REACTION RATES

1. Distinguish between kinetic and thermodynamic regions of a reaction.

2. How does an increase in pressure affect the rate of a gas-phase reaction? What effect on the rate would doubling the pressure of A in a reaction that is second order in A?

3. How does an increase in temperature affect the rate of reaction?

4. What is the reaction rate? How is the rate of disappearance of a reactant related to the rate of reaction?

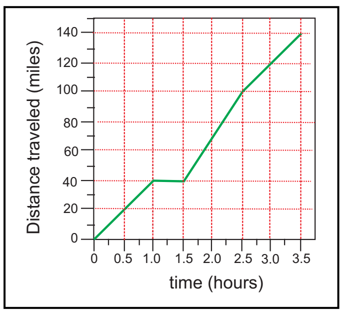
5. Why does the rate of reaction decrease as the reaction proceeds?

6. Sketch the concentrations of X and Y versus time for the first order decomposition of X by the reaction $X \rightarrow 2Y$ with the following equilibrium constants. Label the thermodynamic and kinetic regions.

a) K >> 1 **b)** K < 1

7. Distinguish between average and instantaneous rates of reaction.

8. Consider the following plot of distance traveled versus time:



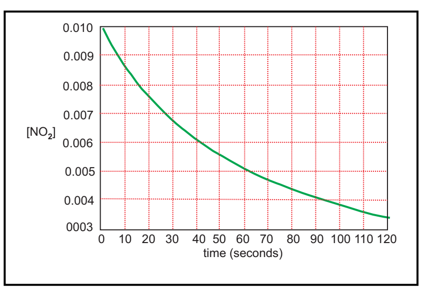
a) What is the average speed of the trip?

b) What is the instantaneous speed at the following times?

i) 0.5 hr ii) 1.2 hr

iii) 2.0 hr iv) 3.0 hr

9. Consider the following plot of $[NO_2]$ versus time.



a) What is the average rate of disappearance of NO_2 over the time of the experiment?

b) Use the graphical methods presented in Section 10.1 to determine the rate of disappearance of NO_2 at 20 seconds and 80 seconds.

10. What is the rate of consumption of oxygen in a combustion reaction carried out in a 10.0-L flask if 3.32 mmol of O_2 is consumed in 18.3 μs?

11. What is the rate of formation ($M \cdot s^{-1}$) of NOBr gas in a reaction in which 13.4 μmol of NOBr is produced in a 38.9 mL-flask in 26.8 minutes?

12. Consider the following reaction: $3O_2(g) + 2N_2(g) \rightarrow 2N_2O_3(g)$. By what factor must the rate of disappearance of N_2 be multiplied to obtain the following:

a) the rate of disappearance of O_2

b) the rate of formation of N_2O_3

c) the rate of the reaction

13. What are the rates of appearance of NO_2 and O_2 at a time when the rate of disappearance of N_2O_5 is $2.0x10^{-5}$ $M{\cdot}s^{-1}$?

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

14. The combustion of ammonia is the first step in the Ostwald process, which is used in the production of nitric acid.

$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$

What is the rate of disappearance of ammonia and the rates of formation of nitric oxide and water at a time when the rate of consumption of oxygen is $2.5x10^{-4}$ $M{\cdot}s^{-1}$?

RATE LAWS

15. What is an exponential decay? What type of kinetics is characterized by an exponential decay?

16. A reaction has the experimentally determined rate law: rate = $k[NO_2][F_2]$. What is the reaction order? What is the order with respect to fluorine?

17. A reaction has the experimentally determined rate law: rate = $k[A][B]^2$. What is the reaction order? What is the order with respect to A and with respect to B?

18. The reaction of hydrogen with iodine monochloride to produce hydrogen chloride and iodine is first order in both hydrogen and iodine monochloride. Write the balanced chemical equation and the rate law.

19. The reaction $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$ is second order in NO_2. What is the second-order rate constant if the rate of formation of O_2 is $5.0x10^{-5}$ $M{\cdot}s^{-1}$when the concentration of NO_2 is 0.012 M?

DETERMINING RATE LAWS

20. The following initial rates data were obtained for

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$.

Experiment	$[NO]_o$	$[O_2]_o$	$-(\Delta[O_2]/\Delta t)_o$ $M{\cdot}s^{-1}$
I	0.0150	0.0100	0.0184
II	0.0300	0.0100	0.0738
III	0.0300	0.0300	0.2214

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

21. The following initial rate data were obtained for

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

Experiment	$[NO]_o$	$[H_2]_o$	$(\Delta[N_2]/\Delta t)_o$ $M{\cdot}s^{-1}$
I	0.326	0.118	0.0859
II	0.109	0.118	0.00954
III	0.326	0.0295	0.0215

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

22. The reaction $5Br^{1-}(aq) + BrO_3^{1-}(aq) + 6H^{1+}(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

has the following initial rates.

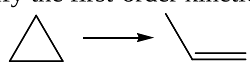
Exp	$[Br^{1-}]_o$	$[BrO_3^{1-}]$	$[H^{1+}]$	$(\Delta[Br^{1-}]/\Delta t)_o$ $M{\cdot}s^{-1}$
I	0.10	0.10	0.10	$6.8x10^{-4}$
II	0.15	0.10	0.10	$1.0x10^{-3}$
III	0.10	0.20	0.10	$1.4x10^{-3}$
IV	0.10	0.10	0.25	$4.3x10^{-3}$

What is the rate law for the reaction, and what is the value of the rate constant at the temperature of the experiments?

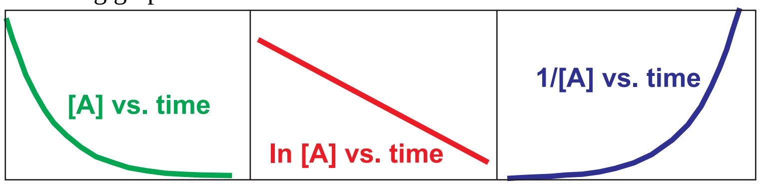
23. The kinetics of the conversion of cyclopropane to propene (see below) were studied at 500 °C by monitoring the concentration of cyclopropane versus time. The following data were obtained:

t	0	7.0	15.0	35.0	57.0	75.0	min
[Δ]	0.256	0.193	0.140	0.0626	0.0259	0.0126	M

Verify the first-order kinetics and determine the rate constant and half-life of the reaction at 500 °C.



24. The kinetics of the reaction 3A $\rightarrow$ B was studied by monitoring the concentration of A as a function of time. The following graphs were constructed from the data:

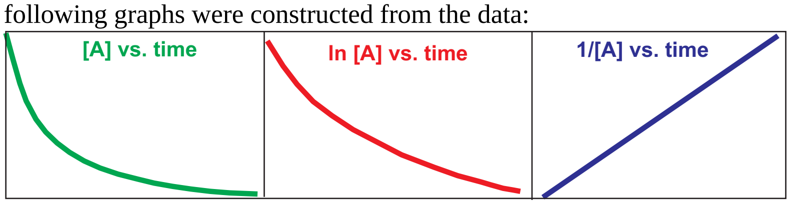


a) What is the rate law for the reaction?

b) Given the following concentrations, determine the specific rate constant for the reaction at the temperature of the experiment.

t	0	1000	10000	s
[A]	0.100	0.0878	0.0273	M

25. The kinetics of the reaction 2A $\rightarrow$ C was studied by monitoring the concentration of A as a function of time. The following graphs were constructed from the data:



a) What is the rate law for the reaction?

b) Given the following concentrations, determine the specific rate constant for the reaction at the temperature of the experiment.

t	0	2.000	5.000	s
[A]	0.2600	0.0892	0.0450	M

26. Nitrosyl bromide decomposes by the reaction $2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$. Show that the following data are consistent with a second-order reaction and determine the second-order rate constant for the reaction.

t	0	5	15	25	30	35	s
[NOBr]	0.0652	0.0514	0.0361	0.0278	0.0249	0.0226	M

What is the rate law for the reaction and the value of the rate constant at the temperature of the experiment?

27. Explain how the rate of a reaction would change if the hydronium ion concentration were doubled and the reaction is

a) First order in H^{1+} **b)** Second order in H^{1+}

28. Consider the first-order reaction $C_2H_6 \rightarrow 2CH_3$ at 500 °C where its half-life is 21 minutes.

a) How long does it take for the concentration of C_2H_6 to drop from 5.0 mM to 1.0 mM and from 1.0 mM to 0.2 mM?

b) If the original concentration of ethane is 5.0 mM, what is the concentration after 2.0 hours?

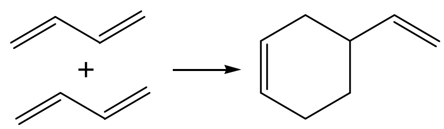
c) How long will it take for the reaction to be 95% complete?

29. Living organisms maintain a constant level of carbon-14, but upon death of the organism, the carbon-14 decays with first-order kinetics with a half-life of 5730 years. The decay is the basis of *carbon dating*. The carbon-14 level in a piece of charcoal at an archeological dig was found to be 62% of the constant level maintained by living organisms. Approximate the age of the charcoal.

30. The hydrolysis of sucrose to glucose and fructose is catalyzed by the enzyme sucrase. The hydrolysis is first order in sucrose with a half-life of 4.8×10^3 s at 20 °C. What fraction of sucrose will be hydrolyzed after 3.0 hours? How long is required to hydrolyze 99% of the sucrose?

31. The gas-phase dimerization of butadiene (see below) was monitored at 326 °C. Determine the order of the reaction and the rate constant at 326 °C.

t	0	10.1	24.	49.5	90.1	135.7	min
$[C_4H_6]$	16.79	14.64	12.26	9.67	7.29	5.67	mM



REACTION MECHANISMS AND RATE LAWS

32. The rate law for the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is rate = $k[NO_2]^2$. Is this reaction a single elementary reaction or does it occur by a more complicated mechanism? Explain.

33. Each of the following is an elementary reaction. Indicate the molecularity and write the rate law for each.

a) $I_2 \rightarrow 2I$ **b)** $2NO_2 \rightarrow NO + NO_3$
c) $CH_3 + I \rightarrow CH_3I$ **d)** $2H_2 \rightarrow 4H$
e) $HO + H \rightarrow H_2O$ **f)** $NO_2Cl \rightarrow NO_2 + Cl$

34. Consider the following three-step mechanism:

i) $2A \rightleftharpoons B + C$ fast

ii) $C + B \rightarrow D$ slow

iii) $D + E \rightarrow F$ fast

a) What is the molecularity of each step?
b) Identify any intermediate(s).
c) What is the reaction?
d) What is the rate law?

35. Consider the following three-step mechanism:

i) $A + B \rightleftharpoons C$ fast

ii) $D + C \rightarrow E$ slow

iii) $E + F \rightarrow G + H$ fast

a) What is the molecularity of each step?
b) Identify any intermediate(s).
c) What is the reaction?
d) What is the rate law?

36. Consider the two-step mechanism below.

i) $I_2 \rightarrow 2I$
ii) $H_2 + 2I \rightarrow 2HI$

a) What is the reaction?
b) Identify all intermediates.
c) What is the molecularity of each step?
d) Based on the mechanism, which step is more likely rate determining? Why?
e) What is the rate law if the first step is rate determining?
f) What is the rate law if the second step is rate determining and the previous step reaches equilibrium?

37. Consider the following two-step mechanism:

i) $NO_2 + Cl_2 \rightarrow NO_2Cl + Cl$

ii) $Cl + NO_2 \rightarrow NO_2Cl$

a) Write the reaction.

b) What is the intermediate?

c) The first step is the rate-determining step. What is the rate law?

38. Nitrogen monoxide also catalyzes the depletion of ozone in the stratosphere by the two-step mechanism shown below:

i) $NO + O_3 \rightarrow NO_2 + O_2$ slow

ii) $NO_2 + O \rightarrow NO + O_2$ fast

a) What is the net reaction?

b) What is the rate law for the reaction?

c) If the activation energy for the first step is 11.9 $kJ \cdot mol^{-1}$, how does the rate of this reaction compare to that catalyzed by Cl? Refer to Figure 10.10.

39. Consider the two mechanisms shown below. The rate law for the reaction is rate = $k[NO_2]^2$. Which mechanism is *not* acceptable? Explain. What is the reaction and what is the rate-determining step?

Mechanism I	Mechanism II
$2NO_2 \rightarrow NO + NO_3$	$NO_2 + F_2 \rightarrow NO_2F + F$
$NO_3 + F_2 \rightarrow NO_2F + OF$	$F + NO_2 \rightarrow NO_2F$
$NO + OF \rightarrow NO_2F$	

40. Consider the mechanisms shown below. The rate law for the reaction is rate = $k[X_2][Y]$. Which mechanism is acceptable? Explain. What is the reaction and what is the rate-determining step?

Mechanism I	Mechanism II	Mechanism III
$X_2 + Z \rightarrow XZ + X$	$Y + Z \rightarrow YZ$	$X_2 + Y \rightarrow XY + X$
$X + Y \rightarrow XY$	$YZ + X_2 \rightarrow XY + XZ$	$X + Z \rightarrow XZ$

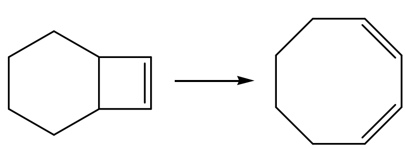
EFFECT OF TEMPERATURE ON REACTION RATES

41. What is an Arrhenius plot? How is it used?

42. What factors dictate the fraction of collisions that lead to the transition state? How are these factors incorporated into the rate law?

43. The following rate constant data were obtained for the isomerization reaction shown below. What is the activation energy for the isomerization?

t (^oC)	236	248	259	267	285
10^4 x k (s^{-1})	0.376	1.08	2.44	4.61	16.6



44. The first-order rate constant for the conversion of cyclopropane to propene at 800 ^oC is 2.7×10^{-3} s^{-1}. If the reaction has an activation energy of 274 $kJ \cdot mol^{-1}$, what is the rate constant at 900 ^oC?

45. The rate constant for $H_2(g) + I_2(g) \rightarrow 2HI(g)$ is 4.3×10^{-7} $M^{-1} \cdot s^{-1}$ at 500 K and 6.3×10^{-2} at 700 K. What is the activation energy for the reaction and what is the rate constant at 600 K?

CATALYSIS

46. What is a catalyst? How does it function?

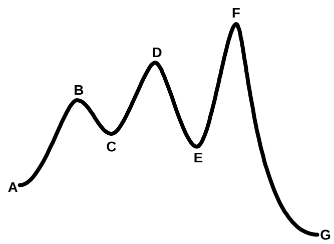
47. Distinguish between a homogeneous catalyst and a heterogeneous catalyst.

48. What effect does a catalyst have on the rate, the mechanism, the activation energy, and the equilibrium constant of a chemical process?

49. What distinguishes a catalyst from an intermediate?

MISCELLANEOUS

50. Given the following reaction diagram indicate whether each labeled position is a reactant, a product, a transition state, or an intermediate. Which intermediate has the best chance of being isolated?



51. Consider the following three-step mechanism:

i. $N_2O_5 \rightarrow NO_2 + NO_3$ — K_1, rapid equilibrium

ii. $NO_2 + NO_3 \rightarrow NO_2 + O_2 + NO$ — RDS

iii. $NO + NO_3 \rightarrow 2NO_2$ — fast

a) What is the reaction?

b) What are the intermediates?

c) What is the rate law?

52. Calculate the activation energy for $N_2O_5 \rightarrow 2NO_2 + {}^{1}/_{2}O_2$ if the specific rate constant for the decomposition is 4.30×10^{-5} s^{-1} at 300. K and 6.97×10^{2} s^{-1} at 500. K. A plot of energy versus reaction coordinate for this reaction consists of several maxima and minima. To what process does this activation energy apply? See Exercise 51 for the mechanism