CH11 | Lecture: **L4-L6** | **(C)** Chen + Class| **(A)** AI-assisted: student + AI | **(T)** Transfer: student, AI closed

I. Chemical reaction and rate:

$aA + bB \rightarrow cC + dD$

$$\textbf{Averaged Rate (M/s)} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

II. Rate law:

Differential rate law:

$$\text{Rate} = k[A]^n[B]^m \text{ not } k[A]^a[B]^b$$

Integrated rate law:

$$-\frac{d[A]}{dt} = k \qquad [A]_t = -kt + c$$

Unit of rate constant ***k*: $M^{1-n}s^{-1}$**, ex: 0 order (Ms^{-1}); 1 order (s^{-1}); 2 order ($M^{-1}s^{-1}$); 3 order ($M^{-2}s^{-1}$)

Table 11-6 | 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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

III. Reaction mechanism:
elementary steps and rate **determine step**
1. Write out the overall balanced eq. identify the **reactants**, **products**, **intermediate**, and/or **catalyst**.
2. Write the rate law by using the rate determine elementary step **directly**
3. If the rate law contains non-reactant, use K_{eq} from other steps to derive the final rate law with **reactants** *if possible*.

IV. Arrhenius equation: note R = 8.314J/mol, T must use *Kelvin* not degree C

$$k = Ae^{-\frac{E_a}{RT}} \qquad ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$lnk = lnA - \frac{E_a}{RT}$$

- Catalyst is the only thing that can change the E_a and only E_a (it does not affect equilibrium).

Ch 11

11.I-II

1. **(L4_C)** What is the reaction order of Br^- for a reaction with the following rate law? Rate = $k[BrO_3^-][Br^-][H^+]^2$ [**first**]
2. **(L4_A)** Consider the reaction with the rate law, Rate = $k[BrO_3^-][Br^-][H^+]^2$.
   By what factor does the rate change if the concentration of H^+ is quadrupled? Just put in the number as a whole number or fraction. [**16**]
3. **(L4_C)** Given the data below for the reaction, 2 A + 2 B + 4 C => D + E + 3 F, the reaction is [x1] order in A, [x2] order in B, [x3] order in C and [x4] order overall. USE WORDS TO FILL IN THE BLANKS NOT NUMBERS (i.e., zero, first, second etc) !!!!! :

Experiment	Initial conc of A, mol/L	Initial conc of B, mol/L	Initial conc of C, mol/L	Initial rate, mol/L.s
1	0.1	0.2	0.4	2×10^{-3}
2	0.2	0.2	0.4	2×10^{-3}
3	0.3	0.4	0.4	4×10^{-3}
4	0.4	0.6	0.2	1.5×10^{-3}

   [**zero, first, two, total three**]
4. **(L5_C)** The reaction, AB => A(g) + B(g), has a rate law, rate = $k[AB]^2$. Calculate the rate constant in L/mol·s. If it takes 120 seconds to reach an [AB] of 0.2 mol/L from an initial concentration of 0.8 mol/L. (Enter your answer to 3 decimal places) [(**0.031**]
5. **(L5_A)** In a first order decomposition in which the rate constant is 0.5 sec^{-1}, how long will it take (in minutes) until 1.6 mol/L of the compound is left, if there was 4 mol/L at the start? Give your answer to 3 decimal places. [**0.031**]

11.III

6. **(L6_C)** Consider the reaction, A + B + C => D, which is found to be first order in A and first order in B. Which step of the proposed mechanism must be slow in order to agree with this rate law?
   1. A(g) + B(g) => X(g)
   2. X(g) + C(g) => Y(g)
   3. Y(g) => D(g)

   [**1**]
7. **(L6_A)** For the reaction $NO_2(g) + CO(g) \Rightarrow NO(g) + CO_2(g)$ at temperatures below 500 K, the rate law is rate = $k[NO_2]^2$. Which mechanism is consistent with this information?
   Mechanism 1
   $NO_2 + NO_2 \Rightarrow NO_3 + NO$ slow
   $CO + NO_3 \Rightarrow CO_2 + NO_2$ fast
   Mechanism 2
   $NO_2 + NO_2 \Rightarrow NO_3 + NO$ fast
   $CO + NO_3 \Rightarrow CO_2 + NO_2$ slow
   [**1**]
8. **(L6_C)** The proposed mechanism for a reaction $ClO^- + I^- \leftrightarrow IO^- + Cl^-$ is:
   $ClO^- + H_2O \leftrightarrow HClO + OH^-$ Fast
   $I^- + HClO \leftrightarrow HIO + Cl^-$ Fast
   $OH^- + HIO \leftrightarrow H_2O + IO^-$ Slow
   Which of the following would be a rate law for the reaction? [**rate = $k[ClO^-][I^-]/[Cl^-]$**]

11.IV

9. **(L6_C)** A first order reaction has an activation energy of 48 kJ/mol and a frequency factor (Arrhenius constant) of 5×10^{10} sec^{-1}. Calculate the rate constant at 27 °C. Use the nearest whole number.[**219**]
10. **(L6_A)** A first order reaction has a rate constant of 0.52 s^{-1} at 34.1 °C. if the activation energy is 63.6kJ, calculate the temperature in °C at which the rate constant is 0.979 s^{-1}.

1. What is the reaction order of Br^- for a reaction with the following rate law? Rate = $k[BrO_3^-][Br^-][H^+]^2$ [**first**]

2. Consider the reaction with the rate law, Rate = $k[BrO_3^-][Br^-][H^+]^2$.
   By what factor does the rate change if the concentration of H^+ is quadrupled? Just put in the number as a whole number or fraction. [**16**]

3. Given the data below for the reaction, 2 A + 2 B + 4 C => D + E + 3 F, the reaction is [x1] order in A, [x2] order in B, [x3] order in C and [x4] order overall. USE WORDS TO FILL IN THE BLANKS NOT NUMBERS (i.e., zero, first, second etc) !!!!! :

Experiment	Initial conc of A, mol/L	Initial conc of B, mol/L	Initial conc of C, mol/L	Initial rate, mol/L.s
1	0.1	0.2	0.4	2×10^{-3}
2	0.2	0.2	0.4	2×10^{-3}
3	0.3	0.4	0.4	4×10^{-3}
4	0.4	0.6	0.2	1.5×10^{-3}

[**zero, first, first, total two**]

4. The reaction, AB => A(g) + B(g), has a rate law, rate = $k[AB]^2$. Calculate the rate constant in L/mol·s. If it takes 120 seconds to reach an [AB] of 0.2 mol/L from an initial concentration of 0.8 mol/L. (Enter your answer to 3 decimal places) [(**0.031**]

5. In a first order decomposition in which the rate constant is 0.5 sec^{-1}, how long will it take (in minutes) until 1.6 mol/L of the compound is left, if there was 4 mol/L at the start? Give your answer to 3 decimal places. [**0.031**]

6. Consider the reaction, A + B + C => D, which is found to be first order in A and first order in B. Which step of the proposed mechanism must be slow in order to agree with this rate law?
   1. A(g) + B(g) => X(g)
   2. X(g) + C(g) => Y(g)
   3. Y(g) => D(g)
   [**1**]

7. For the reaction $NO_2(g) + CO(g) \Rightarrow NO(g) + CO_2(g)$ at temperatures below 500 K, the rate law is rate = $k\,[NO_2]^2$. Which mechanism is consistent with this information?

   Mechanism 1

   $NO_2 + NO_2 \Rightarrow NO_3 + NO$ slow

   $CO + NO_3 \Rightarrow CO_2 + NO_2$ fast

   Mechanism 2

   $NO_2 + NO_2 \Rightarrow NO_3 + NO$ fast

   $CO + NO_3 \Rightarrow CO_2 + NO_2$ slow

   [**1**]

8. The proposed mechanism for a reaction $ClO^- + I^- \leftrightarrow IO^- + Cl^-$ is:

   $ClO^- + H_2O \leftrightarrow HClO + OH^-$ Fast

   $I^- + HClO \leftrightarrow HIO + Cl^-$ Fast

   $OH^- + HIO \leftrightarrow H_2O + IO^-$ Slow

   Which of the following would be a rate law for the reaction? [**rate = *k*$[ClO^-][I^-]/[Cl^-]$**]

9. A first order reaction has an activation energy of 48 kJ/mol and a frequency factor (Arrhenius constant) of 5 x 10^{10} sec $^{-1}$. Calculate the rate constant at 27 ^{o}C. Use the nearest whole number.[**219**]

10. A first order reaction has a rate constant of 0.52 s^{-1} at 34.1 °C. if the activation energy is 63.6kJ, calculate the temperature in °C at which the rate constant is 0.979 s^{-1}.