Chapter 6 Review, pages 396–401

Knowledge

1. (a)
2. (d)
3. (d)
4. (b)
5. (c)
6. (b)
7. (c)
8. (c)
9. (c)

10. False. The instantaneous reaction rate is always *changing during the course of the reaction.*

11. True

12. False. It *is* necessary to break existing bonds in molecules in order to form new bonds.

13. False. Chemical entities *must be in a favorable* orientation during an effective collision.

14. True

15. True

16. False. The rate constant for a zero order reaction has units *of mol/L·s*.

17. False. The rate law for a chemical reaction is always expressed as a product of the initial concentrations of the *reactants* of the reaction.

18. False. The units for the rate law constant, *k*, *depend on the order of the reaction*.

19. False. The reaction mechanism *predicts the sequence of steps in which the* chemical reaction occurs.

20. True

21. The average and instantaneous rates of a reaction usually differ because the instantaneous reaction rate changes continually as the concentration of reactants changes during the chemical reaction.

22. Reaction rate is the rate of change in concentration of a reactant or product during a chemical reaction.

23. Three different methods a chemist might use to quantify the appearance of a product or the disappearance of a reactant are: use pH to measure the change in an acid or base; measure the volume of a gas; and, measure the change in mass of a solid.

24. The purpose of enzymes in our bodies is to allow chemical reactions to occur faster at lower temperatures in cells.

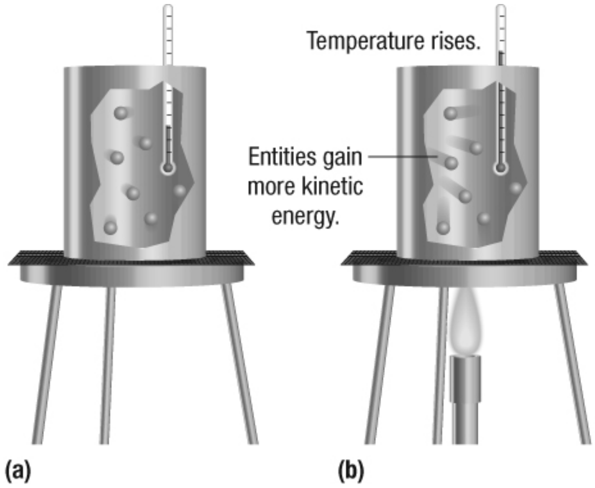
25. (a) A catalyst increases reaction rate by providing an alternative pathway for the reaction that has a lower activation energy. Thus, a much greater fraction of the collisions are effective at a given temperature.

(b) An increase in temperature raises the average kinetic energy levels of the molecules involved in the reaction. This increases reaction rate because the molecules move faster and have more energetic collisions, which increases the probability of effective collisions that can overcome the activation energy required for a chemical reaction.

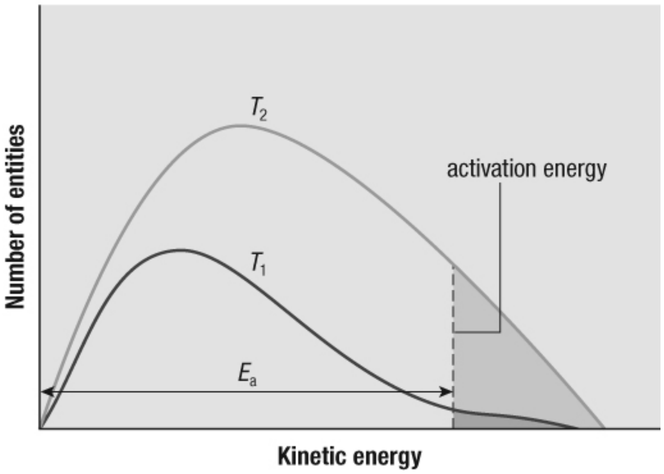
(c) An increase in concentration of the reactants increases reaction rate by increasing the probability of collisions between reactant molecules. There are more reacting particles in a given volume, so there are likely to be more collisions and therefore more effective collisions.

26. A homogeneous catalyst, such as many enzymes in aqueous solutions in cells, has the same phase as the reactants. A heterogeneous catalyst, such as the metal in a catalytic converter, has a different phase than the reactants.

27. Answers may vary. Sample answers:

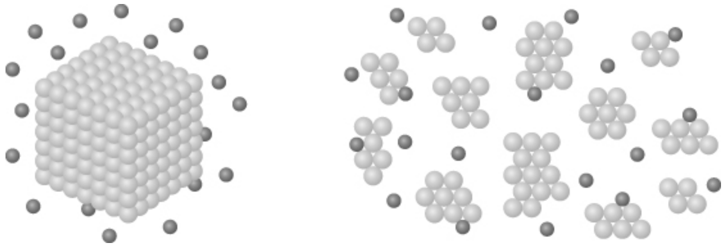

Effect of Temperature of the Reaction System on the Rate of a Reaction

Two molecules will only react if they have enough energy. By heating the mixture, you will raise the average energy levels of the molecules involved in the reaction. (a) Before heating, the entities have only a little kinetic energy. (b) After heating, they have much more kinetic energy. The molecules move faster and have more energetic collisions and therefore the probability increases of effective collisions that can overcome the activation energy required for a chemical reaction.


Maxwell–Boltzmann Distribution at Two Temperatures

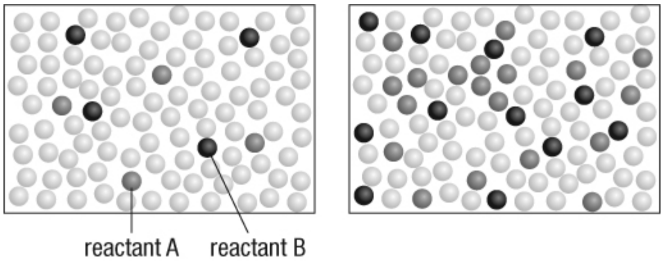
When the temperature of a reaction mixture is increased from T_1 to T_2, the number of entities capable of having effective collisions increases significantly.

Effect of Surface Area on the Rate of a Reaction



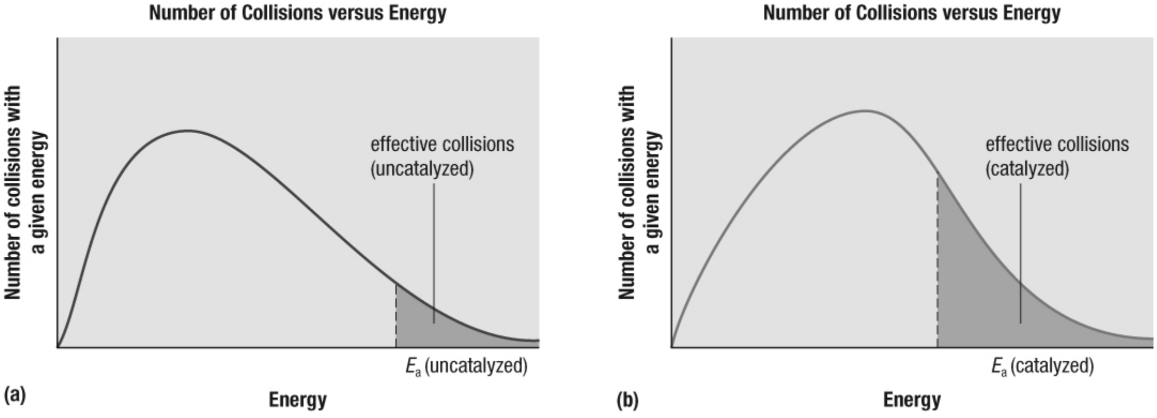
Increasing surface area increases the number of sites available for reactions to occur, so more collisions can occur and therefore more effective collisions are likely to happen. Solids with a smaller particle size (e.g., powders or small chips) react more quickly than solids with a larger particle size (e.g., large chips).

Effect of Concentration on the Rate of a Reaction

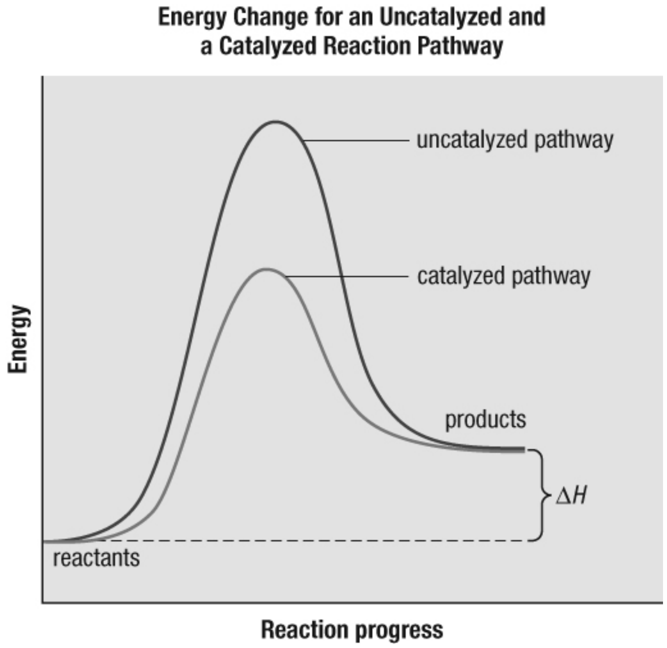


Increasing the concentration of the reactants means there are more reacting particles in a given volume, so there are likely to be more collisions between the reactants and therefore more effective collisions.

Effect of a Catalyst on the Rate of a Reaction



Catalysts speed up chemical reactions by providing an alternative pathway for the reaction—a pathway that has a lower activation energy. A much greater fraction of the collisions are successful at a given temperature for (b) the catalyzed pathway than for (a) the uncatalyzed pathway. This allows reactants to become products at a much higher rate, even if temperature is not increased.



Energy plots for a catalyzed and an uncatalyzed pathway for a given reaction

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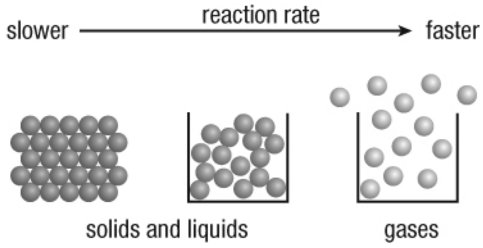
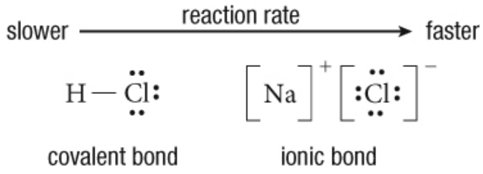
Nature of Reactants and the Rate of a Reaction

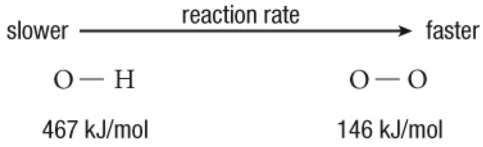
State of matter Gases tend to react faster than solids or liquids. Aqueous ions tend to react faster than species in other states of matter.



Bond type Reactions involving ionic species tend to proceed faster than reactions involving molecular compounds.

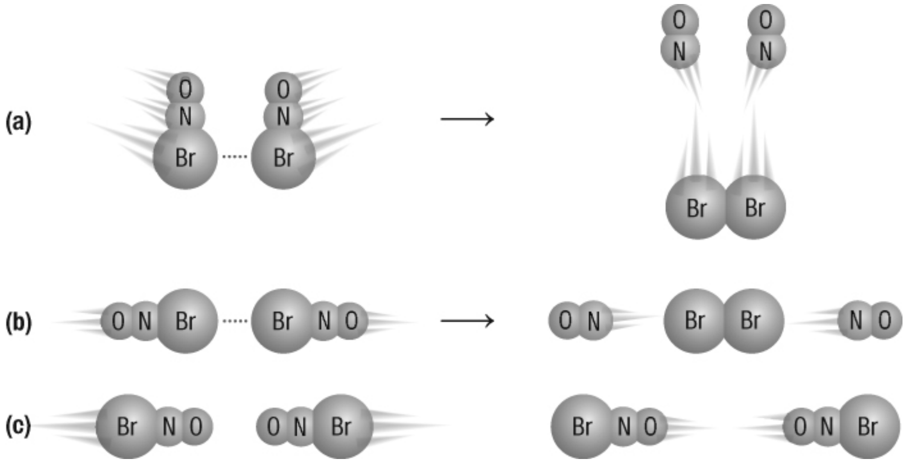


Bond strength Reactions involving the breaking of weaker bonds proceed faster than reactions involving the breaking of stronger bonds.



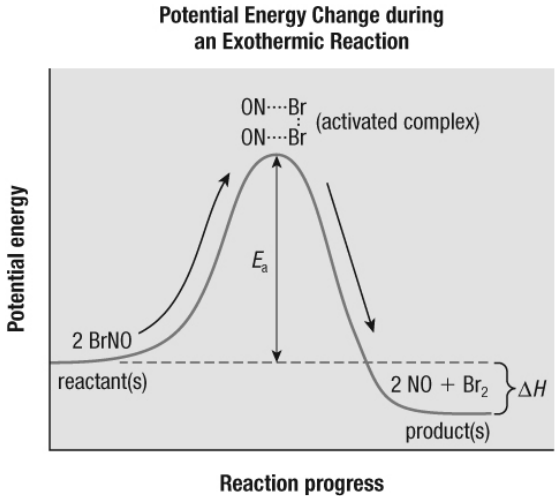
28. For the equation $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$, the rate law will be

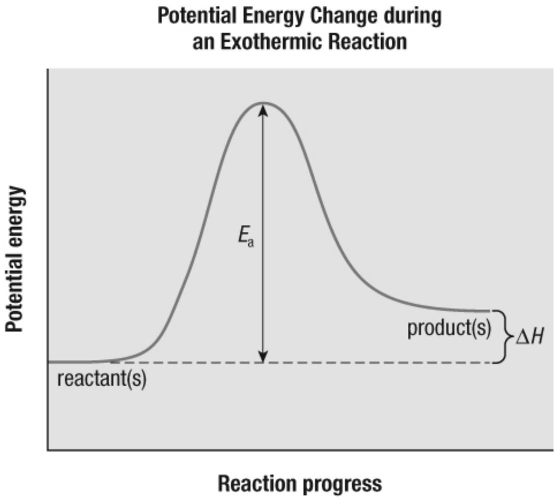
rate = $k[Ag^+(aq)][Cl^-(aq)]$ because the reaction has a single step involving two reactants.
29. Reactions of substances containing covalent bonds take longer than reactions of ions in solution because covalent bonds must be broken before a reaction can occur, while in ionic solutions, the bonds are already broken.
30. Answers may vary. Sample answer: The collision theory states that a chemical reaction occurs when reactants collide in the right orientation and with enough energy to break chemical bonds and make new ones. For example, in (a) and (b) below, the orientations of the bromine atoms allow them to contact one another, so the chemical reaction can occur. In (c), the orientation of the bromine atoms prevents the bromine atoms from interacting, so the molecules move apart without reacting.



31. The Maxwell–Boltzmann distribution is the relationship between the numbers of entities of a gas phase reactant and their kinetic energy.
32. Activation energy is the minimum energy required during a collision in order for a chemical reaction to occur.
33. All chemical reactions have activation energy because all colliding entities must overcome their mutual repulsions before an effective collision to occur.
34. According to the collision theory, two reasons why the rates of most reactions increase with increasing temperature are that a greater proportion of reactant entities will have a quantity of kinetic energy that equals or exceeds the activation energy, so more effective collisions occur, and that the increase in kinetic energy increases the rate and force of collisions between reactants, and this increases the probability that the collisions will be effective.

35. Answers may vary. Sample answer:





36. Answers may vary. Sample answer: A potential drawback to using biocatalysts is that many biological catalysts are sensitive to temperature and pH, so they are difficult to use in industrial processes.

37. The initial rates are used to measure the rate of reaction because at the initiation of the reaction, only reactants are present, because the product is not yet formed.

38. The one-step reaction represented by A + B $\rightarrow$ products has the rate law equation rate = k[A][B], so the reaction is first order with respect to both A and B. The total order of reaction is the sum of the individual orders of reaction for each reactant: 1 + 1 = 2. The total order of reaction is 2.

39. It is unlikely that more than two chemical entities (atoms, ions, or molecules) will be involved in an elementary step because a chemical reaction must involve collision of chemical entities with each other and it is unlikely that three or more entities will come together in a collision with any significant frequency.

40. (a) Average rates of reaction decrease with time because the concentration of reactants decreases as the reaction proceeds.

(b) The instantaneous rate of a reaction generally decreases as over time because the concentration of reactants decreases during the course of the reaction.

(c) Initial rates are used by convention because there is no product in the reaction, so the rate can be determined based only on the reactants.

41. The relationship between the rate law and the reaction mechanism is as follows: Experimental evidence like the determination of the rate law is used to develop a reaction mechanism. A rate law can prove a reaction mechanism wrong but it cannot prove it right. If the rate law for the rate-determining step of the reaction mechanism agrees with the experimentally determined rate law, then one of the two requirements for a plausible reaction mechanism has been met. If the reaction mechanism does not agree with the experimentally determined rate law, the mechanism is not plausible.

42. Answers may vary. Sample answer: The rate of a chemical reaction is the change in concentration of a reactant over time, and has units of $\text{mol/(L}\cdot\text{s)}$. The rate constant, *k*, is the proportionality constant in the rate law equation, and it is related to the concentrations of the reactants. The units for the rate constant depend upon the rate law, because the rate always has units of $\text{mol/(L}\cdot\text{s)}$ and the concentration always has units of mol/L. For a zero-order reaction, $r \propto [\text{A}]^0$ and *k* has units of $\text{mol/(L}\cdot\text{s)}$; for a first-order reaction, $r \propto [\text{A}]^1$ and *k* has units of 1/s; and, for a second-order reaction, $r \propto [\text{A}]^2$ and *k* has units of $\text{L/(mol}\cdot\text{s)}$.

43. When the rate law equation for the rate-determining step agrees with the experimentally determined rate law for the overall reaction, the reaction mechanism is plausible, because the rate-determining step determines the rate of the overall reaction. It follows that the rate law equation for the overall reaction identifies the reactants in the rate-determining step.

44. A reaction mechanism is a series of one or more elementary steps by which a chemical reaction occurs. Each elementary step involves a one-,two-, or in rare cases, three-entity collision that cannot be explained by simpler reactions.

45. An elementary step of a chemical reaction mechanism generally involves one or two chemical entities.

46. It is not effective to simply use a balanced chemical equation to understand a reaction rate because the balanced equation does not give any information about the elementary steps involved in the reaction or the relative rates of elementary steps.

47. It is necessary to consider the atmospheric life span of gas when considering the gas's impact on global warming because a greenhouse gas continues to affect the retention in the atmosphere until it breaks down.

48. The concern surrounding greenhouse gases is that they increase the amount of thermal energy retained by the atmosphere by absorbing incoming solar radiation and infrared radiation re-irradiated from Earth's surface and storing it. An increase in the proportions of greenhouse gases in the atmosphere can increase Earth's average temperature and have an effect on Earth's climates. Gases that persist in the upper atmosphere can make a significant contribution to global warming even in low concentrations.

Analysis and Application

49. Given: (a) $4\ \text{PH}_3(\text{g}) \rightarrow \text{P}_4(\text{g}) + 6\ \text{H}_2(\text{g})$; rate of consumption of $\text{PH}_3(\text{g})$, $\dfrac{\Delta[\text{PH}_3(\text{g})]}{\Delta t} = -0.0024\ \text{mol/L}\cdot\text{s}$ is −0.0024 mol/(L·s)

Required: rate of formation of phosphorus gas and hydrogen gas

Analysis: Scale the rates by the inverse of their coefficients in the balanced chemical equation. Then, substitute the given rate and solve for the required rates.

Solution:

$$\frac{1}{4}\left(-\frac{\Delta[\text{PH}_3(\text{g})]}{\Delta t}\right)=\frac{\Delta[\text{P}_4(g)]}{\Delta t}$$

$$\frac{\Delta[\text{P}_4(\text{g})]}{\Delta t}=-\frac{1}{4}(-0.0024\ \text{mol/(L}\cdot\text{s))}$$

$$\frac{\Delta[\text{P}_4(g)]}{\Delta t}=0.00060\ \text{mol/(L}\cdot\text{s)}$$

$$\frac{1}{4}\left(-\frac{\Delta[\text{PH}_3(\text{g})]}{\Delta t}\right)=\frac{1}{6}\left(\frac{\Delta[\text{H}_2(\text{g})]}{\Delta t}\right)$$

$$\frac{\Delta[\text{H}_2(\text{g})]}{\Delta t}=-\frac{6}{4}(-0.0024\ \text{mol/(L}\cdot\text{s))}$$

$$\frac{\Delta[\text{H}_2(\text{g})]}{\Delta t}=0.0036\ \text{mol/(L}\cdot\text{s)}$$

Statement: The rate of formation phosphorus gas is $0.00060\ \text{mol/(L}\cdot\text{s)}$ and the rate of formation of hydrogen gas is $0.0036\ \text{mol/(L}\cdot\text{s)}$.

50. (a) Given: $[\text{B}]_{\text{initial}}=0.0431\ \text{mol/L}$; $[\text{B}]_{t=11.3\ \text{min}}=0.0307\ \text{mol/L}$

Required: average rate of consumption of B for first 11.3 min

Analysis: Since the average rate of consumption of a reactant will be a negative number, use the following equation: $\text{rate}_\text{A}=-\dfrac{\Delta[\text{A}]}{\Delta t}$.

Solution:

$$\begin{aligned}\text{rate}_\text{B}&=-\frac{\Delta[\text{B}]}{\Delta t}\\&=-\left(\frac{[\text{B}]_{t=11.3\ \text{min}}-[\text{B}]_{t=0\ \text{min}}}{11.3\ \text{min}-0\ \text{min}}\right)\\&=-\left(\frac{0.0431\ \text{mol/L}-0.0307\ \text{mol/L}}{11.3\ \text{min}}\right)\\&=-0.00110\ \text{mol/(L}\cdot\cancel{\text{min}})\times\frac{1\ \cancel{\text{min}}}{60\ \text{s}}\\\text{rate}_\text{B}&=-1.83\times10^{-5}\ \text{mol/(L}\cdot\text{s)}\end{aligned}$$

Statement: The average rate of consumption of B is $1.83\times10^{-5}\ \text{mol/(L}\cdot\text{s)}$.

(b) Given: $\text{A} + 2\ \text{B} \rightarrow 3\ \text{C} + 4\ \text{D}$; $\text{rate}_\text{B}=-1.83\times10^{-5}\ \text{mol/(L}\cdot\text{s)}$

Required: average rate of formation of C

Analysis: Scale the rates by the inverse of their coefficients in the balanced chemical equation. Then, substitute the given rate and solve for the required rate.

Solution: $\frac{1}{2}\left(-\frac{\Delta[\text{B}]}{\Delta t}\right)=\frac{1}{3}\left(\frac{\Delta[\text{C}]}{\Delta t}\right)$

$$\frac{\Delta[\text{C}]}{\Delta t}=-\frac{3}{2}(-1.83\times10^{-5}\ \text{mol/(L}\cdot\text{s))}$$

$$\frac{\Delta[\text{C}]}{\Delta t}=2.74\times10^{-5}\ \text{mol/(L}\cdot\text{s)}$$

Statement: The average rate of formation of C is $2.74\times10^{-5}\ \text{mol / (L}\cdot\text{s)}$.

51. Given: A + 2 B → 3 C + 4 D; $[\text{A}]_{\text{initial}}$ = 0.0367 mol/L; $[\text{A}]_{t\,=\,21.8\text{ min}}$ = 0.0240 mol/L
Required: average rate of disappearance of B, in $\text{mol/(L}\cdot\text{s)}$

Analysis: Since the average rate of disappearance of a reactant will be a negative number, use the equation $\text{rate}_\text{A}=-\frac{\Delta[\text{A}]}{\Delta t}$ to find the average rate of disappearance of A. Then, scale the rates by the inverse of their coefficients in the balanced chemical equation, substitute the calculated rate, and solve for the required rate.

Solution: $\text{rate}_\text{A}=-\frac{\Delta[\text{A}]}{\Delta t}$

$$-\left(\frac{[\text{A}]_{t=21.8\text{ min}}-[\text{A}]_{t=0\text{ min}}}{21.8\text{ min}-0\text{ min}}\right)$$

$$=-\left(\frac{0.0367\text{ mol/L}-0.0240\text{ mol/L}}{21.8\text{ min}}\right)$$

$$=-5.8257\times10^{-4}\ \text{mol/L}\cdot\cancel{\text{min}}\times\frac{1\ \cancel{\text{min}}}{60\text{ s}}$$

$$\text{rate}_\text{A}=-9.7095\times10^{-6}\ \text{mol/(L}\cdot\text{s)}\ \text{(two extra digits carried)}$$

$$\frac{1}{2}\left(-\frac{\Delta[\text{B}]}{\Delta t}\right)=-\left(\frac{\Delta[\text{A}]}{\Delta t}\right)$$

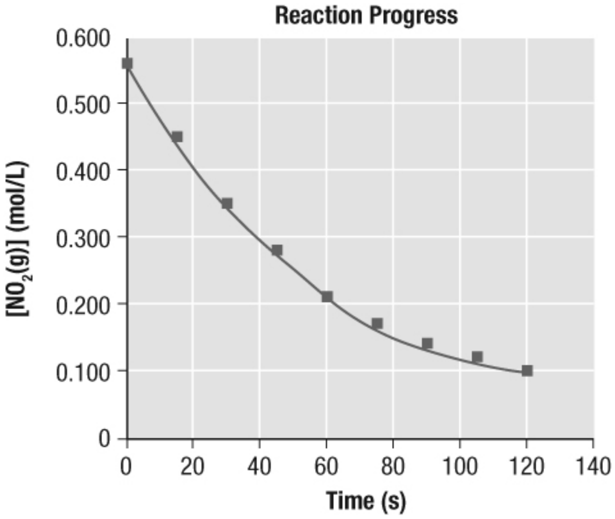
$$\frac{\Delta[\text{B}]}{\Delta t}=2(-9.7095\times10^{-6}\ \text{mol/(L}\cdot\text{s))}$$

$$\frac{\Delta[\text{B}]}{\Delta t}=-1.94\times10^{-5}\ \text{mol/(L}\cdot\text{s)}$$

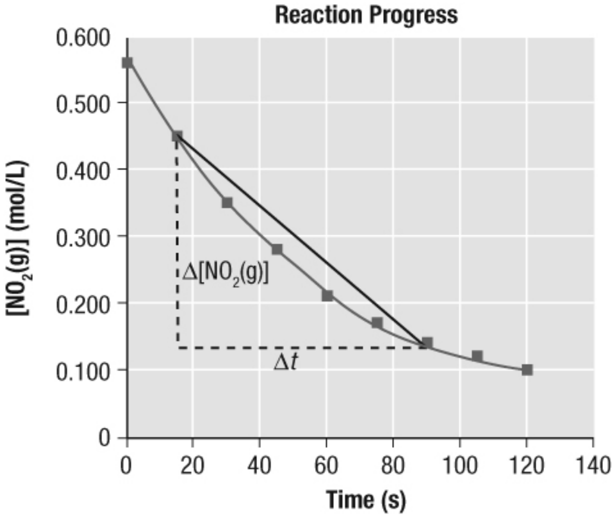
Statement: The average rate of disappearance of B is $1.94\times10^{-5}\ \text{mol/(L}\cdot\text{s)}$.

52. (a) There are 2 reactants, A and B.
(b) There is 1 product, C.
(c) $[\text{A}]_{\text{initial}}$ = 0.100 00 mol/L; $[\text{B}]_{\text{initial}}$ = 0.050 00 mol/L; $[\text{C}]_{\text{initial}}$ = 0.00 mol/L
(d) Based on the graph, the balanced chemical equation for the reaction is 2 A + B → 3 C because Δ[A] = 2 Δ[B] and Δ[C] = −1.5 Δ[A].

53. (a) Graphs will be curves of best fit and may vary. Sample graph:



(b) Answers may vary, as graphs in (a) may vary. Sample answer:
Given: Graph in (a)
Required: average rate of consumption of nitrogen dioxide gas between 15 s and 90 s
Analysis: Interpolate the concentrations of nitrogen dioxide gas at 15 s and 90 s from the graph in (a). Draw a secant to the curve at *t* = 15 s and *t* = 90 s and calculate the slope of this line which is, by definition, the average rate of reaction.



Solution: From the graph, the concentration of nitrogen dioxide gas at 15 s is 0.445 mol/L and at 90 s is 0.142 mol/L.

$$\begin{aligned}\text{rate}_{\text{NO}_2\text{(g)}} &= \frac{\Delta y}{\Delta x} \\ &= \frac{\Delta[\text{NO}_2\text{(g)}]}{\Delta t} \\ &= \frac{0.142\ \text{mol/L} - 0.445\ \text{mol/L}}{90\ \text{s} - 15\ \text{s}} \\ \text{rate}_{\text{NO}_2\text{(g)}} &= -4.0 \times 10^{-3}\ \text{mol/(L} \cdot \text{s)}\end{aligned}$$

Statement: The average rate of consumption of nitrogen dioxide gas between 15 s and 90 s is 4.0×10^{-3} mol/(L · s) .

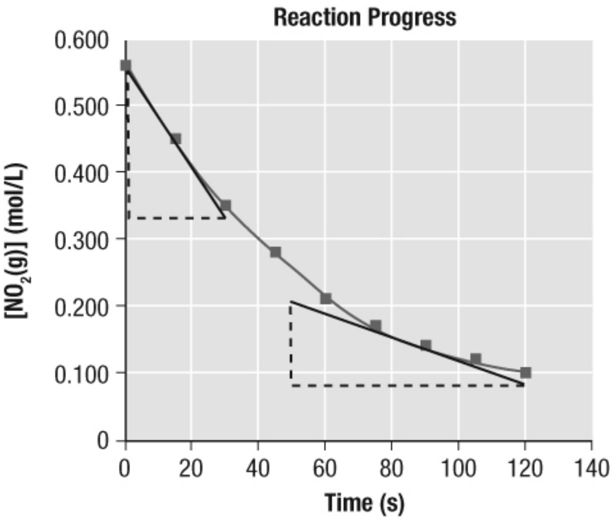
(c) & (d) Answers may vary, as graphs, tangent lines, and points used in calculations may vary. Sample answer:

Given: Graph in (a)

Required: (c) instantaneous rate of appearance of nitrogen dioxide gas at 15 s

(d) instantaneous rate of appearance of nitrogen dioxide gas at 90 s

Analysis: Draw tangents to the curve at t = 15 s and t = 90 s. Each tangent line is the hypotenuse of a right triangle. Δy is the change in concentration, and Δx is the change in time. Substitute these values for Δy and Δx in the slope formula to get the instantaneous rate of appearance of hydrogen gas at 15 s and 90 s.



Solution: (c) To calculate the instantaneous rate at $t = 15$ s, use the points (0 s, 0.560 mol/L) and (30 s, 0.350 mol/L) on the tangent to the curve at 15 s.

$$\begin{aligned}\text{rate}_{\text{instantaneous at } t=15\text{ s}} &= \text{slope of the tangent at 15 s}\\ &= \frac{\Delta y}{\Delta x} \text{ at 15 s}\\ &= \frac{0.350 \text{ mol/L} - 0.560 \text{ mol/L}}{30 \text{ s} - 0 \text{ s}}\\ \text{rate}_{\text{instantaneous at } t=15\text{ s}} &= -7.0 \times 10^{-3} \text{ mol/(L}\cdot\text{s)}\end{aligned}$$

(d) To calculate the instantaneous rate at $t = 90$ s, use the points (50 s, 0.205 mol/L) and (120 s, 0.090 mol/L) on the tangent to the curve at 90 s.

$$\begin{aligned}\text{rate}_{\text{instantaneous at } t=90\text{ s}} &= \text{slope of the tangent at 90 s}\\ &= \frac{\Delta y}{\Delta x} \text{ at 90 s}\\ &= \frac{0.090 \text{ mol/L} - 0.205 \text{ mol/L}}{120 \text{ s} - 50 \text{ s}}\\ \text{rate}_{\text{instantaneous at } t=90\text{ s}} &= -1.6 \times 10^{-3} \text{ mol/(L}\cdot\text{s)}\end{aligned}$$

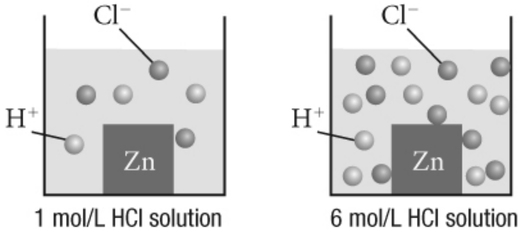
Statement: The instantaneous rate of disappearance of nitrogen dioxide gas at 15 s is 7.0×10^{-3} mol/L·s, and at 90 s is 1.6×10^{-3} mol/(L·s).

(e) The rate of reaction slowed dramatically because the concentration of reactant decreased significantly.

54. Diagrams may vary. Sample answer:

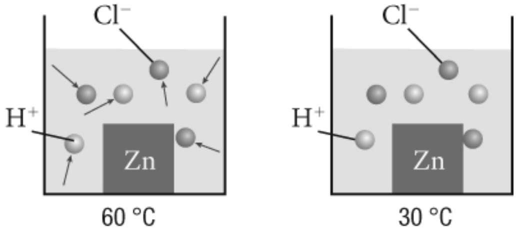
For the reaction 2 HCl(aq) + Zn(s) → H_2(g) + $ZnCl_2$(aq) + thermal energy:

(a) Increasing the concentration of hydrochloric acid will increase the reaction rate because the probability of collisions, and thus of effective collisions, will increase.



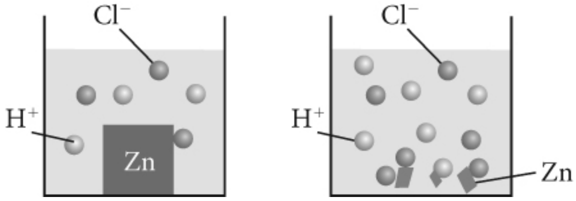
Increasing the concentration of HCl(aq) increases the frequency of collisions.

(b) Cooling the reaction mixture will decrease the reaction rate because the kinetic energy of the reactant entities will decrease and thus the probability of collisions will decrease.



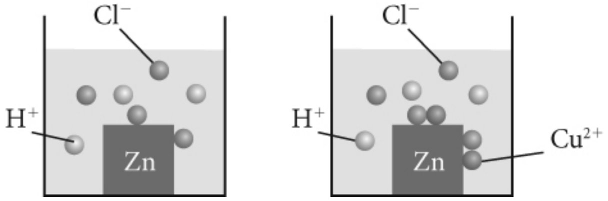
Cooling the reaction mixture decreases the energy and frequency of collisions.

(c) Using finely ground zinc instead of large chunks of zinc will increase the reaction rate because the frequency of collisions will increase.



Increasing the surface area of Zn increases the frequency of collisions.

(d) Using a solution of copper(II) sulfate as a catalyst will increase the reaction rate because it will lower the activation energy for the reaction by providing a new mechanism through which the reaction can proceed.



Using $CuSO_4$ as a catalyst provides an alternative pathway for the reaction with a lower activation energy.

55. During the process of making bread, temperature affects the action of yeast and baking as follows: The fermentation of sugar by yeast produces carbon dioxide gas to create a light and airy texture in the bread and alcohol to enhances the flavour of the bread. While the yeast is acting on the dough, a warmer temperature increases the rate of chemical reactions of the yeast, but if the temperature is too high, the yeast will die. During baking, the higher temperature of the oven is needed to cause the bubbles of carbon dioxide gas trapped in the dough to expand rapidly, and then to kill the yeast cells. As the bread is heated in the oven, the yeast inside the dough continues feeding on the sugars in the flour, and the pockets of gas in the dough continue to expand. As the temperature of the dough rises, the yeast eventually dies, the gluten in the flour hardens, and the dough solidifies.

56. Dust control is an important part of industrial safety because a fine mist of combustible dust can be highly flammable. The reaction rate is proportional to both surface area and concentration. Dusts have a very large surface area compared to their mass, and if the dust is suspended in the air at a high concentration, very rapid combustion can cause an explosion if there is an ignition source (for example, an electrical spark). An example is coal dust, which is explosive when suspended in air; coal dust explosions have been the cause of some serious mining accidents.

57. (a) Copper is commonly used in plumbing because copper is unreactive with water, but unlike mercury, it is solid, and unlike gold and silver, it is relatively inexpensive.

(b) If copper were not available, tin or iron might be suitable to make plumbing pipes. Gold and silver are too expensive, mercury is a liquid, lead is toxic, and the other metals are too reactive with water.

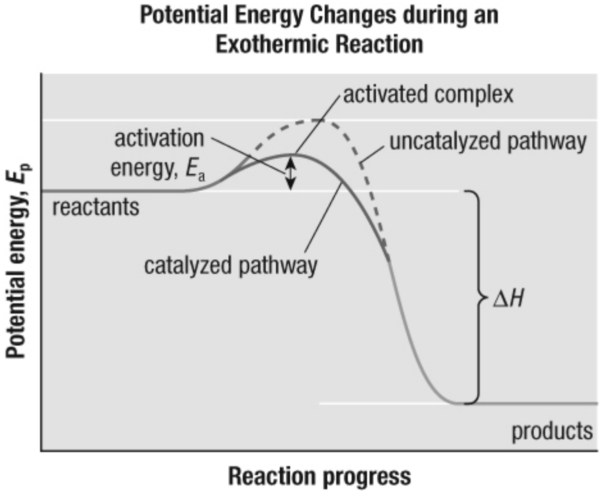
58. (a) & (b)

Increasing the Rate of Reaction of Each Step in the Wet Sulfuric Acid Process

Reactant(s)	Step(s)	Change	Benefits	Expenses
S(s)	1	– increase surface area	– All changes will lead to faster production and reduce the cost of producing H_2SO_4(aq.	– Increasing the temperature and pressure will make the steps in the reaction less safe. – The catalyst will cost something (but will reduce costs).
O_2(g), SO_2(g), SO_3(g)	1, 2, 3	– increase concentration (pressure)		
SO_2(g)	2	– add V_2O_5(s) as a catalyst		
all	all	– increase temperature of reaction system		

59. It is possible for the instantaneous rate of a highly exothermic reaction to be higher after the reaction has proceeded for a time than at the start of the reaction because the reaction rate will increase as the temperature increases due to thermal energy produced by the reaction.

60.



A catalyst provides an alternative pathway for the reaction, which has a lower activation energy. Thus, at any given temperature, a larger fraction of the entities of the reactants will have kinetic energy equal to or greater than this lower activation energy. There are a greater number of effective collisions, and so the reaction rate is increased.

61. Large piles of timber in a lumberyard do not catch fire spontaneously, even though they are surrounded by oxygen, because the surface area of the logs is small compared to their mass and the activation energy is high enough to keep the reaction from occurring.

62. (a) Three ways that you could increase the rate of the reaction $Co(s) + Cl_2(aq) \rightarrow CoCl_2(aq)$ are: 1) Increase the concentration of $Cl_2(aq)$, which will increase the probability of collisions between reactant molecules, and thus the probability of effective collisions; 2) decrease the particle size of the Co(s), which will increase surface area and thus the probability of effective collisions; and, 3) increase the temperature of the reaction system, so more entities in the sample will have enough kinetic energy to break the bonds of the reactants and form an activation complex, and the rate and force of collisions between reactants will also increase, which will increase the probability of effective collisions.

(b) One technique you could use to measure the rate of this reaction is to measure the decrease in concentration of $Cl_2(aq)$ or increase in concentration of $CoCl_2(aq)$ by measuring the change in colour intensity with a spectrophotometer. By collecting spectrophotometric data at various times after the solutions are mixed, you could determine the reaction rate. Another technique you could use would be to measure the decrease in Co(s) by determining the initial mass and then isolating the solid after a given time, measuring the unreacted mass, and calculating the average rate.

63. (a) Since the reaction is second order with respect to chlorine dioxide and first order with respect to hydroxide ions, the rate equation for the reaction is

$\text{rate} = k[ClO_2(aq)]^2[OH^-(aq)]$

(b) The total order of reaction is 2 + 1 = 3.

(c) Doubling the concentration of chlorine dioxide would quadruple the reaction rate.

(d) Doubling the concentration of hydroxide ions would double the reaction rate.

64. Answers may vary. Sample answer:
The steps you need to follow to determine the exponents of the reactant concentrations in the rate law equation are:

- Run the reaction several times, varying the concentrations of reactants one by one.
- Calculate the reaction rate change for an increase in one reactant while keeping the other reactant concentrations constant.
- Determine the exponent of the change in reaction rate divided by the change in concentration for the first reactant.
- Repeat for each additional reactant, using runs in which the reactant's concentration changes.

65. Given: RX + OH^- → products; experimental data provided in Table 2
Required: order of reaction with respect to RX and OH^- and the rate law equation
Analysis: $\text{rate} = k[\text{RX}]^m[\text{OH}^-]^n$
To determine the order of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for *m* and *n* into the rate equation.
Solution: Step 1. Find *m*.
Look at the data from runs 1 and 3, because the initial concentration of RX changed while the concentration of OH^- remained constant. When the initial concentration of RX doubled, the rate of reaction doubled. The exponent *m* in the rate law equation is therefore 1, and the order of reaction with respect to RX is 1.
Step 2. Find *n*.
Look at the data from runs 1 and 2, because the initial concentration of OH^- changed while the concentration of RX remained constant. When the initial concentration of OH^- doubled, the rate of reaction doubled. The exponent *n* in the rate law equation is therefore 1, and the order of reaction with respect to OH^- is 1.
Step 3. Therefore, for this reaction,
$\text{rate} = k[\text{RX}][\text{OH}^-]$
Statement: The reaction is first order with respect to both RX and OH^-, and the rate law equation is $\text{rate} = k[\text{RX}][\text{OH}^-]$.
66. (a) The reaction is zero order with respect to [A] because the rate is not affected by concentration.
(b) The reaction is first order with respect to [A] because the rate increases linearly with the concentration.
(c) The order of the reaction is greater than one with respect to [A] but cannot be determined exactly without coordinates.
(d) The reaction is second order with respect to [A] because the square of the rate increases linearly with concentration.
67. (a) According to the rate law $r = k[\text{Cl}_2(\text{g})][\text{NO(g)}]^2$, the reaction is first order with respect to $Cl_2(g)$ and second order with respect to NO(g).
(b) The total order of reaction is 3.
(c) Since the total reaction order is 3, the units of the rate constant will be $\text{L}^2/(\text{mol}^2 \cdot \text{s})$.

68. (a) Given: 2 Mg(s) + O_2(g) → 2 MgO(s); experimental data provided in Table 3
Required: the rate law equation, the rate constant, and the total order of reaction
Analysis: $\text{rate} = k[\text{Mg(s)}]^m[\text{O}_2\text{(g)}]^n$

To determine the order of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes. Then, insert values for *m* and *n* into the rate equation along with 1 set of data from the table. The total order of reaction is the sum of the individual orders of reaction for each reactant.

Solution: Find *m*. In runs 1 and 2, the initial concentration of magnesium changed while the concentration of oxygen gas remained constant. When the initial concentration of magnesium doubled, the rate of reaction doubled. The exponent *m* in the rate law equation is therefore 1, and the order of reaction with respect to Mg(s) is 1.

Find *n*. In runs 1 and 3, the initial concentration of oxygen gas changed while the concentration of magnesium remained constant. When the initial concentration of oxygen gas doubled, the rate of reaction quadrupled. The exponent *n* in the rate law equation is therefore 2, and the order of reaction with respect to O_2(g) is 2.

Therefore, for this reaction, $\text{rate} = k[\text{Mg(s)}][\text{O}_2\text{(g)}]^2$.

The total order of reaction is 1 + 2 = 3.

$$\begin{aligned}k &= \frac{\text{rate}}{[\text{Mg(s)}][\text{O}_2\text{(g)}]^2}\\ &= \frac{2.0\times10^{-3}\ \text{mol/(L}\cdot\text{s)}}{(0.10\ \text{mol/L})(0.10\ \text{mol/L})^2}\\ k &= 2.0\ \text{L}^2/(\text{mol}^2\cdot\text{s})\end{aligned}$$

Statement: The rate law equation is $\text{rate} = k[\text{Mg(s)}][\text{O}_2\text{(g)}]^2$; the rate constant, *k,* is $2.0\ \text{L}^2/(\text{mol}^2\cdot\text{s})$; and the total order of reaction is 3.

69. The most likely factor the researcher changed is the temperature, since this is a gas phase reaction and the concentration is the same in all of the runs. Decreasing the temperature would decrease the reaction rate.

70. (a) The reaction is first order for both reactants, so
rate = $k[\text{CH}_3\text{CSNH}_2\text{(aq)}][\text{OH}^-\text{(aq)}]$

(b) The total order of reaction is 1 + 1 = 2.

(c) Given: the chemical equation for a two-step reaction and the rate determining step

$$\begin{array}{l}\text{CH}_3\text{CSNH}_2\text{(aq)} + \text{OH}^-\text{(aq)} \rightarrow \text{CH}_3\text{CONH}_2\text{(aq)} + \text{HS}^-\text{(aq)} \quad \text{slow}\\ \qquad\qquad\qquad ? \quad \rightarrow \quad ?\\ \hline \text{CH}_3\text{CSNH}_2\text{(aq)} + 2\,\text{OH}^-\text{(aq)} \rightarrow \text{CH}_3\text{CO}_2^-\text{(aq)} + \text{HS}^-\text{(aq)} + \text{NH}_3\text{(g)}\end{array}$$

Required: equation for the second step
Analysis: The balanced equation is the sum of the elementary steps, minus any reaction intermediates.

Solution:

$$\begin{array}{l} \quad CH_3CSNH_2(aq) + OH^-(aq) \rightarrow \cancel{CH_3CONH_2(aq)} + HS^-(aq) \\ \quad \cancel{CH_3CONH_2(aq)} + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + NH_3(g) \\ \hline CH_3CSNH_2(aq) + 2\,OH^-(aq) \rightarrow CH_3CO_2^-(aq) + HS^-(aq) + NH_3(g) \end{array}$$

Statement: The equation for the second step in the reaction is
$CH_3CONH_2(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + NH_3(g)$

71. (a) Given: $2\text{ A} + \text{B} + \text{C} \rightarrow 2\text{ D} + \text{E}$; experimental data provided in Table 4

Required: order of reaction with respect to each reactant

Analysis: $\text{rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^p$

To determine the orders of reaction, look for pairs of data in which the initial concentration of only 1 reactant changes.

Solution: Find *m*. In runs 2 and 4, the initial concentration of A changed while the concentrations of B and C remained constant. When the initial concentration of A doubled, the rate of reaction quadrupled. The exponent *m* in the rate law equation is therefore 2, and the order of reaction with respect to A is 2.

Find *n*. In runs 1 and 3, the initial concentration of B changed while the concentrations of B and C remained constant. When the initial concentration of B was multiplied by 4, the rate of reaction remained the same. The exponent *n* in the rate law equation is therefore 0, and the order of reaction with respect to B is 0.

Find *p*. In runs 1 and 2, the initial concentration of [C] changed while the other concentrations remained constant. When the initial concentration of [C] doubled, the rate of reaction doubled. The exponent *p* in the rate law equation is therefore 1, and the order of reaction with respect to [C] is 1.

Statement: The reaction is second order with respect to A, zero order with respect to B, and first order with respect to C.

(b) Given: $\text{rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^p$; orders of reaction: A = 2, B = 0, C = 1

Required: the specific rate law equation, including units for *k*

Analysis: Use the orders of reaction to write the rate law equation. To find *k*, rearrange the rate law equation to solve for *k* and enter values provided in Table 3.

Solution: $\text{rate} = k[\text{A}]^2[\text{C}]$

$$\begin{aligned} k &= \frac{\text{rate}}{[\text{A}]^2[\text{C}]} \\ &= \frac{0.0060\text{ mol/(L}\cdot\text{s)}}{(0.025\text{ mol/L})^2(0.022\text{ mol/L})} \\ k &= 440\text{ L}^2/(\text{mol}^2\cdot\text{s}) \end{aligned}$$

Statement: The specific rate law equation is $(440\text{ L}^2/(\text{mol}^2\cdot\text{s}))[\text{A}]^2[\text{C}]$.

(c) Step 3 is the slowest step, so it is the rate-determining step.

(d) The reaction intermediates are F and G.

(e) This mechanism results in the overall reaction:

$$\begin{array}{l} \mathrm{A + C \rightarrow D + \cancel{F} + \cancel{G}} \\ \mathrm{\cancel{F} + B \rightarrow E} \\ \mathrm{A + \cancel{G} \rightarrow D} \\ \hline \mathrm{2\ A + B + C \rightarrow 2\ D + E} \end{array}$$

(f) Yes, the reaction mechanism agrees with the experimental rate law because the reactants in the rate-determining step are A and G. The reaction step that forms G involves A and C, so there the mechanism is second order in A and first order in C.

(g) No, this mechanism is not correct. It satisfies the one of the two requirements for a plausible mechanism, that the elementary steps in the reaction mechanism add up to the overall balanced equation for the reaction. However, it does not satisfy the second requirement. The equation for the rate-determining step, k[A][G] does not match the experimentally determined rate law, $k[\mathrm{A}]^2[\mathrm{C}]$.

72. Answers may vary. Sample answer: A + B → P

Evaluation

73. (a)

Time (s)	**$[\mathrm{MnO_4^-(aq)}]$ (mol/L)**	**$[\mathrm{H_2C_2O_4(aq)}]$ (mol/L)**	**$[\mathrm{Mn^{2+}(aq)}]$ (mol/L)**
0	0.100	1.00	0.000
10	0.049	0.87	0.051
20	0.024	0.81	0.076
30	0.011	0.78	0.089
40	0.005	0.76	0.095

Sample calculation:

Given:

$$2\ \mathrm{MnO_4^-(aq)} + 5\ \mathrm{H_2C_2O_4(aq)} + 6\ \mathrm{H_3O^+(aq)} \rightarrow 2\ \mathrm{Mn^{2+}(aq)} + 10\ \mathrm{CO_2(aq)} + 14\ \mathrm{H_2O(l)}$$

$[\mathrm{MnO_4^-(aq)}]_{t=0\ \mathrm{s}} = 0.100\ \mathrm{mol/L}$; $[\mathrm{H_2C_2O_4(aq)}]_{t=0\ \mathrm{s}} = 1.00\ \mathrm{mol/L}$;

$[\mathrm{MnO_4^-(aq)}]_{t=10\ \mathrm{s}} = 0.049\ \mathrm{mol/L}$

Required: $[\mathrm{H_2C_2O_4(aq)}]_{t=10\ \mathrm{s}}$; $[\mathrm{Mn^{2+}\ (aq)}]_{t=10\ \mathrm{s}}$

Analysis: According to the balanced chemical equation, the permanganate ion, oxalic acid, and manganese(II) ion react in a 2:5:2 ratio.

Solution: During the first 10 s, the permanganate ion concentration decreased by:
0.100 mol/L – 0.049 mol/L = 0.051 mol/L

Since the permanganate and manganese(II) ions are in a 2:2 ratio, 0.051 mol/L of $\mathrm{Mn^{2+}(aq)}$ is produced.

The concentration of oxalic acid that reacted is given by:

$$\left[\mathrm{H_2C_2O_4}\left(\mathrm{aq}\right)\right]_{\mathrm{reacted}} = \frac{5}{2}(0.051\ \mathrm{mol/L})$$

$$\left[\mathrm{H_2C_2O_4}\left(\mathrm{aq}\right)\right]_{\mathrm{reacted}} = 0.13\ \mathrm{mol/L}$$

The concentration of oxalic acid remaining is
1.00 mol/L – 0.13 mol/L = 0.87 mol/L

Statement: The concentration of oxalic acid and manganese(II) at 10 s is 0.87 mol/L and 0.051 mol/L.

(b) Given: $[\mathrm{MnO_4^-(aq)}]_{t=0\text{ s}} = 0.10\text{ mol/L}$; $[\mathrm{MnO_4^-(aq)}]_{t=30\text{ s}} = 0.011\text{ mol/L}$

Required: average rate of disappearance of permanganate ion over the first 30 s

Analysis: Since the average rate of disappearance of a reactant will be a negative number, use the following equation:

$$\text{rate}_{\mathrm{A}} = -\frac{\Delta[\mathrm{A}]}{\Delta t}$$

Solution:
$$\begin{aligned}
\text{rate}_{\mathrm{MnO_4^-(aq)}} &= -\left(\frac{\Delta[\mathrm{MnO_4^-(aq)}]}{\Delta t}\right)\\
&= -\left(\frac{[\mathrm{MnO_4^-(aq)}]_{t=30\text{ s}} - [\mathrm{MnO_4^-(aq)}]_{\mathrm{t=0\ s}}}{30\text{ s} - 0\text{ s}}\right)\\
&= -\left(\frac{0.10\text{ mol/L} - 0.011\text{ mol/L}}{30\text{ s}}\right)\\
\text{rate}_{\mathrm{MnO_4^-(aq)}} &= -2.967\times 10^{-3}\text{ mol/(L}\cdot\text{s) (two extra digits carried)}
\end{aligned}$$

Statement: The average rate of disappearance of permanganate ion over the first 30 s of the reaction is $3.0\times 10^{-3}\text{ mol/(L}\cdot\text{s)}$.

(c) Given:

$2\ \mathrm{MnO_4^-(aq)} + 5\ \mathrm{H_2C_2O_4(aq)} + 6\ \mathrm{H_3O^+(aq)} \rightarrow 2\ \mathrm{Mn^{2+}(aq)} + 10\ \mathrm{CO_2(aq)} + 14\ \mathrm{H_2O(l)}$;

$$\frac{\Delta[\mathrm{MnO_4^-(aq)}]}{\Delta t} = -2.967\times 10^{-3}\text{ mol/(L}\cdot\text{s)}$$

Required: average rate of disappearance of $\mathrm{H_2C_2O_4(aq)}$ and appearance of $\mathrm{CO_2(aq)}$

Analysis: Scale the rates by the inverse of their coefficients in the balanced chemical equation. Then, substitute the given rate and solve for the required rates.

Solution:
$$\begin{aligned}
\frac{1}{2}\left(-\frac{\Delta[\mathrm{MnO_4^-(aq)}]}{\Delta t}\right) &= \frac{1}{5}\left(\frac{\Delta[\mathrm{H_2C_2O_4(aq)}]}{\Delta t}\right)\\
\frac{\Delta[\mathrm{H_2C_2O_4(aq)}]}{\Delta t} &= \frac{5}{2}(-2.967\times 10^{-3}\text{ mol/(L}\cdot\text{s))}\\
\frac{\Delta[\mathrm{H_2C_2O_4(aq)}]}{\Delta t} &= -7.4\times 10^{-3}\text{ mol/(L}\cdot\text{s)}
\end{aligned}$$

$$\begin{aligned}
\frac{1}{2}\left(-\frac{\Delta[\mathrm{MnO_4^-(aq)}]}{\Delta t}\right) &= \frac{1}{10}\left(\frac{\Delta[\mathrm{CO_2(aq)}]}{\Delta t}\right)\\
\frac{\Delta[\mathrm{CO_2(aq)}]}{\Delta t} &= -\frac{10}{2}(-2.967\ \times\ 10^{-3}\text{ mol/(L}\cdot\text{s))}\\
\frac{\Delta[\mathrm{CO_2(aq)}]}{\Delta t} &= 1.5\times 10^{-2}\text{ mol/(L}\cdot\text{s)}
\end{aligned}$$

Statement: The average rate of disappearance of $H_2C_2O_4(aq)$ is 7.4×10^{-3} mol/(L · s) and the average rate of appearance of $CO_2(aq)$ is 1.5×10^{-2} mol/(L · s).

(d) No, measuring colour intensity is not the only way to determine concentration of reactants and products over time for this reaction. Because H_3O^+ is a reactant, the reaction could be monitored by pH change.

74. Answers may vary. Sample answer: Yes, I think the clerk is using the term "catalyst" correctly because the accelerant could be a catalyst that speeds up the reaction of the paint with air when it is spread onto the wall.

75. Answers may vary. Sample answer: No, I think the statement "a gas station is much more likely to catch fire spontaneously on a hot day than on a cold day" is not accurate. Higher temperatures would cause more gasoline to become a vapour, increasing the concentration in the air, and the higher temperature means the molecules will collide with more energy. However, an ignition source like a spark is still required to start the fire regardless of whether the air temperature is hot or cold.

Reflect on Your Learning

76. Answers may vary. Student answers should relate aspects of chemical kinetics to everyday life through examples of reactions with controlled rates, such as biochemical reactions in cells or chemical reactions in cooking. Other examples could include combustion of fuels.

77. Answers may vary. Sample answer: Three examples of ways to control reaction rate are: increasing temperature during cooking to make chemical changes in the food occur more rapidly; increasing the concentration of air in a fireplace to increase the rate of fuel combustion; and adding lemon juice to sliced fruit to slow down discoloration.

78. Answers may vary based on student experience.

Research

79. Answers may vary. Sample answer: Heterogeneous catalysts are used in hydrogenation of carbon–carbon double bonds. The catalyst is a solid metal or metal salt that the liquid and/or gas passes over. Heterogeneous catalysts are used to hydrogenate vegetable oils to make margarine. In this case, nickel is used as a catalyst. Catalytic converters in vehicles use other metals as heterogeneous catalysts to convert harmful molecules in exhaust into more harmless molecules, such as carbon dioxide.

Homogeneous catalysts are used to catalyze reactions between ions in solution; for example, to create certain chemicals, such as ethanol and esters. Homogeneous catalysts are used in various parts of the petrochemical industry. Enzymes are a type of homogenous catalyst, and are used in industrial processes to make cheese and other food products.

In general, industrial processes use heterogeneous catalysts, which can be easily recovered and reused. It can be expensive and difficult to recover catalysts in solution from a solution that also contains the reactant and the product.

80. Answers may vary. Sample answer: In autocatalysis, the product of the reaction is also a catalyst for the reaction. An example is the reduction of permanganate ions, MnO_4^-, to Mn^{2+} ions, which is catalyzed by Mn^{2+}. This reaction is carried out as part of the process of manufacturing some types of circuit boards to "desmear" the boards. A medical example is the release of the hormone oxytocin during labour and childbirth. Contractions cause the release of oxytocin, which induces more contractions, causing increased release of the hormone. The result is a positive feedback loop that leads away from homeostasis to the conditions necessary for childbirth.

81. Answers may vary. Sample answers:

(a) Ozone, $O_3(g)$, is toxic to living things because it is a strong oxidizing agent, so it damages body tissues such as the lungs of animals and the leaves of plants.

(b) The mechanics of the reactions that lead to the production of ozone are as follows:

$N_2(g) + O_2(g) \rightarrow 2\ NO(g)$ (in the presence of heat, such as in car engines)

$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$ (spontaneous, in air)

$NO_2(g) \rightarrow NO(g) + O(g)$ (in bright light or UV light)

$O(g) + O_2(g) \rightarrow O_3(g)$ (spontaneous)

(c) The connection between the production of ozone and kinetics is that two steps in the formation of ozone are spontaneous. A third step relies on heat, which is always present in internal combustion engines, so does not slow the reaction down. The fourth step relies on light, such as sunlight. Ozone concentrations are often highest in the afternoon when the Sun's effect is strongest.

82. Answers may vary. Sample answer: John Polanyi is a Canadian scientist who was awarded the Nobel prize for his work in chemical kinetics. In a statement, the Royal Swedish Academy stated that Polanyi received the award for developing "the method of infrared chemiluminescence," that is, measuring and analyzing the very weak infrared fields of molecules that have just formed. Polanyi has used this method to learn more about how energy is transferred and transformed during chemical reactions. His experiments have also included investigations into gaseous reaction dynamics, and using spectroscopy to observe transition states.

John Polanyi was born in 1929 and educated in England, and studied in the United States before becoming a member of the faculty of Chemistry at the University of Toronto. He has received numerous other honours for his work. He also dedicates much of his time to the peace movement,

In his acceptance speech for the Nobel prize, Polanyi said: "When … we fear science, we really fear ourselves. Human dignity is better served by embracing knowledge."