

VC210 FALL2018 RECITATION CLASS

Final Review

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December 11, 2018

Outline

① Reaction Rate

② Reaction Order

③ Rate Law

④ Reaction Mechanism

Steady-state approximation

Pre-equilibria approximation

⑤ Models of Reaction

Arrhenius Equation

Activation Energy

Collision Theory and Transient State Theory

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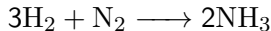
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The reaction rate is the speed at which reactants are converted into products. It is described as the decrement of reactants or increment of products.



Average reaction rate:

$$r = -\frac{\Delta[\text{H}_2]}{3\Delta t} = -\frac{\Delta[\text{N}_2]}{\Delta t} = \frac{\Delta[\text{NH}_3]}{2\Delta t}$$

Instantaneous reaction rate:

$$r = -\frac{d[\text{H}_2]}{3dt} = -\frac{d[\text{N}_2]}{dt} = \frac{d[\text{NH}_3]}{2dt}$$

The reaction rate **depends** on the stoichiometry coefficients of the equation!

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The exponential sum of the concentrations in the rate law

rate law	reaction order
$r = k$	0
$r = k[A]$	1
$r = k[A]^2$ or $k[A][B]$ or $k[A]^3[B]^{-1}$	2
...	...

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Determine the reaction order with experimental data

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Exp.	Initial Conc. ($\text{mol}\cdot\text{L}^{-1}$)			Initial rate
	BrO_3^-	Br^-	H_3O^+	$\text{mmol BrO}_3^- \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
1	0.10	0.10	0.10	1.2
2	0.20	0.10	0.10	2.4
3	0.10	0.30	0.10	3.5
4	0.20	0.10	0.15	5.5

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	BrO ₃ ⁻	Br ⁻	H ₃ O ⁺	mmol BrO ₃ ⁻ · L ⁻¹ · s ⁻¹
1	0.10	0.10	0.10	1.2
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$$\text{Assume } \text{rate} = k[\text{BrO}_3^-]^\alpha [\text{Br}^-]^\beta [\text{H}_3\text{O}^+]^\gamma$$

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Assume $rate = k[BrO_3^-]^\alpha [Br^-]^\beta [H_3O^+]^\gamma$
 Exp.(1,2) : $[BrO_3^-] \times 2 \rightarrow rate \times 2 \Rightarrow \alpha=1$;

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 Exp.(1,2) : $[BrO_3^-] \times 2 \rightarrow rate \times 2 \Rightarrow \alpha=1$;
 Exp.(1,3) : $[Br^-] \times 3 \rightarrow rate \approx \times 3 \Rightarrow \beta=1$;

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$$\text{Assume } \text{rate} = k[\text{BrO}_3^-]^\alpha [\text{Br}^-]^\beta [\text{H}_3\text{O}^+]^\gamma$$

$$\text{Exp. (1,2)} : [\text{BrO}_3^-] \times 2 \rightarrow \text{rate} \times 2 \Rightarrow \alpha=1;$$

$$\text{Exp. (1,3)} : [\text{Br}^-] \times 3 \rightarrow \text{rate} \approx \times 3 \Rightarrow \beta=1;$$

$$\text{Exp. (2,4)} : [\text{H}_3\text{O}^+] \times 1.5 \rightarrow \text{rate} \approx \times 2.25 \Rightarrow \gamma=2;$$

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$$\text{Assume } \text{rate} = k[\text{BrO}_3^-]^\alpha [\text{Br}^-]^\beta [\text{H}_3\text{O}^+]^\gamma$$

$$\text{Exp. (1,2)} : [\text{BrO}_3^-] \times 2 \rightarrow \text{rate} \times 2 \Rightarrow \alpha = 1;$$

$$\text{Exp. (1,3)} : [\text{Br}^-] \times 3 \rightarrow \text{rate} \approx \times 3 \Rightarrow \beta = 1;$$

$$\text{Exp. (2,4)} : [\text{H}_3\text{O}^+] \times 1.5 \rightarrow \text{rate} \approx \times 2.25 \Rightarrow \gamma = 2;$$

$$\text{Simpler method: } \left(\frac{[\text{H}_3\text{O}^+]_4}{[\text{H}_3\text{O}^+]_2} \right)^\gamma = \left(\frac{5.5}{2.4} \right)$$

$$\gamma = \log_{1.5} \frac{5.5}{2.4}$$

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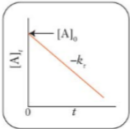
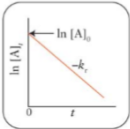
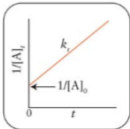
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Rate Law

TABLE 7B.1 Integrated Rate Laws, Rate Law Plots, and Half-Lives

	Order of reaction		
	0	1	2
Rate law	$\text{Rate} = k_r$	$\text{Rate} = k_r[A]$	$\text{Rate} = k_r[A]^2$
Integrated rate law	$[A]_t = -k_r t + [A]_0$	$[A]_t = [A]_0 e^{-k_r t}$	$[A]_t = \frac{[A]_0}{1 + k_r t [A]_0}$ $\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_r t$
Plot to determine order			
Slope of the line plotted	$-k_r$	$-k_r$	k_r
Half-life	$t_{1/2} = \frac{[A]_0}{2k_r}$ <p>(not used)</p>	$t_{1/2} = \frac{\ln 2}{k_r} \approx \frac{0.693}{k_r}$	$t_{1/2} = \frac{1}{k_r [A]_0}$ <p>(not used)</p>

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Determine the rate constant for each of the following first-order reactions, in each case expressed for the rate of loss of A:

- a) $A \longrightarrow B$, given that the concentration of A decreases to one-half its initial value in 1000.s;
- b) $A \longrightarrow B$, given that the concentration of A decreases from 0.67 mol/L to 0.53 mol/L in 25s;
- c) $2A \longrightarrow B + C$, given that $[A]_0 = 0.153$ mol/L and that after 115s the concentration of B rises to 0.034 mol/L.

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The concentration of highly active intermediates does not change over time.

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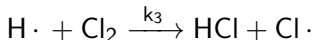
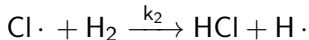
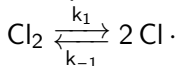
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The concentration of highly active intermediates does not change over time.

Example

Determine the rate law of the reaction $\text{H}_2 + \text{Cl}_2 \longrightarrow 2 \text{HCl}$ with provided mechanism.



Reaction Mechanism

Steady-state approximation

The concentration of highly active intermediates does not change over time.

Example

Reaction Mechanism

Steady-state approximation

The concentration of highly active intermediates does not change over time.

Example

$$\frac{d[\text{Cl}\cdot]}{dt} = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Cl}_2] - k_{-1}[\text{Cl}\cdot]^2 = 0 \quad (1)$$

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Cl}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Cl}_2] = 0 \quad (2)$$

Reaction Mechanism

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The concentration of highly active intermediates does not change over time.

Example

$$\frac{d[\text{Cl}\cdot]}{dt} = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Cl}_2] - k_{-1}[\text{Cl}\cdot]^2 = 0 \quad (1)$$

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Cl}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Cl}_2] = 0 \quad (2)$$

substitute (2) into (1)

$$2k_1[\text{Cl}_2] - 2k_{-1}[\text{Cl}\cdot]^2 = 0$$

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$$\frac{d[\text{Cl}\cdot]}{dt} = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Cl}_2] - k_{-1}[\text{Cl}\cdot]^2 = 0 \quad (1)$$

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Cl}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Cl}_2] = 0 \quad (2)$$

substitute (2) into (1)

$$2k_1[\text{Cl}_2] - 2k_{-1}[\text{Cl}\cdot]^2 = 0$$

$$[\text{Cl}\cdot] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Cl}_2]^{1/2}$$

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Steady-state approximation

The concentration of highly active intermediates does not change over time.

Example

$$\frac{d[\text{Cl}\cdot]}{dt} = 2k_1[\text{Cl}_2] - k_2[\text{Cl}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Cl}_2] - k_{-1}[\text{Cl}\cdot]^2 = 0 \quad (1)$$

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Cl}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Cl}_2] = 0 \quad (2)$$

substitute (2) into (1)

$$2k_1[\text{Cl}_2] - 2k_{-1}[\text{Cl}\cdot]^2 = 0$$

$$[\text{Cl}\cdot] = \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Cl}_2]^{1/2}$$

$$\text{Therefore, } r = -\frac{d[\text{H}_2]}{dt} = k_2 \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Cl}_2]^{1/2} [\text{H}_2]$$

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Tips

When choosing which substance to represent reaction rate:

- i) appears in the rate-determining step
- ii) appears the least in the mechanism

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Pre-equilibria approximation

Opposing steps prior to the rate-determining step reaches equilibrium. Steps after the rate-determining step do not affect the net reaction rate.

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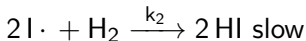
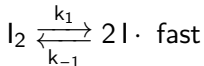
Reaction Mechanism

Pre-equilibria approximation

Opposing steps prior to the rate-determining step reaches equilibrium. Steps after the rate-determining step do not affect the net reaction rate.

Example

Determine the rate law of the reaction $\text{H}_2 + \text{I}_2 \longrightarrow 2 \text{HI}$ with provided mechanism.



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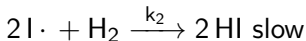
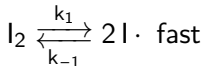
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Opposing steps prior to the rate-determining step reaches equilibrium. Steps after the rate-determining step do not affect the net reaction rate.

Example

Determine the rate law of the reaction $\text{H}_2 + \text{I}_2 \longrightarrow 2 \text{HI}$ with provided mechanism.



The first step reaches equilibrium

$$k_1[\text{I}_2] = k_{-1}[\text{I} \cdot]^2$$

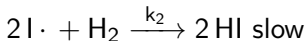
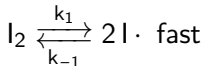
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Determine the rate law of the reaction $\text{H}_2 + \text{I}_2 \longrightarrow 2 \text{HI}$ with provided mechanism.



The first step reaches equilibrium

$$k_1[\text{I}_2] = k_{-1}[\text{I} \cdot]^2$$

Therefore,

$$r = \frac{d[\text{HI}]}{2dt} = k_2[\text{H}_2][\text{I} \cdot]^2 = \frac{k_2 k_1}{k_{-1}} [\text{H}_2][\text{I}_2]$$

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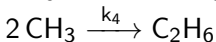
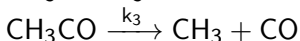
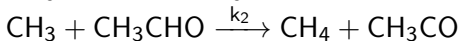
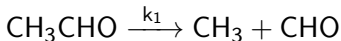
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Exercise

Dissociation reaction of acetaldehyde $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$ is composed of the following steps



deduce the rate law with steady-state approximation:

$$r = k_2 \left(\frac{k_1}{2k_4} \right)^{1/2} [\text{CH}_3\text{CHO}]^{3/2}$$

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Arrhenius Equation

$$k = Ae^{-\frac{E_a}{RT}} \quad \ln k = -\frac{E_a}{RT} + \ln A$$

Two points Arrhenius Equation

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

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Elementary reactions:

$$E_a = E^\star - E_R$$

E^\star is the energy of the transient and E_R is the energy of the initial state.

Complex reactions: The net activation energy is the specific combination of the activation energies of the constituent elementary reactions.

$$k = \frac{k_1 k_2}{k_{-1}} \Rightarrow E_a = E_{a,1} + E_{a,2} - E_{a,-1}$$

Models of Reaction

Collision Theory and Transient State Theory

Collision Theory

Reaction occurs when **activated** molecules collide into each other.

The theory explains the effect of molecule size, temperature, and orientation of molecules on the reaction rate.

Transient State Theory

Atoms rearrange as molecules approach each other. The transient state is the state where atoms are partially rearranged. This state has the highest energy throughout the process.

Be careful with your calculations and units!

Good luck for your final!