

# Ch 14: Chemical Kinetics

↳ study of the rate at which a chemical process occurs : how the reaction occurs (reaction mechanism)

## 1. Factors that affect reaction rates

### (A) Physical state of the reactants

(1) In order to react, molecules must come into contact with each other

(2) The more homogeneous the mixture of reactants, the faster the molecules can react

### (B) Concentration of reactants

(1) As the concentration of reactants increases, the faster the reaction. **Why?**

↑ concentration = more stuff to react

### (C) Temperature

(1) Rates increase as temperature increases. **Why?**  
↑ KE ↑ collisions ↑ rate

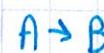
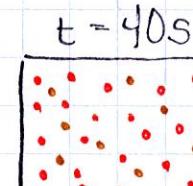
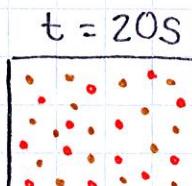
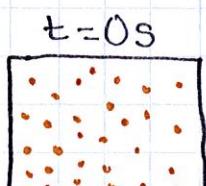
### (D) Presence of a Catalyst

(1) Catalysts speed up a reaction by changing the reaction mechanism

(2) Catalysts are NOT consumed during the reaction

## 2. Reaction Rates - speed of a chemical reaction

can be determined by monitoring the change in concentration of either reactants or products as a function of time.



$$\text{avg. rate of appearance of } B = \frac{\Delta [B]}{\Delta t} = \frac{(0.46\text{ mol} - 0\text{ mol})}{(20\text{ s} - 0\text{ s})} = \frac{0.46\text{ mol}}{20\text{ s}} = 0.023\text{ mol/s}$$

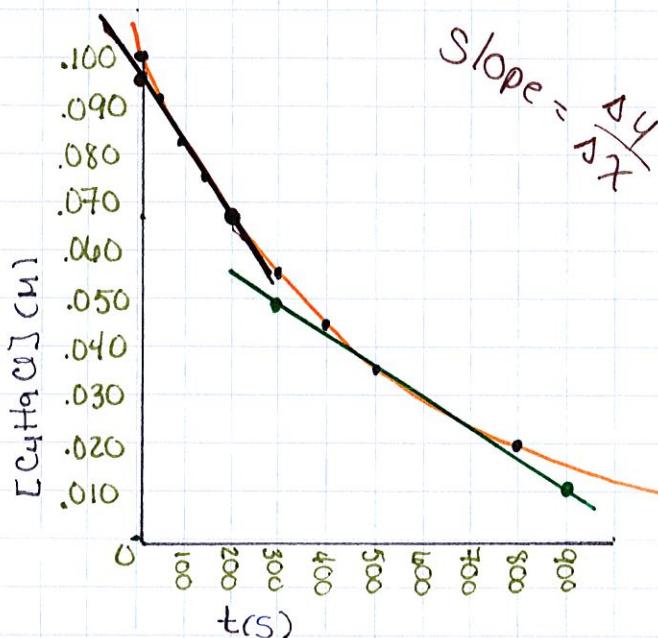
$$\text{avg. rate of disappearance of } A = \frac{-\Delta [A]}{\Delta t} = \frac{-(0.54\text{ mol} - 1.00\text{ mol})}{(20\text{ s} - 0\text{ s})} = \frac{0.46\text{ mol}}{20\text{ s}} = 0.023\text{ mol/s}$$



| time, t(s) | $[\text{C}_4\text{H}_9\text{Cl}](\text{M})$ | Avg. rate = $\frac{-\Delta[\text{C}_4\text{H}_9\text{Cl}]}{\Delta t}$                |
|------------|---|--|
| 0          | 0.1000                                      |  |
| 50.0       | 0.0905                                      | $\frac{(.0905 - .1000)}{(50\text{s} - 0\text{s})} = 1.90 \times 10^{-4} \text{ M/s}$ |
| 100.0      | 0.0820                                      | $1.70 \times 10^{-4} \text{ M/s}$  |
| 150.0      | 0.0741                                      | $1.58 \times 10^{-4} \text{ M/s}$  |
| 200.0      | 0.0671                                      | $1.40 \times 10^{-4} \text{ M/s}$  |
| 300.0      | 0.0549                                      | $1.22 \times 10^{-4} \text{ M/s}$  |
| 400.0      | 0.0448                                      | $1.01 \times 10^{-4} \text{ M/s}$  |
| 500.0      | 0.0368                                      | $8.00 \times 10^{-5} \text{ M/s}$  |
| 800.0      | 0.0200                                      | $5.6 \times 10^{-5} \text{ M/s}$   |
| 10,000.0   | 0   | $2.17 \times 10^{-6} \text{ M/s}$  |

what happens to the average rate as the reaction proceeds and why?  
 rate decreases b/c there is less reactants to react.

3. Instantaneous Rate - rate at a particular moment in time.



• found by taking the slope of a line tangent to the curve at any point.

• all reactions slow down over time

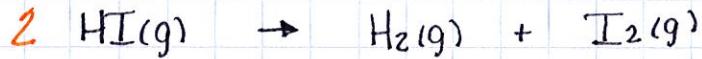
\* • best indicator of rate is the instantaneous rate near the beginning of a reaction.

$$\text{rate} @ 100\text{s} = \frac{(0.068\text{M} - 0.095\text{M})}{(200\text{s} - 0\text{s})} = \\ = -1.35 \times 10^{-4} \text{ M/s}$$

$$\text{rate} @ = \frac{(0.010\text{M} - 0.049\text{M})}{(900\text{s} - 300\text{s})} \\ = -6.5 \times 10^{-5} \text{ M/s}$$

From now on, when we say rate, we mean instantaneous rate!

4. Reaction Rates & Stoichiometry - what happens when the stoichiometric relationships are not 1 to 1.

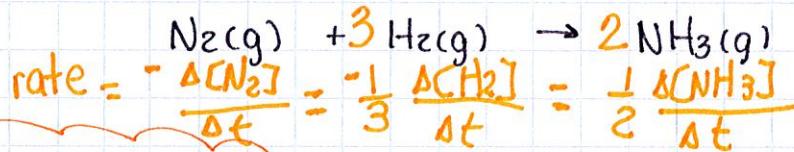


2 mol HI disappear for each mole of H<sub>2</sub> or I<sub>2</sub> that appear

For a general reaction:  $aA + bB \rightarrow cC + dD$

$$\text{the rate will be: rate} = -\frac{1}{a} \frac{\Delta [A]}{\Delta t} = -\frac{1}{b} \frac{\Delta [B]}{\Delta t} = \frac{1}{c} \frac{\Delta [C]}{\Delta t} = \frac{1}{d} \frac{\Delta [D]}{\Delta t}$$

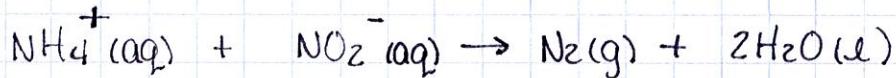
Ex(i) Write the rate expression for the following reactions:



See next page (3.5)

5. The Rate Law: the effect of concentration on rate

↳ gaining information about a reaction rate by seeing how the rate changes with concentration.



| Exp | $[\text{NH}_4^+]^\circ (\text{M})$ | $[\text{NO}_2^-]^\circ (\text{M})$ | Initial Rate (M/s)    |
|-----|------------------------------------|------------------------------------|-----------------------|
| 1   | .0100                              | .200                               | $5.4 \times 10^{-7}$  |
| 2   | .0200                              | .200                               | $10.8 \times 10^{-7}$ |
| 3   | .0400                              | .200                               | $21.5 \times 10^{-7}$ |
| 4   | .200                               | .0202                              | $10.8 \times 10^{-7}$ |
| 5   | .200                               | .0404                              | $21.6 \times 10^{-7}$ |
| 6   | .200                               | .0808                              | $43.3 \times 10^{-7}$ |

Compare Exp 1 & 2:  $[\text{NH}_4^+]$  doubles,  $[\text{NO}_2^-]$  constant, rate doubled

Compare Exp 5 & 6:  $[\text{NH}_4^+]$  constant,  $[\text{NO}_2^-]$  doubles, rate doubled

what does that mean?

$$\begin{aligned} \text{rate} &\propto [\text{NH}_4^+] \\ \text{rate} &\propto [\text{NO}_2^-] \end{aligned}$$

rate law

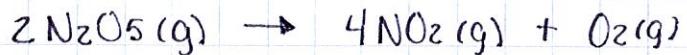
$$\therefore \text{rate} \propto [\text{NH}_4^+][\text{NO}_2^-]$$

$$\Rightarrow \text{Rate} = k [\text{NH}_4^+][\text{NO}_2^-]$$

rate constant

$$-\frac{1}{2} \frac{\Delta [N_2O_5]}{\Delta T} = \frac{1}{4} \frac{\Delta [NO_2]}{\Delta T} = \frac{\Delta [O_2]}{\Delta T}$$

Ex (2) The decomposition of  $\text{N}_2\text{O}_5$  proceeds according to the equation:



$$-\frac{1}{2} \left( 4.2 \times 10^{-7} \text{ M/s} \right) = \frac{1}{4} \frac{\Delta [\text{NO}_2]}{\Delta t}$$

$$2(4.2 \times 10^{-7} \text{ M/s}) = \frac{\Delta [\text{NO}_2]}{\Delta t}$$

$$= \frac{\Delta [NO_2]}{\Delta t}$$

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5. (A) Rate Laws - show the relationship b/w the reaction rate and the concentrations of reactants

(1) exponents - tell the order of the reaction w/ respect to each reactant

$$\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

1<sup>st</sup> order in  $[NH_4^+]$

1<sup>st</sup> order in  $[NO_2^-]$

(2) overall order - found by adding the exponents on the reactants in the rate law

$$\text{rate} = k[\text{NH}_4^+][\text{NO}_2^-] \quad \text{2nd order overall}$$

**★** (3) exponents tell how the rate is affected by the concentration of each reactant

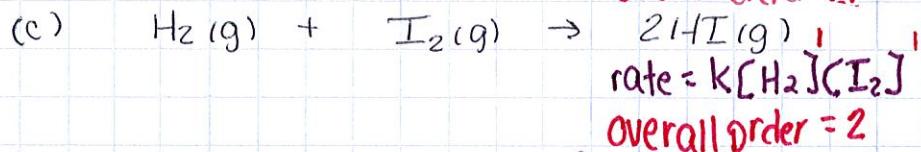
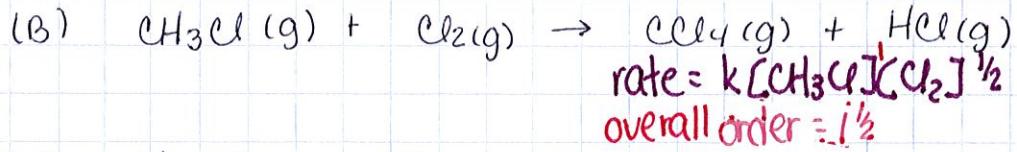
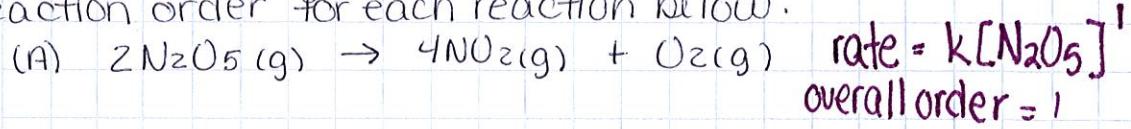
(a) 1<sup>ST</sup> order - rate doubles when concentration doubles

(b) 2<sup>nd</sup> order - rate quadruples when concentration doubles

(c) 0<sup>o</sup> order - rate is not affected by concentration changes

(d) sometimes the exponents in the rate law are the coefficients in the balanced equation BUT the values must be determined experimentally. (3)

Ex (3) what is the order of each reactant and the overall reaction order for each reaction below.



Ex (4) Determine the Rate Law from Initial Rate Data

The initial rate for a reaction,  $A + B \rightarrow C$  was measured for several different starting concentrations of  $A + B$ .

| EXP | <u><math>[A]</math> (m)</u> | <u><math>[B]</math> (m)</u> | <u>Initial Rate (m/s)</u> |
|-----|-----------------------------|-----------------------------|---------------------------|
| 1   | ( .100 )                    | ( .100 )                    | ( $4.0 \times 10^{-5}$ )  |
| 2   | ( .100 )                    | ( .200 )                    | ( $4.0 \times 10^{-5}$ )  |
| 3   | .200                        | .100                        | ( $16.0 \times 10^{-5}$ ) |

Using this data, determine

(A) the rate law.

(B) the rate constant

(C) the rate of the reaction when  $[A] = .050\text{M}$  and  $[B] = .100\text{M}$ .

(A) rate =  $k[A]^2[B]^{1/2} = k[A]^2$

(B) rate =  $k[A]^2$   
 $4.0 \times 10^{-5} \text{ M/s} = k[.100\text{M}]^2$

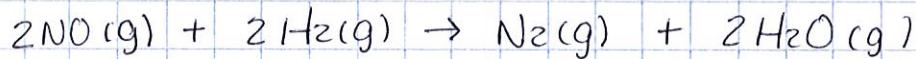
$$\frac{4.0 \times 10^{-5} \text{ M/s}}{[.100\text{M}]^2} = k$$

$$4.00 \times 10^{-3} \frac{1}{\text{M s}} = k$$

(C) rate =  $k[A]^2$

$$\text{rate} = \left(4.00 \times 10^{-3} \frac{1}{\text{M s}}\right) (.050\text{M})^2 = 1.0 \times 10^{-5} \text{ M/s}$$

Ex (5) The following data were measured for the reaction :



| <u>Exp</u> | <u>[NO]<sub>0</sub>(M)</u> | <u>[H<sub>2</sub>](M)</u> | <u>Initial Rate (M/s)</u> |
|------------|----------------------------|---------------------------|---------------------------|
| 1          | .10                        | .10                       | $1.23 \times 10^{-3}$     |
| 2          | .10                        | .20                       | $2.46 \times 10^{-3}$     |
| 3          | .20                        | .10                       | $4.92 \times 10^{-3}$     |

Determine

- the rate law
- the rate constant
- calculate the rate when [NO]<sub>0</sub> = .050M and [H<sub>2</sub>] = .150M.