Unit 5 Study guide

Reaction rate and rate laws

1. For this reaction, $CH_3NC \rightarrow CH_3CN$, and using the data in the table below, calculate the average rate of reaction, in M/s, for the time interval between each measurement.

Time (s)	**[CH3NC] (M)**	**Average rate (M/s)**
0	0.0165	
2 000	0.0110	
5 000	0.00591	
8 000	0.00314	
12 000	0.00137	
15 000	0.00074	

2. For each reaction shown below, write the rate expression in terms of the appearance of each product or the disappearance of each reactant (the rate expression has all the delta signs).
   a. $2SO_2 + O_2 \rightarrow 2SO_3$
   b. $2NO + 2H_2 \rightarrow N_2 + 2H_2O$

3. $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate law is first order in N_2O_5. At 64 degrees, the rate constant is $4.82\times10^{-3}\ s^{-1}$.
   a. Write the rate law for the reaction.
   b. What is the rate of the reaction when $[N_2O_5] = 0.0240$ M?
   c. What happens to the rate when the concentration of N_2O_5 is doubled to 0.0480 M?

4. To study the rate of this reaction, A + B → C, a student makes measurements of the initial rates under the following conditions:

Trial 1	[A] = 1.0 M	[B] = 1.0 M
Trial 2	[A] = 2.0 M	[B] = 1.0 M

   a. What reactant concentration could be used for Trial 3 in order to determine the rate law, assuming that the rate law is of this form: rate = $k[A]^x[B]^y$
   b. For this reaction, A + B + C → products, the following observations are made; doubling the concentration of A doubles the rate; tripling the concentration of B has no effect on the rate, and tripling the concentration of C increases the rate by a factor of 9. By what factor will the rate change if the concentrations of A, B, and C are all halved?

5. For this reaction, $OCl^- + I^- \rightarrow OI^- + Cl^-$, the following data were collected:

$[OCl^-]$, M	$[I^-]$, M	Rate, M/s
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{4}
3.0×10^{-3}	1.5×10^{-3}	2.72×10^{4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{4}

   a. Write the rate law for this reaction.
   b. Calculate the rate constant with units.
   c. Calculate the rate when $[OCl^-] = 1.0 \times 10^{-3}$ M and $[I^-] = 5.0 \times 10^{-4}$ M.

6. For this reaction, $2ClO_2 + 2OH^- \rightarrow ClO_3^- + ClO_2^- + H_2O$, the following data were collected:

$[ClO_2]$, M	$[OH^-]$, M	Rate, M/s
.060	.030	.0248
.020	.030	.00276
.020	.090	.00828

   a. Write the rate law for this reaction.
   b. Calculate the rate constant with units.
   c. Calculate the rate when $[ClO_2] = 0.010$ M and $[OH^-] = 0.015$ M.

7. For this reaction, $BF_3 + NH_3 \rightarrow F_3BNH_3$, the following data were collected:

Experiment	$[BF_3]$ (M)	$[NH_3]$, M	Initial Rate, M/s
1	.250	.250	.2130
2	.250	.125	.1065
3	.200	.100	.0682
4	.350	.100	.1193
5	.175	.100	.0596

   a. Write the rate law for this reaction.
   b. What is the overall order of the reaction?
   c. What is the value of the rate constant for the reaction?

Half-life problems

The reaction A → B is first order in [A]. Consider the following data.

time (s)	[A] (M)
0.0	1.60
10.0	0.40
20.0	0.10

1. The rate constant with units for this reaction is _____________.

2. The half-life for this reaction is ______________.

3. The rate constant of a first-order process that has a half-life of 225 s is ________________.

4. At elevated temperatures, nitrogen dioxide decomposes to nitrogen oxide and oxygen:

   $NO_2\,(g) \rightarrow NO\,(g) + \frac{1}{2}O_2\,(g)$

   The reaction is second order in NO_2 with a rate constant of 0.543 $M^{-1}s^{-1}$ at 300˚C. If the initial $[NO_2]$ is 0.260 M, it will take ______________ s for the concentration to drop to 0.100 M.

5. The reaction below is first order in $[H_2O_2]$:

   $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$

   A solution originally at 0.600 M H_2O_2 is found to be 0.075 M after 54 min. The half-life for this reaction is _______________ min.

6. A second-order reaction has a half-life of 18 s when the initial concentration of reactant is 0.71 M. The rate constant for this reaction is ____________ $M^{-1}s^{-1}$.

Mechanism practice

$2\ NO_2 \rightarrow NO_3 + NO$ (slow)
$NO_3 + CO \rightarrow NO_2 + CO_2$ (fast)

1. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

   $O_3 \leftrightarrow O + O_2$ (fast)
   $O + O_3 \rightarrow 2O_2$ (slow)

2. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute. (The rate law will look very strange, unlike anything you've seen. But it is correct.)

$Br_2 + NO \rightarrow NOBr_2$ (slow)
$NOBr_2 + NO \rightarrow 2\ BrNO$ (fast)

3. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

$2NO \leftrightarrow N_2O_2$ (fast equilibrium)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)
$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

4. Based on the above two-step mechanism, write the overall equation and predict the rate for the reaction. Note that an intermediate CANNOT be in the rate law. Substitute.

MC practice

1. Hydrogen iodide decompose to give a mixture of hydrogen and iodine:

$2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

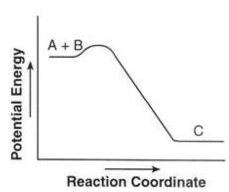
Trial	[HI] (M)	Initial Rate (M/sec)
1	1.0×10^{-2}	4.0×10^{-6}
2	2.0×10^{-2}	1.6×10^{-5}
3	3.0×10^{-2}	3.6×10^{-5}

The order of the decomposition of HI in the gas phase is

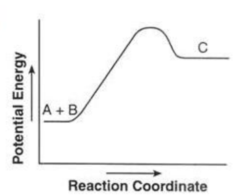
   a. 0
   b. 1
   c. 2
   d. 3
   e. 4

2. Which of the following is a graph that describes the pathway of reaction that is exothermic and has relatively high activation energy?

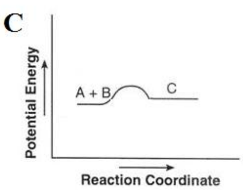
A



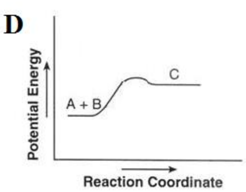
B



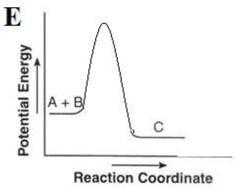
C



D



E



4. Which of the following, if increased, does not increase reaction rate?
    a. Reactant concentration
    b. Surface area
    c. Pressure
    d. Activation energy
    e. Temperature

5. The rate constant
    a. Always shows an exponential increase with the Kelvin or absolute temperature
    b. Increase with increasing concentration
    c. Usually increases with increased pressure for gases
    d. Never changes (it is constant)
    e. Is the same for a given reaction at the same Kelvin or absolute temperature

6. The reaction

    $2NO_{2(g)} + F_{2(g)} \rightarrow 2NO_2F_{(g)}$

    Follows the mechanism below:

    $NO_2 + F_2 \rightarrow NO_2F + F$ **(slow)**

    $NO_2 + F \rightarrow NO_2F$ **(fast)**

    The rate law would be consistent with

    a. Rate= $k[NO_2]^3[F_2]^2$
    b. Rate= $k[NO_2]^2[F_2]$
    c. Rate= $k[NO_2][F_2]$
    d. Rate= $k[NO_2]^2[F_2]^2$
    e. Rate= $k[NO_2][F_2]^2$

7. A reaction is first order with respect to [X] and second order with respect to [Y]. When [X] is 0.20 M and [Y] is 0.20 M the rate is 8.00×10^{-3} M/min. the value of the rate constant, including units, is
    a. 1.00 M min^{-1}
    b. 1.00 M^{-2} min^{-1}
    c. 2.00 M^{-1} min^{-1}
    d. 2.0 M^{-2} min^{-1}
    e. 8.00×10^{-3} min^{-3}

8. Which of the following rate laws has a rate constant with units of L mol^{-1} sec^{-1}?
    a. Rate=k[A]
    b. Rate=$k[A]^2$
    c. Rate=$k[A]^2[B]$
    d. Rate=$k[A][B]^2$
    e. Rate=$k[A]^0$

9. A first order reaction has a half-life of 85 s. What factors of the reactant is left after 255 s?
    a. ½
    b. ¼
    c. ⅛
    d. ⅓
    e. ⅞

10. If a reactant's concentration is doubled and the reaction rate increases by a factor of 8, the exponent for that reactant in the rate law should be
    a. 3
    b. 2
    c. 1
    d. 0
    e. ½

11. A graph of the reciprocal of reactant concentration versus time will give a straight-line for
    a. A zero order reaction
    b. A first order reaction
    c. A second order reaction
    d. Both A and C
    e. A, B and C

12. The activated complex may be described as
    a. An elementary reaction in a mechanism
    b. The shape of the molecules at the moment of collision
    c. The shape of the reaction product
    d. The phase- liquid, solid, or gas- in which a reaction takes place
    e. The final state

13. The Molecularity of an elementary step
    a. Specifics that the particles taking part in the reaction are molecules
    b. Indicates the order of the reaction
    c. Specifies the number of reacting species participating in that step
    d. Is a measure of the energy released or absorbed in the reaction
    e. Indicates the size of the reacting particles; a high Molecularity meaning a small particle size

14. Which of the following statements is false?
    a. An exothermic reaction always goes faster than an endothermic reaction
    b. A catalyst provides a different route by which the reaction can occur
    c. Some reactions may never reach completion (100% products)
    d. The rate of a reaction depends upon the height of the energy barrier
    e. Increase in temperature usually increases the rate of a reaction

15. A graph of the natural log of reactant concentration versus time will give a straight-line for
    a. A zero order reaction
    b. A first order reaction
    c. A second order reaction
    d. Both A and C
    e. A, B and C

16. Addition of a catalyst to a reaction mixture
    a. Increases the activation energy of a reaction
    b. Decreases the energy required to activate the reaction
    c. Has no effect of the activation energy of a reaction
    d. Decreases the frequency of collisions that are effective
    e. Has not effect on the frequency of collisions that are effective

17. A possible mechanism for the overall reaction $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ is the following:

    $NO(g) + NO(g) \rightarrow N_2O_2(g)$ (slow)

    $N_2O_2(g) + O_2(g) \rightarrow 2\ NO_2(g)$ (fast)

    Which of the following rate expressions agrees best with this possible mechanism?

    a. Rate = $k[NO]^2$
    b. Rate = $k[NO]/[O_2]$
    c. Rate = $k[NO]^2/[O_2]$
    d. Rate = $k[NO]^2[O_2]$
    e. Rate = $k[N_2O_2][O_2]$

For questions 18-21

Consider the following reaction between hydrogen gas and nitrous oxide:

$$2H_2(g) + 2\ NO(g) \rightarrow 2\ H_2O(g) + N_2(g)$$

The rate law for this reaction is

$$\text{Rate} = k[H_2][NO]^2$$

18. What is the order of this reaction in respect to NO?
    a. 0
    b. 1
    c. 2
    d. 3
    e. 4

19. What is the overall order of the reaction?
    a. 0
    b. 1
    c. 2
    d. 3
    e. 4

20. If the concentration of NO is tripled, the reaction rate will increase by a factor of
    a. 3
    b. 9
    c. 27
    d. 54
    e. 81

21. The following are three mechanisms by which the reaction can proceed. On the basis of the observed rate law, which mechanism(s) can be ruled out?

Mechanism I

$H_2 + NO \rightarrow H_2O + N$ (slow)

$N + NO \rightarrow N_2 + O$ (fast)

$O + H_2 \rightarrow H_2O$ (fast)

Mechanism II

$H_2 + 2\ NO \rightarrow N_2O + H_2O$ (slow)

$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

Mechanism III

$2\ NO \leftrightarrow N_2O_2$ (fast equilibrium)

$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

$N_2O + H_2 \rightarrow N_2 + H_2O$ (fast)

    a. I only
    b. II only
    c. III only
    d. I and II
    e. II and III

FRQ practice

Free response 1:

$2\ ClO_2(aq) + 2\ OH^-(aq) \rightarrow ClO_3^-(aq) + ClO_2^-(aq) + H_2O(l)$

A series of experiments were conducted to study the above reaction. The initial concentrations and rates are reported in the table below.

EXPERIMENT	INITIAL CONCENTRATION (mol/L)		INITIAL RATE OF FORMATION OF ClO_3^- (mol/L min)
	$[OH^-]$	$[ClO_2]$	
1	0.030	0.020	0.166
2	0.060	0.020	0.331
3	0.030	0.040	0.661

a.
   i. Determine the order of the reaction with respect to each reactant. Make sure you explain your reasoning.
   ii. Give the rate law for the reaction.

b. Determine the value of the rate constant. Include units.

c. Calculate the initial rate of disappearance of ClO_2 in experiment 1.

d. The following has been proposed as a mechanism for this reaction. Which step is the rate-determining step?

   Step 1: $ClO_2 + ClO_2 \leftrightarrow Cl_2O_4$ (fast equilibrium)
   Step 2: $Cl_2O_4 + OH^- \rightarrow ClO_3^- + HClO_2$ (slow)
   Step 3: $HClO_2 + OH^- \rightarrow ClO_2^- + H_2O$ (fast)

e. Show that this mechanism is consistent with:
   i. The overall rate law for the reaction, and
   ii. The overall stoichiometry of the reaction

Free response 2:

Initial rate data were collected for the following reaction in which iodide ion is oxidized to triiodide by peroxydisulfate ion:

$S_2O_8^{2-}{}_{(aq)} + 3I^-{}_{(aq)} \rightarrow 2SO_4^{2-}{}_{(aq)} + I_3^-{}_{(aq)}$

Experiment	**$[S_2O_8^{2-}]$ (M)**	**$[I^-]$ (M)**	**Initial rate (M/sec)**
1	0.080	0.034	2.2×10^{-4}
2	0.080	0.017	1.1×10^{-4}
3	0.160	0.017	2.2×10^{-4}
4	0.280	???	5.7×10^{-4}

a. Write the rate law for the overall reaction.
b. Determine the value of the rate constant, *k*, for the reaction. Include units with your answer.
c. Calculate the initial concentration of I^- for experiment 4.
d. What is the overall order of this reaction?
e. What does the overall order indicate about the slow step of the reaction mechanism?

Free response 3:

Consider the proposed mechanism for the reaction between nitrogen monoxide and hydrogen gas. Assume the mechanism is correct

Step 1:	$2\ NO \rightarrow N_2O_2$
Step 2:	$N_2O_2 + H_2 \rightarrow N_2O + H_2O$
Step 3:	$N_2O + H_2 \rightarrow N_2 + H_2O$

a. Use the steps in the mechanism to determine the overall balanced equation for the reaction. Clearly show your method

b. If step 2 is the rate-determining step, write the rate law for the reaction, explain your answer

c. If the observed rate law is rate= $k[NO]^2[H_2]^2$, which step is rate determining? Explain your reasoning

d. If the first step is the rate-determining step, what is the order of reaction with respect to each reactant?

Free response 4:

$C_2H_4(g)$ reacts readily with $HCl(g)$ to produce $C_2H_5Cl(g)$, as represented by the following equation:

$C_2H_4(g) + HCl(g) \rightarrow C_2H_5Cl(g)$ $\Delta H^\circ = -72.6$ kJ/mol

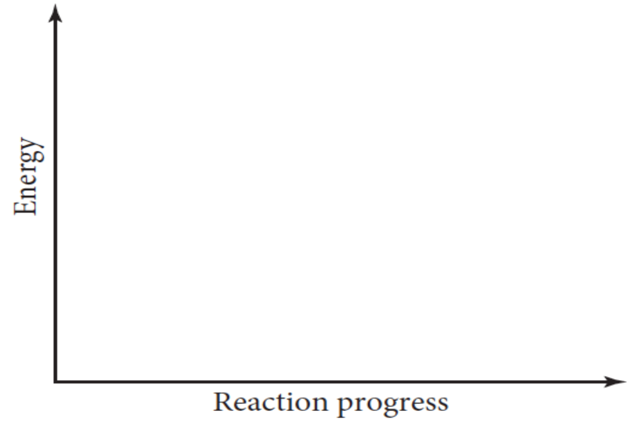
It is proposed that he formation of $C_2H_5Cl(g)$ proceeds via the following two step reaction mechanism:

Step 1: $C_2H_4 + HCl \rightarrow C_2H_5^+ + Cl^-$ (rate determining step)

Step 2: $C_2H_5^+ + Cl^- \rightarrow C_2H_5Cl$ (fast step)

a. Write the rate law for the reaction that is consistent with the reaction mechanism above.
b. Identify an intermediate in the reaction mechanism above.

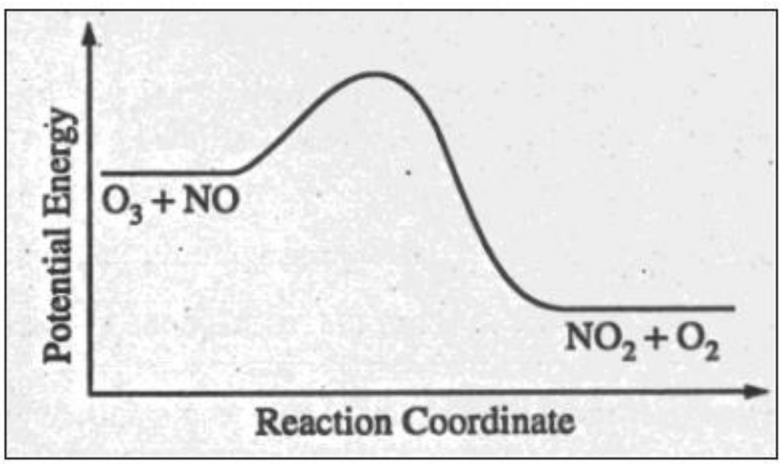
c. Using the axes provided below, draw a curve that shows the energy changes that occur during the progress of the reaction. The curve should illustrate both the proposed two step mechanism and the enthalpy change of the reaction.



d. On the diagram above, clearly indicate the activation energy, E_a, for the rate determining step in the reaction.

Free response 5:

Answer the following questions regarding the kinetics of chemical reactions.



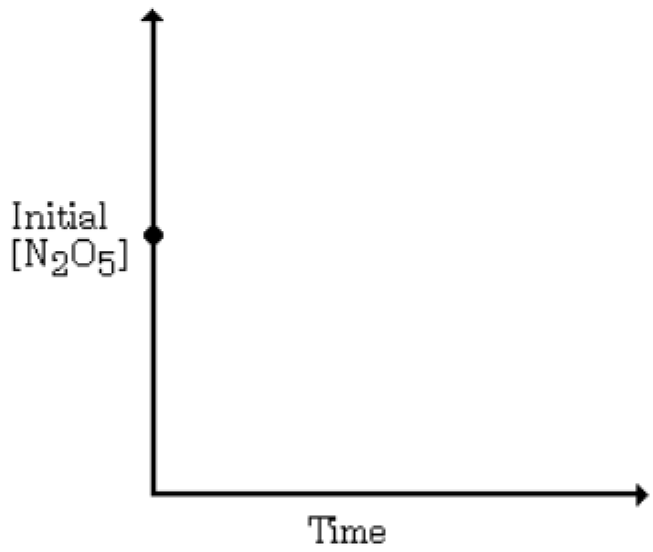
a. The diagram above shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$. Clearly label the following directly on the diagram.

   i. The activation energy (E_a) for the forward reaction

   ii. The enthalpy change (ΔH) for the reaction.

b. The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.

   i. Using the axis, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.

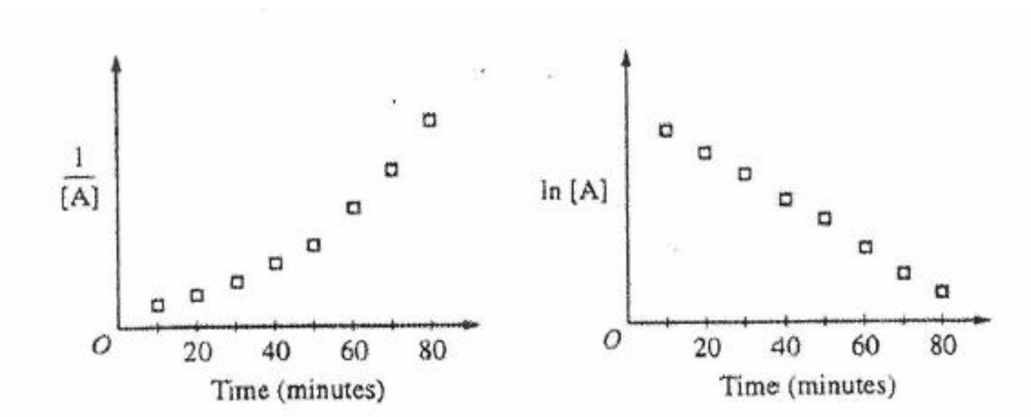


ii. Describe how the graph in (i) could be used to find the reaction rate at a given time t.

iii. Considering the rate law and the graph in (i), describe how the value of the rate constant, k, could be determined.

iv. If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k? Explain.

c. Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of the data.



Use the information in the graphs above to answer the following.

i. Write the rate-law expression for the reaction. Justify your answer.

ii. Describe how to determine the value of the rate constant for the reaction.