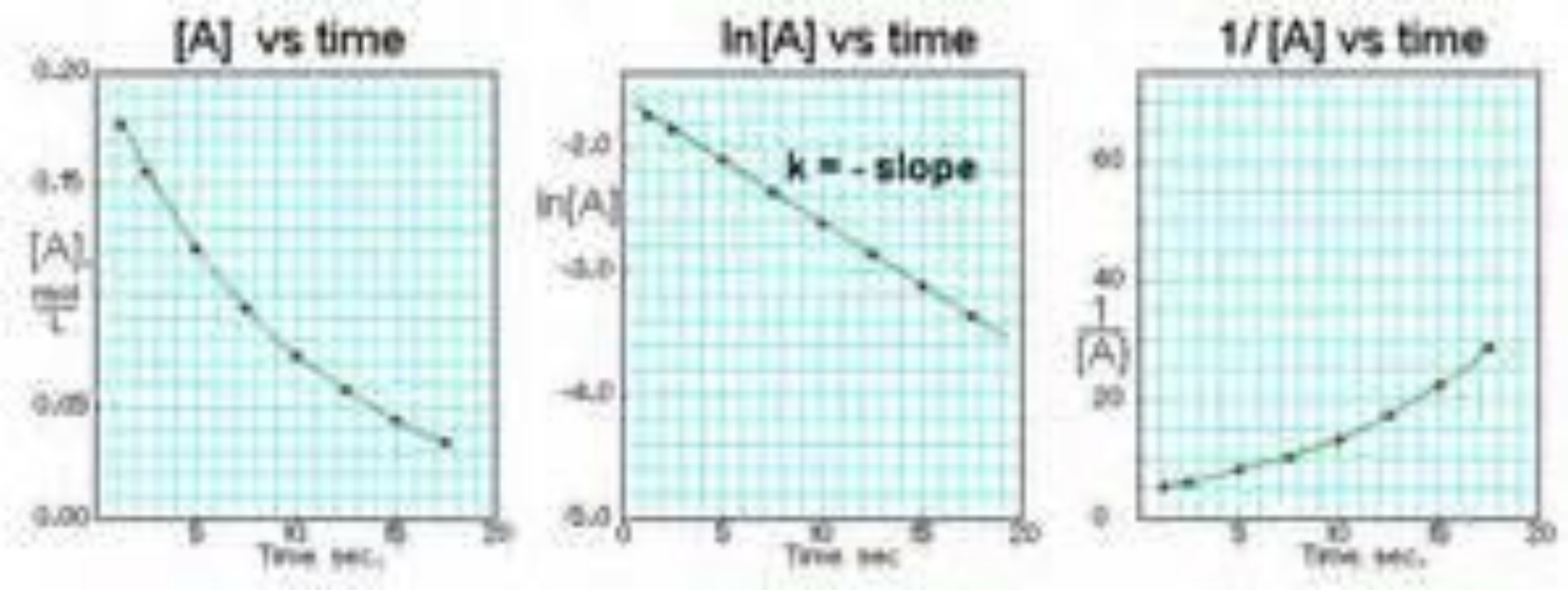
**only gives initial rate!!

Concentration vs. Time

TABLE 12.6 Summary of the Kinetics for Reactions of the Type aA → Products That Are Zero, First, or Second Order in [A]

	Order		
	Zero	*First*	*Second*
Rate Law:	Rate = k	Rate = $k[A]$	Rate = $k[A]^2$
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Plot Needed to Give a Straight Line:	[A] versus t	ln[A] versus t	$\frac{1}{[A]}$ versus t
Relationship of Rate Constant to the Slope of Straight Line:	Slope = $-k$	Slope = $-k$	Slope = k
Half-life:	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

Should be able to interpret these graphs



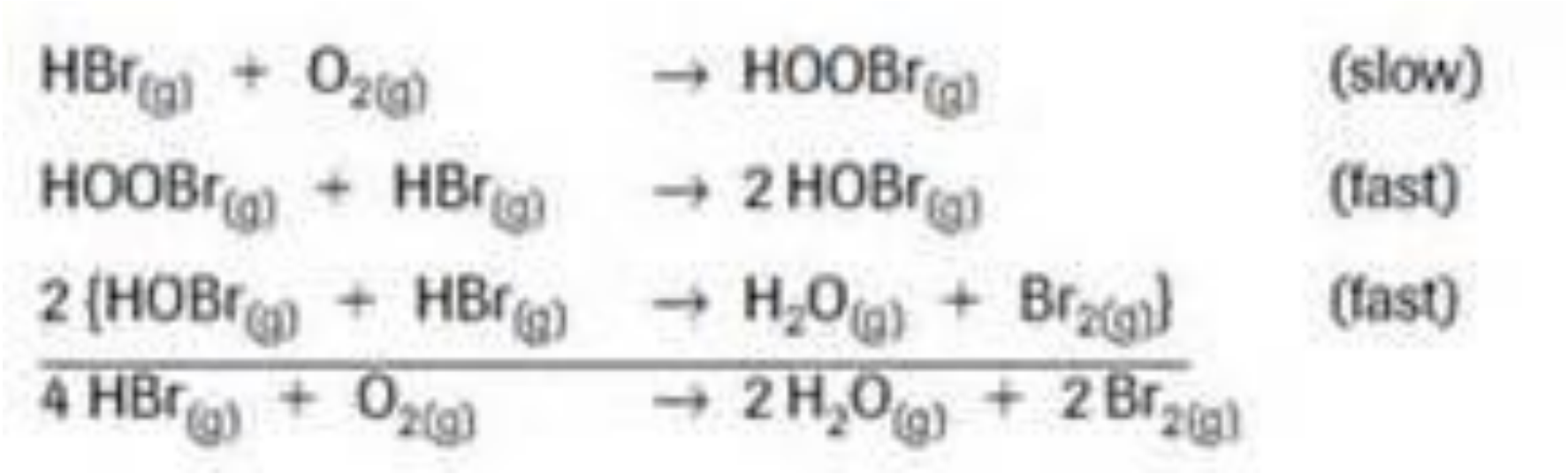
Half life

- Most Half lives are 1^{st} order.

- $T_{1/2} = 0.693/K$

Reaction Mechanisms

- Should be able to write out a rate law from elementary steps
- Slow step and any prior step will increase slow step.
- Be able to identify catalyst and intermediates



Multiple choice

6. A kinetics experiment is set up to collect the gas that is generated when a sample of chalk, consisting primarily of solid $CaCO_3$, is added to a solution of ethanoic acid, CH_3COOH. The rate of reaction between $CaCO_3$ and CH_3COOH is determined by measuring the volume of gas generated at 25°C and 1 atm as a function of time. Which of the following experimental conditions is most likely to increase the rate of gas production?

   (A) Decreasing the volume of ethanoic acid solution used in the experiment

   (B) Decreasing the concentration of the ethanoic acid solution used in the experiment

   (C) Decreasing the temperature at which the experiment is performed

   (D) Decreasing the particle size of the $CaCO_3$ by grinding it into a fine powder

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- D. Answer is based upon collision theory

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

24. Consider the following mechanism for the reaction represented above.

Step 1: $2\,NO \rightleftarrows N_2O_2$ (*fast reversible*)

Step 2: $N_2O_2 + O_2 \rightarrow 2\,NO_2$ (*slow*)

Which of the following statements is true?

(A) Step 1 represents a unimolecular reaction.
(B) Increasing the concentration of NO will decrease the overall rate of the reaction.
(C) Raising the temperature will have no effect on the numerical value of the rate constant.
(D) The rate law that is consistent with the mechanism is $rate = k[NO]^2[O_2]$.

- Determine the answer?

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- D: Reaction mechanisms. Slow step is increased by 2 NO and 1 O_2. NO increases concentration of intermediate which increases slow step!

Step 1: $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$

Step 2: $ClO(g) + O(g) \rightarrow Cl(g) + O_2(g)$

53. A proposed mechanism for destruction of ozone gas in the stratosphere is represented above. Which of the following is evidence that the mechanism is occurring?

(A) The presence of $Cl(g)$ increases the rate of the overall reaction.

(B) The presence of $Cl(g)$ decreases the rate of the overall reaction.

(C) The presence of $Cl(g)$ increases the equilibrium constant of the overall reaction.

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- Determine the Answer

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A: Cl is a catalyst. And therefore should increase the rate of the reaction.

$$2\,N_2O_5(g) \rightarrow 4\,NO_2(g) + O_2(g)$$

57. A sample of N_2O_5 was placed in an evacuated container, and the reaction represented above occurred. The value of $P_{N_2O_5}$, the partial pressure of $N_2O_5(g)$, was measured during the reaction and recorded in the table below.

Time (min)	$P_{N_2O_5}$ (atm)	$\ln(P_{N_2O_5})$	$\frac{1}{P_{N_2O_5}}$ (atm^{-1})
0	150	5.0	0.0067
100	75	4.3	0.013
200	38	3.6	0.027
300	19	2.9	0.053

Which of the following correctly describes the reaction?

(A) The decomposition of N_2O_5 is a zero-order reaction.

(B) The decomposition of N_2O_5 is a first-order reaction.

(C) The decomposition of N_2O_5 is a second-order reaction.

(D) The overall reaction order is 3.

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- Looking for a consistent change that would indicate a constant slope…. Which would indicate the correct order.
- Zero is decreasing in half every time (exponential)
- 2nd is doubling every time. (exponential)
- 1st order is showing consistent change every time. 8 units