CH11.

I. Chemical reaction and rate:

$aA + bB \rightarrow cC + dD$

$$\text{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

II. Rate law:

Differential rate law:

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

Integrated rate law:

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

Unit of rate constant: 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	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$

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III. Reaction mechanism:
elementary steps and rate determine step
1. Write out the overall balanced eq. identify the reactants, products, and intermediate
2. Write the rate law by using the rate determine step
3. If the rate law contains non-reactant, use K_{eq} from other steps to derive the final rate law *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 10

11.I-II

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, two, total three**]
4. The reaction, AB => A(g) + B(g), has a rate law, rate = $[AB]^2$. 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**]

11.III

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 = $k[ClO^-][I^-]/[Cl^-]$**]

11.IV

9. 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. A first order reaction has a rant 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) !!!!! :

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

4. The reaction, AB => A(g) + B(g), has a rate law, rate = $[AB]^2$. 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**]

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   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?

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   $NO_2 + NO_2 \Rightarrow NO_3 + NO$ slow

   $CO + NO_3 \Rightarrow CO_2 + NO_2$ fast

   Mechanism 2

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   $CO + NO_3 \Rightarrow CO_2 + NO_2$ 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

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

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