Nuggets: Methods to determine Rate Law: 6. Mechanisms; Reaction Coordinate Diagrams; Arrhenius Equation/Graph, Catalysts

DIFFERENT METHODS TO DETERMINE RATE LAW (i.e., find the order, k, initial concentration)
   I. Initial rates method  (see Help Sheet #6)
   II. Description  (see Help Sheet #6)
   III. Integrated Rate Laws – Graphs  (see Help Sheet #7)
   IV. Half-life, \( t_{1/2} \): \([A]\) versus time – Graphs  (see Help Sheet #7)
   V. Rate versus Concentration – Graphs  (see Help Sheet #7)
   VI. Mechanisms  (see below: this Help Sheet)

From Kinetic Molecular Theory, for a reaction to proceed:
   1. Collision must occur
   2. Correct molecular orientation
   3. Sufficient energy

VI. MECHANISMS: series of chemical steps called elementary steps, elementary reactions, or elementary processes; Molecularity: number of species that collide; nanoscale view; molecular transformations:
   - Unimolecular step: \( A \rightarrow \) products
   - Bimolecular step: \( A + B \rightarrow \) products or \( A + A \rightarrow \) products
   - Termolecular step: \( A + B + C \rightarrow \) products or \( A + A + B \rightarrow \) products (very unlikely to occur)

The rate law for an elementary reaction, \( nA + mB \rightarrow \) products, is written: \( \text{Rate} = k[A]^n[B]^m \)
where \( n \) and \( m \) are stoichiometric coefficients, that is, numbers! For the elementary reaction: \( A + A \rightarrow A_2 \),
Rate = \( k[A]^2 \); this method of writing rate laws applies only to elementary reactions not overall reactions.

Intermediate: initially appears as product in the mechanism and then as a reactant; does not appear in final rxn
Catalysis: initially appears as reactant in the mechanism and then as a product; does not appear in final rxn

Rate-determining step: the slow step in a reaction mechanism is usually the step with the largest activation energy; use the rate-determining step in the mechanism to determine rate law. All chemicals in the rate law must be reactants or products in the overall reaction, or be a catalyst; no intermediates are allowed in the rate law; if an intermediate is present, then a substitution is needed

Temperature: changes both the rate of the reaction and \( k \); for every 10˚C \( \rightarrow \) reaction rate doubles (about)

Valid Mechanism: must satisfy all three criteria
   1. Unimolecular and bimolecular steps (termolecular steps too unlikely!)
   2. Steps when added yield the overall reaction
   3. Experimental rate law matches rate law predicted from the mechanism

Example 1 (slow step is first step): Given the mechanism below, a. Write overall reaction.  b. Identify each chemical as a reactant, product, intermediate, or catalyst.  c. Determine the rate law.

Answer 1:
   a. Overall reaction (just add reactions together and cancel out where possible):
      \( A_2 + B \rightarrow AB + A \) slow
      \( A_2 + B + A + B \rightarrow AB + A + AB \); simplifies to: \( A_2 + 2B \rightarrow 2AB \)
   b. overall rxn = reactants & products: \( A_2, B = \) reactants; \( AB = \) product; \( A = \) intermediate:
      it does not appear in the overall rxn and 1st appeared as a product in Step 1
   c. From slow step: rate = \( k_1[A_2]^1[B]^1 \) (\( k_1 \) is Step 1 rate constant)
**Example 2 (slow step is the second step):** Using the same mechanism above but with slow and fast steps changed determine the rate law. *(This ends up with an intermediate in the rate law; solved by making a substitution for the intermediate in the rate law.)*

Step 1: \[ A_2 + B \rightleftharpoons AB + A \] fast, equilibrium

Step 2: \[ A + B \rightarrow AB \] slow

**Answer 2:**

- **a.** From slow step: rate \( = k_2[A][B]^1 \) (\( k_2 \) is Step 2 rate constant)

- **b. Problem:** A is an intermediate and not allowed in a rate law. **Assumption** (fast equilibrium step): Rate forward = Rate reverse

- **c.** Rate reverse = \( k_{-1}[AB][A] \) (\( k_{-1} \) is rate constant for the reverse reaction of Step 1)

- **d.** Rate forward = \( k_1[A_2][B] \) (\( k_1 \) is rate constant for the forward reaction of Step 1)

- **e.** set Rate forward = Rate reverse: \( k_1[AB][A] = k_1[A_2][B] \)

- **f. factor out \([A]\):** \( [A](k_{-1}[AB]) = k_1[A_2][B] \) and solve for \([A]\): \[ [A] = \frac{k_1[A_2][B]}{k_{-1}[AB]} \]

- **g. substitute \([A]\) into original rate law above:** rate \( = k_2[A][B] \) \rightarrow rate \( = k_2\left(\frac{k_1[A_2][B]}{k_{-1}[AB]}\right)[B] \)

- **h. simplify:** rate \( = k_2\left(\frac{k_1}{k_{-1}}\right)\left(\frac{[A_2][B][B]}{[AB]}\right) \rightarrow rate = k \left[\frac{[A_2][B]^2}{[AB]}\right] \) where \( k = \frac{k_2k_1}{k_{-1}} \); note: \( \frac{k_1}{k_{-1}} = K \) (equilibrium constant)

**REACTION COORDINATE DIAGRAMS**

- Be able to label: reactants, products, intermediates, axes, transition state (TS), \( \Delta_r E \) (\( \Delta_r H \)), \( E_a \), \( E_a \) forward, \( E_a \) reverse

- **Endothermic:** products higher \( E \) than reactants (uphill); **Exothermic:** products lower \( E \) than reactants (downhill);

- **Fast reaction \( \rightarrow \) small \( E_a \); Slow reaction \( \rightarrow \) large \( E_a \**

**Activation Energy, \( E_a \)** - energy required to get over the "barrier"

**Transition state, TS** - complex at the top of the curve; TS is also sometimes called an **activated complex** and is sometimes represented by this graphic: [ ]

**Catalyst:** Changes to a reaction coordinate diagram when a catalyst is added – note how the forward and reverse \( E_a \) are reduced in size; the smaller \( E_a \) allows both the forward and reverse reactions to proceed faster since the barrier is smaller in both directions
ARRHENIUS EQUATION: $k = Ae^{-E_a/RT}$, which can be algebraically manipulated to:

$$\ln k = -\frac{E_a}{R} \left(\frac{1}{T}\right) + \ln A$$

this is an equation of a line, $y = mx + b$ with

- $A =$ frequency factor (same units as $k$);
- $E_a =$ activation energy (J or kJ);
- $R =$ 8.314 J/molK;
- $k =$ rate constant;
- $T$ in K

$y$ (axis) = $\ln k$, $x$ (axis) = $1/T$, slope = $-\frac{E_a}{R}$, and y-intercept = $\ln A$

activation energy needed to: allow collisions, rearrange bonds, and overcome steric hindrance (molecular shape)

$e^{-\frac{E_a}{RT}}$ represents the fraction of molecules that have sufficient energy to react

this equation can be algebraically manipulated to yield: $\ln \left(\frac{k_1}{k_2}\right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

(see this to find: $E_a$, $T_1$, $T_2$, $k_1$, or $k_2$ given the other 4 values)

when $T$ increases and reaction rate doubles with concentrations unchanged $\to k_{(\text{higher } T)} = 2 \times k_{(\text{lower } T)}$

$E_a \uparrow \to$ Rate $\downarrow$ (as the activation barrier, $E_a$, increases $\to$ rate decreases)

$T \uparrow \to k \uparrow \to$ Rate $\uparrow$ (as the temperature increases $\to$ $k$ increases $\to$ rate increases)

1. For a reaction to occur, what 3 criteria must be met?

2. Given the reaction below between hydrogen and iodine:

   $$\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$$

which of the following will increase the rate of the reaction?

- a. increasing the temperature
- b. adding a catalyst
- c. increase reactant concentrations
- d. both a and c
- e. a, b, and c

3. Assume that the mechanism for the reaction, $\text{NO} + \text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$, is

   Slow I. $\text{NO} + \text{Br}_2 \rightarrow \text{Br}_2\text{NO}$ ($\Delta H_1 = 50 \text{ kJ/mol}$)
   
   Fast II. $\text{Br}_2\text{NO} + \text{NO} \rightarrow 2\text{NOBr}$ ($\Delta H_{II} = -100 \text{ kJ/mol}$)

Draw the reaction coordinate diagram for the above mechanism. Include the axes' labels, identify the reactants and products for each step, the activation energies for each step (just label these $E_a$ - no numbers needed), note the $\Delta H$ values for each step and for the overall reaction, and identify where the activated complexes are.
4. Use the following mechanism to answer the questions below.

Rxn 1: \[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \] slow, endothermic
Rxn 2: \[ \text{O} + \text{NO}_2 \rightarrow \text{NO}_3 \] fast, exothermic
Rxn 3: \[ \text{NO}_3 + \text{CO} \rightarrow \text{NO}_2 + \text{CO}_2 \] fast, exothermic

a. Write the overall reaction.
b. What catalyst, if any, is present in the above mechanism?
c. What intermediate(s), if any, are present in the above mechanism?
d. What are the product(s) in the overall reaction?
e. What is the rate law as determined from the above mechanism?
f. Draw the reaction coordinate diagram assuming the overall reaction is exothermic. Label the axis; write in the specific reactants, products, and intermediates; identify where the transition states/activated complexes are; and mark the activation energies of all forward reactions and the enthalpy of reaction.

5. Use the following mechanism to answer the questions below.

Rxn 1: \[ \text{N}_2 + \text{O} \rightleftharpoons \text{NO} + \text{N} \] fast, equilibrium
Rxn 2: \[ \text{N} + \text{O} \rightarrow \text{NO} \] slow

a. Write the overall reaction.
b. What catalyst, if any, is present in the above mechanism?
c. What intermediate(s), if any, are present in the above mechanism?
d. What are the reactant(s) in the overall reaction?
e. What is the rate law as determined from the above mechanism?

6. Use the following mechanism to answer the questions below.

Rxn 1: \[ 2\text{NO} \rightleftharpoons \text{N}_2\text{O}_2 \] fast, equilibrium
Rxn 2: \[ \text{N}_2\text{O}_2 + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} \] slow

a. Write the overall reaction.
b. What catalyst, if any, is present in the above mechanism?
c. What intermediate(s), if any, are present in the above mechanism?
d. What are the reactant(s)?
e. What are the products(s)?
f. What is the rate law as determined from the above mechanism?

7. a. Describe briefly how increasing the temperature increases the rate of reaction.
b. Describe briefly how adding a catalyst increases the rate of reaction.

8. For a chemical reaction that has a \( \Delta_r H = -100 \text{kJ} \), the activation energy is 25kJ. What is the activation energy for the reverse reaction? (Hint: Draw a simple one-step reaction coordinate diagram and add the energies listed in the problem.)

9. During a certain reaction, it was found that the rate constant at 18.0°C was \( 1.50 \times 10^{-3} \text{min}^{-1} \) and that at 25.0°C it increased to \( 9.00 \times 10^{-3} \text{min}^{-1} \). What is the activation energy for this reaction?

10. For a first order gas-phase reaction, the activation energy was determined to be 72.5kJ/mol, and the rate constant at 25.5°C was \( 7.85 \times 10^{-2} \text{hr}^{-1} \). What would be the rate constant at 58.5°C?

11. In a reaction it was determined that the rate would triple when the temperature was increased 10°C from 35°C. What is the activation energy for the reaction?
12. Using the plot of ln(k) versus 1/T, answer the following questions. Assume the graph values have 4 sig figs.

I. What is the value of the frequency factor, A?
   a. 3067  
   b. 8.41  
   c. 368.9  
   d. 4492  
   e. None of these

II. What is the value of the activation energy in J/mol?
   a. 3067  
   b. 251.8  
   c. 25,500  
   d. 8.41  
   e. 368.9

III. What is the value of the rate constant at 400K?
   a. 0  
   b. 0.7422  
   c. 2.101  
   d. 9.602 x 10^6  
   e. none of these

IV. What is the order of the reaction?
   a. 0 order  
   b. 1st order  
   c. 2nd order  
   d. Can’t be determined from info given.

ANSWERS
1. A collision must occur with sufficient energy and with the correct orientation.

2. e
4. a. NO₂ + CO → NO + CO₂
b. none
c. NO₃ and O  \{first appears as a product, then a reactant; does not appear in the overall reaction\}
d. NO and CO₂
e. rate = k₁[NO₂] \{use slow step: rate = k₁[NO₂]¹; since NO₂ is a reactant the rate law is done\}

f. 

5. a. N₂ + 2O → 2NO
b. none
c. N  \{first appears as a product, then a reactant; does not appear in the overall reaction\}
d. N₂, O
e. rate = k \left( \frac{[N₂][O]^2}{[NO]} \right) \quad \text{with} \quad k = \frac{k₂k₁}{k₋₁}  \quad \text{\{from slow step: rate = k₂[N][O]; [N] is intermediate: need to make a substitution for [N]\}}

\text{set rate forward = rate reverse: } k₁[N₂][O] = k₋₁[NO][N];

\text{rearrange to solve for } [N]: k₁[N₂][O] = [N](k₋₁[NO]); \quad [N] = \frac{k₁[N₂][O]}{k₋₁[NO]};

\text{substitute into original rate law: } \text{rate} = k₂ \left( \frac{k₁[N₂][O]}{k₋₁[NO]} \right) [O];

\text{simplify: } \text{rate} = k₂ \left( \frac{k₁[N₂][O][O]}{[NO]} \right); \quad \text{rate} = k \left( \frac{[N₂][O]^2}{[NO]} \right) \quad \text{where} \quad k = \frac{k₂k₁}{k₋₁} \}
6. a. $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
b. none
c. $\text{N}_2\text{O}_2$  (first appears as a product, then a reactant; does not appear in the overall reaction)
d. $\text{NO}; \text{H}_2$
e. $\text{N}_2\text{O}; \text{H}_2\text{O}$
f. $\text{rate} = k[\text{NO}][\text{H}_2]$ with $k = \frac{k_2k_1}{k_{-1}}$  
   \text{from slow step: rate} = k_2[\text{N}_2\text{O}_2][\text{H}_2]; [\text{N}_2\text{O}_2]$ is an \textit{intermediate} so need to make a substitution for $[\text{N}_2\text{O}_2]$;

   $\text{set rate forward} = \text{rate reverse: } k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$;  
   \text{rearrange to solve for } [\text{N}_2\text{O}_2]:  
   \begin{align*}
   [\text{N}_2\text{O}_2] &= \frac{k_1[\text{NO}]^2}{k_{-1}} \\
   \text{simplifying into original rate law above: } \text{rate} &= k_2\left(\frac{k_1[\text{NO}]^2}{k_{-1}}\right)[\text{H}_2] \\
   \text{where } k &= \frac{k_2k_1}{k_{-1}}
   \end{align*}$

7. a. As the temperature is increased, the molecules move faster. As they move faster, the number of collisions increases (\textit{i.e.}, frequency of collisions increases) and the energy at which the molecules collide increase (\textit{i.e.}, more molecules will have energy greater than $E_a$). If there are more collisions and they occur with greater energy, the number of molecules that react (as opposed to simply bouncing off) will increase.
b. A catalyst provides another mechanism at lower energy for the reaction to occur; that is, the $E_a$ is lowered. If the $E_a$ is lowered, then the number of molecules that can react increases since more will have sufficient energy to complete the reaction.

8. $125\text{kJ}$  \(\{25 + 100 = 125\text{kJ}; \text{the negative sign for the exothermic rxn is not used during the calculation because you're measuring a distance; see diagram}\}$

[Diagram of Reaction Coordinate]

\[
\begin{align*}
\text{Ea} &= 25\text{kJ} \\
\Delta H &= -100\text{kJ} \\
\text{Ea(rev)} &= ?
\end{align*}
\]

\[
\ln \left( \frac{k_1}{k_2} \right) = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) ;
\ln \left( \frac{9.0 \times 10^{-3}}{1.5 \times 10^{-3}} \right) = \frac{E_a}{8.314} \left( \frac{1}{273+18} - \frac{1}{273+25} \right) ;
\ln(6) = \frac{E_a}{8.314} \left( \frac{1}{291} - \frac{1}{298} \right) ;
\]

\[
14.8970 = E_a \left( 0.003436 \right) - \left( 0.003356 \right) ;
14.8970 = E_a \left( 0.00008072 \right) ;
E_a = 184.552\text{J} \times (1\text{kJ}/1000\text{J}) = 184.55\text{kJ}
\]
10. \(1.43\text{hr}^{-1}\) \(\{\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\}; \ln\left(\frac{k_1}{7.85 \times 10^{-2}}\right) = 8720\left(\frac{1}{298.7} - \frac{1}{331.7}\right)\); \(\ln\left(\frac{k_1}{7.85 \times 10^{-2}}\right) = 8720(0.0033478 - 0.0030148)\); \(\ln\left(\frac{k_1}{7.85 \times 10^{-2}}\right) = 2.9038\);

\[e^{\ln\left(\frac{k_1}{7.85 \times 10^{-2}}\right)} = e^{2.9038} \quad \frac{k_1}{7.85 \times 10^{-2}} = 18.243; \quad k_1 = 1.432\text{hr}^{-1}\}

11. \(89.5\text{kJ}\) \(\{\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)\}; \ln\left(\frac{k_1}{3k_1}\right) = \frac{E_a}{8.314}\left(\frac{1}{(273+45)} - \frac{1}{(273+35)}\right)\); \(\ln\left(\frac{1}{3}\right) = \frac{E_a}{8.314}\left(\frac{1}{318} - \frac{1}{308}\right)\);

\[\ln\left(\frac{1}{3}\right) = E_a (-0.00001228); \quad E_a = 89464\text{J} \times (1\text{kJ/1000J}) = 89.46\text{kJ}\}

12. I. d \{from \(y = mx + b\); \(\ln k = \frac{E_a}{RT} \left(\frac{1}{T}\right)\) + ln(A), \(b = \ln(A)\) and hence, \(\ln(A) = 8.41\); \(e^{\ln(A)} = e^{8.41}; \quad A = 4492\}\)

II. c \{slope = -3067.12; \(\text{slope} = -E_a/R\); -3067.12 = -\(E_a/8.314\); \(E_a = (3067.12)(8.314) = 25,500\text{J}\}\)

III. c \{\ln(k) = -3067.12\left(\frac{1}{T}\right) + 8.41; \quad T = 400\text{K}; \quad \frac{1}{T} = 0.0025; \quad \ln(k) = -3067.12(0.0025) + 8.41; \quad \ln(k) = 0.7422; \quad e^{\ln(k)} = e^{0.7422}; \quad k = 2.101\}

IV. d \{a plot of \([A]\) versus time, \(\ln[A]\) versus time, or \(1/[A]\) versus time will reveal the order of a chemical – not a plot of \(\ln k\) vs \(1/T\)\}