1. The factors affecting the rates of chemical reactions are

    1. Concentration of and nature of reactants
    2. Surface area of reactants (for heterogeneous reactions)
    3. Temperature
    4. Catalysts (concentration for homogeneous catalysis or surface area for heterogeneous catalysis.)

6. rate = $k[I^-][H_3ASO_4][H^+]$ and the reaction is 3rd order overall.

7. The reaction is 2nd order with respect to the reactant.

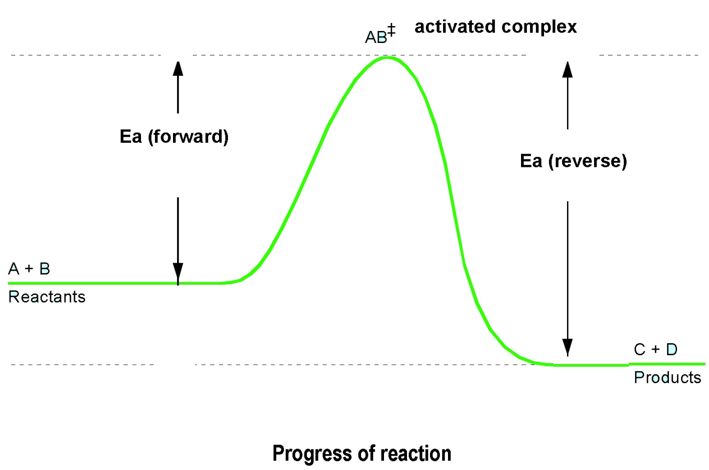
8. The rate would be increased by a factor of $2^{1/2}$ or 1.414.

9. The half-life is 25 s, so it takes 2 half-lives or 50 s for the concentration of A to decrease to 1/4 of its original value. It takes another half-life (3 in all or 75 s) for the concentration of A to decrease to 1/8 of its original value.

10. For a first order reaction, the half-life is given by: $t_{1/2} = \frac{\ln 2}{k}$, and is independent of reactant concentration. For a second order reaction, the half-life is given by: $t_{1/2} = \frac{1}{k\,[A]_o}$ and increases with decreasing reactant concentration.

11. The energy of the collision and the orientation of the molecules determine whether a collision will result in reaction.

12. On this diagram, the vertical axis is an energy axis.



16. There is no necessary relationship between the rate law for a reaction and its stoichiometry, unless the reaction is an elementary (one-step) reaction. Most reactions take place in a series of steps.

17. If this reaction took place in a single step (if it were an elementary reaction), the rate law would be rate = k $[NO_2Cl]^2$. Since the observed rate law is rate = k $[NO_2Cl]$, the reaction does not take place in a single step.

18. The rate determining or rate limiting step is the elementary reaction in a reaction mechanism that is the slowest, and therefore limits the rate at which the reaction proceeds.

23. a. Two other rate expressions are: $\text{rate} = \frac{-d[A]}{dt}$ and $\text{rate} = \frac{d[B]}{dt}$

b. No. The rate of depletion of A would be 1.5 times faster than the rate of appearance of B.

c. $\text{rate} = -\frac{1}{3}\frac{d[A]}{dt} = \frac{1}{2}\frac{d[B]}{dt}$

25. a. Since the reaction is second order with respect to A, rate = k $[A]^2$.

b. Since the smaller container has a larger concentration of A and the rate is proportional to $[A]^2$, the rate will be greater in the smaller container.

c. For a second order reaction, the half-life is inversely proportional to the concentration

$t_{1/2} = \frac{1}{k[A]_o}$, so the half-life will be shorter in the container with the larger concentration.

The half-life will be shorter in the smaller container.

d. Since the concentration of A in the smaller container is twice that in the larger container and the rate is proportional to $[A]^2$, the rate in the smaller container will be 4 times that in the larger.

e. The containers initially contain the same number of A atoms, but the reaction in the smaller container is faster. Therefore, after any given time interval, the smaller container will contain fewer A atoms.

27. a. Since the rate is insensitive to a change in [A], it must be zero order on A, x= 0.

b. Doubling rate with doubling [A] implies first order with respect to A, x = 1.

c. A 27 fold increase in rate while tripling [A] implies third order, x = 3.

29. a. The rate of the reaction is nearly constant in region C .

b. The rate is greatest in region A. The slope of the tangent to the curve (first derivative) is greatest in this region.

31. Here we need to vary [B], keeping [A] constant with respect to either experiment 1 or 2. We could use initial concentrations of [B] = 2.0 *M* and [A] = 1.0 *M* and compare the results of experiment 3 to the results of experiment 1, for example.

33. $$-\frac{1}{2}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

35. $$-\frac{1}{5}\frac{d[Br^-]}{dt} = \frac{-d[BrO_3^-]}{dt}$$

37. $$\text{average rate} = -\frac{\Delta[NH_4^+]}{\Delta t} = \frac{0.500\ \underline{M} - 0.432\ \underline{M}}{3.00\ \text{hr}} = 0.0227\ \frac{\underline{M}}{\text{hr}}$$

39. $$\text{average rate} = -\frac{\Delta[CH_3NNCH_3]}{\Delta t} = \frac{0.0150\ \underline{M} - 0.0101\ \underline{M}}{7.00\ \text{min}} = 7.0 \times 10^{-4}\ \frac{\underline{M}}{\text{min}}$$

$$7.00 \times 10^{-4}\ \frac{\underline{M}}{\text{min}} \times \frac{1\ \text{min}}{60\ \text{s}} = 1.2 \times 10^{-5}\ \frac{\underline{M}}{\text{s}}$$

41. Rate = k $[H_2S][Cl_2]$

This reaction is first order with respect to H_2S and Cl_2, respectively, and second order overall.

43. Rate = k $[MnO_4^-][H_2C_2O_4]$

This reaction is first order with respect to MnO_4^- and $H_2C_2O_4$, respectively, zero order with respect to H^+ and second order overall.

45. Doubling the concentration of CH_3NNCH_3 doubles the rate of reaction, so the reaction is first order in CH_3NNCH_3 and rate = k $[CH_3NNCH_3]$. The value of k can be obtained from the rate law and results of either experiment.

$$k = \frac{\text{rate}}{[CH_3NNCH_3]} = \frac{2.8 \times 10^{-6}\ \frac{\text{mol}}{\text{L}\cdot\text{s}}}{1.13 \times 10^{-2}\ \frac{\text{mol}}{\text{L}}} = 2.5 \times 10^{-4}\ \text{s}^{-1}$$

47. Doubling [NO] approximately quadruples the rate, so the reaction is second order in NO. Doubling $[H_2]$ doubles the rate, so the reaction is first order in H_2.

Rate = k $[NO]^2\,[H_2]$

The value of k can be obtained from the rate law and results of any of the experiments.

$$k = \frac{\text{rate}}{[NO]^2\,[H_2]} = \frac{2.6 \times 10^{-5}\ M \cdot s^{-1}}{(6.4 \times 10^{-3}\ M)^2\ (2.2 \times 10^{-3}\ M)} = 2.9 \times 10^2\ M^{-2} \cdot s^{-1}$$

49. Tripling $[ClO_2]$ increases the rate by a factor of 9, so the reaction is second order in ClO_2. Tripling $[OH^-]$ triples the rate, so the reaction is first order in OH^-.

Rate = k $[ClO_2]^2\,[OH^-]$

The value of k can be obtained from the rate law and results of any of the experiments.

$$k = \frac{\text{rate}}{[ClO_2]^2\,[OH^-]} = \frac{0.0248\ M \cdot s^{-1}}{(0.060\ M)^2\ (0.030\ M)} = 2.3 \times 10^2\ M^{-2} \cdot s^{-1}$$

51. For a first order reaction, $\ln [A] = -kt + \ln [A]_o$ or

$$\ln [SO_2Cl_2]_t = -(2.2 \times 10^{-5}\ s^{-1})(7\underline{2}00\ s) + \ln (0.0248)$$

$$\ln [SO_2Cl_2]_t = -(2.2 \times 10^{-5}\ s^{-1})(7\underline{2}00\ s) - 3.697)$$

$$\ln [SO_2Cl_2]_t = -0.1\underline{5}8 - 3.697 = -3.8\underline{5}5$$

$$[SO_2Cl_2]_t = 0.021\ M$$

53. For a second order reaction, $\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_o}$

$$\frac{1}{[A]_t} = 0.225\ \frac{L}{mol \cdot s} \times 35.4\ s + \frac{1}{0.293\ M}$$

$$\frac{1}{[A]_t} = 7.9\underline{6}5\ M^{-1} + 3.4\underline{1}2\ M^{-1} = 11.3\underline{7}7\ M^{-1}$$

$$[A]_t = \frac{1}{11.3\underline{7}7\ M^{-1}} = 0.08790\ M$$

55. Use the initial concentration and the concentration at 155 s to calculate k. Then use k and the time to calculate the concentration at 256 s.

$$\ln(0.000670) = -k(155\ s) + \ln(0.00100)$$

$$\ln \frac{0.000670}{0.00100} = -k(155\ s)$$

$$\frac{4.00\underline{4}8}{155\ s} = k = 2.5\underline{8}4 \times 10^{-3}\ s^{-1}$$

$$\ln [CH_3CH_2Cl]_t = -(2.5\underline{8}4 \times 10^{-3}\ s^{-1})(256\ s) + \ln(0.00100)$$

$$\ln [CH_3CH_2Cl]_t = -(0.66\underline{1}4) - 6.908 = -7.569$$

$$[CH_3CH_2Cl]_t = e^{-7.569} = 5.16 \times 10^{-4}\ M$$

57. For a first order reaction, $t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$

$$t_{1/2} = \frac{0.693}{6.3 \times 10^{-4}\ s^{-1}} = 1.1 \times 10^3\ s$$

For the concentration to decrease to 50.% (1/2) of the original value requires 1 half-life or 1.1×10^3 s. For the concentration to decrease to 25.0% (1/4) of the original value requires 2 half-lives or 2.2×10^3 s. The second of these is solved mathematically.

$$\ln \frac{1/4\ [CH_3NC]_o}{[CH_3NC]_o} = -6.3 \times 10^{-4}\ s^{-1} \times t$$

$$t = \frac{-1.38\underline{6}3}{-6.3 \times 10^{-4}\ s^{-1}} = 2.2 \times 10^3\ s$$

59. $t_{1/2} = \frac{0.693}{2.0 \times 10^{-6}\ s^{-1}} = 3.\underline{4}65 \times 10^5\ s \times \frac{1\ hr}{3600\ s} = 9\underline{6}.25\ hr$

25.0% (1/4) left = 2 half-lives = 1$\underline{9}$2 hr = 190 hr

12.5% (1/8) left = 3 half-lives = 2$\underline{8}$9 hr = 290 hr

6.25% (1/16) left = 4 half-lives = 3$\underline{8}$5 hr = 380 hr

3.125% (1/32) left = 5 half-lives = 4$\underline{8}$1 hr = 480 hr

61. For a second order reaction, $t_{1/2} = \dfrac{1}{k[A]_o}$

$$t_{1/2} = \frac{1}{0.413\ M^{-1}\cdot s^{-1}\ x\ 5.25\ x\ 10^{-3}\ M} = 461\ s$$

63. 85.0% reaction means that only 15.0% of the original Cr^{3+} remains, i.e. $[Cr^{3+}]_t = 0.150[Cr^{3+}]_o$

$$\ln \frac{0.150\ [Cr^{3+}]_o}{[Cr^{3+}]_o} = -2.0\ x\ 10^{-6}\ s^{-1}\ x\ t$$

$$t = \frac{-1.897}{-2.0\ x\ 10^{-6}\ s^{-1}} = 9.\underline{4}8\ x\ 10^5\ s\ x\ \frac{1\ hr}{3600\ s} = 2.6\ x\ 10^2\ hr$$

65. For a zero order reaction: $[A]_t = -kt + [A]_o$

$$1.0\ x\ 10^{-2}\,M = -8.1\ x\ 10^{-2}\,M\cdot s^{-1}\ t + 0.10\,M$$

$$-0.09\,M = -8.1\ x\ 10^{-2}\,M\cdot s^{-1}\ t$$

$$t = \frac{-0.09\ M}{-8.1\ x\ 10^{-2}\ M\ s^{-1}} = \underline{1}.1\ s$$

71. $\ln \dfrac{k_1}{k_2} = \dfrac{-E_a}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

$$\ln \frac{1.4\ x\ 10^{-4}\ s^{-1}}{5.0\ x\ 10^{-4}\ s^{-1}} = \frac{-E_a}{8.314\ \frac{J}{K\cdot mol}}\left(\frac{1}{308\ K} - \frac{1}{318\ K}\right)$$

$$E_a = \frac{(1.27)\ (8.314\ \frac{J}{K\cdot mol})}{\left(\frac{1}{308\ K} - \frac{1}{318\ K}\right)} = 1.03\ x\ 10^5\ J\cdot mol^{-1} = 103\ kJ\cdot mol^{-1}$$

$$\ln \frac{k_{55}}{5.0\ x\ 10^{-4}\ s^{-1}} = \frac{-1.03\ x\ 10^5 \frac{J}{mol}}{8.314\ \frac{J}{K\cdot mol}}\left(\frac{1}{328\ K} - \frac{1}{318\ K}\right)$$

$$\ln \frac{k_{55}}{5.0\ x\ 10^{-4}\ s^{-1}} = 1.19$$

$$k_{55} = e^{1.19}\ x\ 5.0\ x\ 10^{-4}\ s^{-1} = 1.6\ x\ 10^{-3}\ s^{-1}$$

73. $$\ln 2 = \frac{-E_a}{8.314 \frac{J}{K\cdot mol}} \left(\frac{1}{308\ K} - \frac{1}{298\ K}\right)$$

$$\frac{(0.693)\ (8.314 \frac{J}{K\cdot mol})}{\frac{1}{308\ K} - \frac{1}{298\ K}} = -E_a$$

$E_a = 5.29 \times 10^4$ J/mol = 52.9 kJ/mol

77. $NOCl_2$ is the reaction intermediate since it is formed in one step (the first) and used up in a subsequent step (the second). The overall reaction is the sum of the elementary reactions: $2\ NO + Cl_2 \rightarrow 2\ NOCl$

79. The molecularity is simply the number of particles taking part in the elementary reaction.

a. molecularity = 2 (bimolecular)
b. molecularity = 2 (bimolecular)
c. molecularity = 1 (unimolecular)
d. molecularity = 3 (termolecular)

81. ***For elementary reactions only, the rate law can be obtained from the balanced equation.*** The rate law is given by the rate constant times the concentration of each particle raised to a power equal to the value of its stoichiometric coefficient.

a. rate = k $[O_3]$

b. rate = k $[NOCl_2][NO]$

83. The rate law of the overall reaction is the same as the rate law for the rate-determining (slowest) step. In this instance, the rate law is simply rate = k $[C_3H_6]^2$. Note that we can't write the rate law of an overall reaction in terms of any intermediates. If the rate-determining step (RDS) is the second or subsequent step, we would have to derive a rate law which would be expressed in terms of reactants, products and/or catalysts only. See problem 77.

85. Here, the rate law for the RDS is rate = k $[I]^2\ [H_2]$, but since I is an intermediate, the rate law for the overall reaction cannot be written in a form involving its concentration. we must derive an expression for [I] in terms of $[H_2]$, $[I_2]$ and/or [HI].

Since step 1 is at equilibrium, the forward and reverse rates are equal: $k_1\ [I_2] = k_{-1}\ [I]^2$

$$[I]^2 = \frac{k_1}{k_{-1}} [I_2]$$

Substituting this expression into the first equation yields:

$$\text{rate} = \frac{k_1\ k_2}{k_{-1}} [I_2][H_2] = k\ [I_2][H_2]$$

where k_1, k_{-1}, and k_2 have all been lumped into a single rate constant, k.

87. The overall reaction is: $2\ H_2O_2 \rightarrow 2\ H_2O + O_2$. Br^- is acting as a catalyst since it is consumed in one step and regenerated in a subsequent step and BrO^- is an intermediate, since it is produced in one step and consumed in a subsequent step.

93. $$\ln \frac{[CH_3COOCH_3]_t}{[CH_3COOCH_3]_o} = -kt$$

$$\ln \frac{0.35}{1} = -1.26 \text{ x } 10^{-4} \text{ s}^{-1} \text{ x t}$$

$$t = \frac{-1.05}{-1.26 \text{ x } 10^{-4} \text{ s}^{-1}} = 8.33 \text{ x } 10^3 \text{ s} = 2.31 \text{ hr}$$

95. $$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.26 \text{ x } 10^{-4} \text{ s}^{-1}} = 5.5 \text{ x } 10^3 \text{ s} = 1.5 \text{ hr}$$

97. $$\ln \frac{0.0250}{0.0350} = -k \text{ x } 65 \text{ s}$$

$$k = \frac{-0.336}{65 \text{ s}} = -5.2 \text{ x } 10^{-3} \text{ s}^{-1}$$

$$\ln \frac{[X]_t}{0.0350 \text{ M}} = -5.2 \text{ x } 10^{-3} \text{ s}^{-1} \text{ x } 88 \text{ s} = -0.46$$

$$[X]_t = 0.0350\ M \text{ x } e^{-0.46} = 0.0221\ M$$

107. $$\ln \frac{0.498\ (M\cdot s)^{-1}}{1.81\ (M\cdot s)^{-1}} = \frac{-E_a}{8.314\ \frac{J}{K\cdot mol}} \left(\frac{1}{592\ K} - \frac{1}{627\ K}\right)$$

$$E_a = \frac{(1.290)\ (8.314\ \frac{J}{K\cdot mol})}{(\frac{1}{592\ K} - \frac{1}{627\ K})} = 1.14\ x\ 10^5\ J\cdot mol^{-1} = 114\ kJ\cdot mol^{-1}$$

$$\ln k_1 = \ln A - \frac{E_a}{RT_1}$$

Using either combination of k and T:

$$\ln 0.498 = \ln A - \frac{1.14\ x\ 10^5\ \frac{J}{mol\cdot K}}{(8.314\ \frac{J}{mol\cdot K})(592\ K)}$$

$\ln A = -0.697 + 23.\underline{1}6 = 22.5$

$A = e^{22.5} = 6\ x\ 10^{9}$

$$\ln k_{420} = 22.5 - \frac{1.114\ x\ 10^5\ \frac{J}{mol}}{(8.314\ \frac{J}{K\cdot mol})(693\ K)} = 3.\underline{1}6$$

$k_{420} = e^{3.\underline{1}6} = 2\ x\ 10^1\ M\cdot s^{-1}$

109. The rate law should be rate = k $[NO_2][CO]$ if the reaction takes place in a single step.

111. rate = k $[NO_2Br]$

113. The rate law for the overall reaction will be given by the rate law for the RDS, rate = k_2 $[NH_3][HOCN]$. However, since HOCN is an intermediate, we cannot write the rate law in this manner. Since the first step is in equilibrium:

$k_1\ [NH_4^+][OCN^-] = k_{-1}\ [NH_3][HOCN]$

$$[HOCN] = \frac{k_1}{k_{-1}} \frac{[NH_4^+][OCN^-]}{[NH_3]}$$

$$rate = k_2\ [NH_3][HOCN] = \frac{k_1\ k_2}{k_{-1}} \frac{[NH_3][NH_4^+][OCN^-]}{[NH_3]} = k[NH_4^+][OCN^-]$$

115. The reaction is first order in O_2, because doubling $[O_2]$ doubles the rate. Since the reaction is first order in O_2 and doubling both No and O_2 increases the rate by a factor of 8, the reaction must be second order in NO.

rate = k $[NO]^2[O_2]$

$$k = \frac{\text{rate}}{[NO]^2\ [O_2]} = \frac{0.080\ \frac{\text{mol}}{\text{L}\cdot\text{s}}}{(0.045\ \frac{\text{mol}}{\text{L}})^2\ (0.022\ \frac{\text{mol}}{\text{L}})} = 1.8 \times 10^3\ \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}\quad (\text{M}^{-2}\cdot\text{s}^{-1})$$

$$\text{rate}_4 = 1.8 \times 10^3\ \frac{\text{L}^2}{\text{mol}^2\cdot\text{s}}\ (0.38\ \frac{\text{mol}}{\text{L}})^2\ (0.0046\ \frac{\text{mol}}{\text{L}}) = 1.2\ M\ \text{s}^{-1}$$

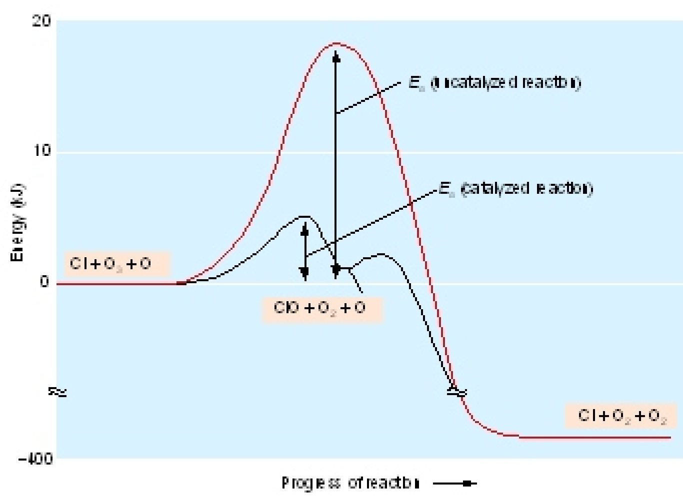
117. a. i. OH^- consumes H_3O^+, decreasing its concentration and slows the reaction.

ii. Adding water dilutes the reactants and slows the reaction.

b. i. The introduction of a catalyst provides an alternative path with a smaller activation energy. k for the catalyzed reaction will be larger than k for the uncatalyzed reaction.

ii. k decreases as the temperature decreases.

119. The catalyst speeds up the reaction by providing an alternate mechanism whose steps have smaller activation energies, thus speeding up the reaction.



121. The rate of a chemical reaction is a measure of how fast products are formed or reactants are consumed. The rate of a reaction normally changes with time because the concentration of reactants decreases with time, and the rate is often dependent on the concentration of at least some of the reactants. This is not the case in a zero order reaction where the rate of the reaction is constant and equal in value to the rate constant, k.