14. (c)
15. (a)
16. (b)
17. (d)
18. (b)

CHAPTER 6 REVIEW

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Understanding Concepts

1. pressure or volume, conductivity, absorbency of light
2. concentration, temperature, catalysis, chemical nature of reactants
3. Additional surface area $= 18 \times 1\ \text{cm}^2$

   Total surface area $= 24\ \text{cm}^2$

   Proportional change in surface area $= \dfrac{24\ \text{cm}^2}{6\ \text{cm}^2} = 4$

   The rate would be multiplied by a factor proportional to the surface area change:
   $r = 4 \times 20$ mL/s
   $r = 80$ mL/s
4. (a) rate increases
   (b) rate decreases
   (c) rate increases
   (d) rate increases
5. (a) $r = \dfrac{\Delta V}{\Delta t}$

   $= \dfrac{44.2\ \text{mL}}{30.0\ \text{s}}$

   $r = 1.47$ mL/s

   (b) (i) With a 5°C increase in temperature, the rate could be doubled and the time halved.
   (ii) Without the catalyst, the reaction might be imperceptibly slow.
6. (a) $r = k\,[ClO_{2(aq)}]^2[OH^-_{(aq)}]$
   (b) This is a third-order reaction.
   (c) The rate would quadruple.
   (d) The rate would double.
7. (a) When we compare Trials 1 and 2, we see that as $[Cl_2]$ is doubled, rate is multiplied by 2; therefore, rate depends on $[Cl_2]^1$.
   When we compare Trials 2 and 3, we see that as [NO] is doubled, rate is multiplied by 4; therefore, rate depends on $[NO]^2$.
   Overall, $r = k\,[Cl_2]^1[NO]^2$.
   (b) The rate-determining step is most likely to be
   $2\,NO_{(g)} + Cl_{2(g)} \rightarrow$ product or intermediate

   (c) $k = \dfrac{r}{[NO]^2\,[Cl_2]}$

   $= \dfrac{1.8 \times 10^{-2}\ \text{mol/(L•s)}}{(0.10\ \text{mol/L})^2 \times 0.10\ \text{mol/L}}$

   $k = 18\ \text{L}^2/(\text{mol}^2\text{•s})$

   (d) $r = k\,[NO]^2\,[Cl_2]$

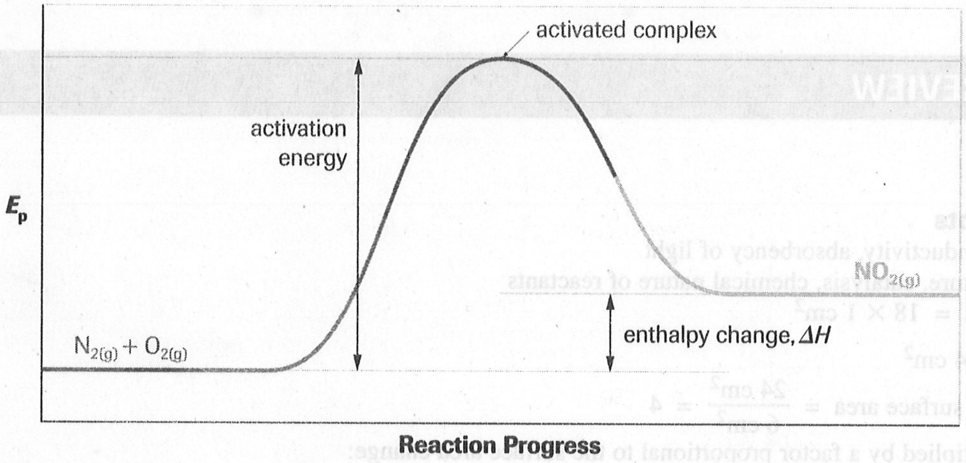
   $= 18\ \text{L}^2/(\text{mol}^2\text{•s})\ (0.30\ \text{mol/L})^2 \times 0.40\ \text{mol/L}$

   $r = 0.65\ \text{mol/(L•s)}$

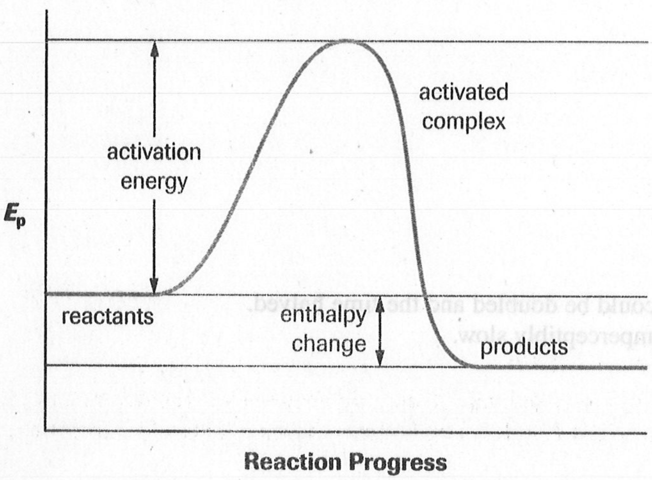
8. (a) Half-life is the amount of time for one-half the mass of a radioisotope to decay.
   (b) 14.0 a is four half-lives. The percentage remaining is $100\% \times (\frac{1}{2})^4 = 6.25\%$.

9.

Potential Energy Diagram of Formation of Nitrogen Dioxide



10. **Potential Energy Diagram of an Exothermic Reaction**



11. (a) There are generally one, two, or three particles involved in each elementary step.
    (b) Collisions of more particles at the same point in time and space are much less probable as the number of particles increases. Four-body collisions are effectively impossible as contributors to a reaction process.
12. (a) A catalyst might be consumed in one step of a mechanism as long as it is regenerated in a subsequent step.
    (b) Homogeneous catalysts, like acid in aqueous solution, are in the same phase as reactants. Heterogeneous catalysts, like platinum in gases, are in different phases from reactants.
13. (a) catalyst (necessary in first step but regenerated): $Cu^{2+}_{(aq)}$

    intermediates (produced but then consumed): $Cu^{+}_{(aq)}$, $I_{(aq)}$, $CuSO^{+}_{4(aq)}$

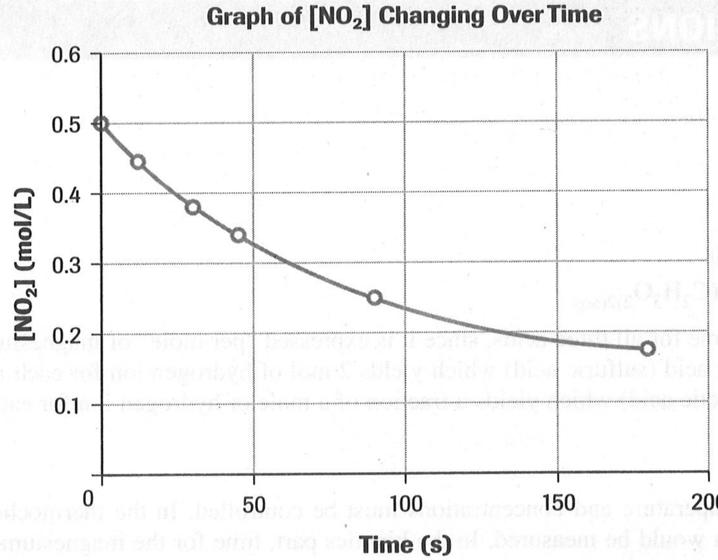
    (b) $S_2O^{2-}_{8(aq)} + 2\,I^{-}_{(aq)} \rightarrow I_{2(aq)} + 2\,SO^{2-}_{4(aq)}$

    (c) Since the $I^{-}_{(aq)}$ is not part of the rate-determining (slow) step, increasing its concentration will have no effect on the overall rate.

    (d) Since the $S_2O^{2-}_{8(aq)}$ is part of the rate-determining (slow) step, increasing its concentration will increase the overall rate.

Applying Inquiry Skills

14. (a)



(b) Average rate, $r_{ave(t = 10 - 60)} = \frac{\Delta c}{\Delta t}$

$= (0.45–0.30)/(10–60)$

$r_{ave(t = 10 - 60)} = 0.003$ mol/(L•s)

(c) Instantaneous rate, $r_{ins(c = 0.46)} = \frac{\Delta c}{\Delta t}$

$r_{ins(c = 0.46)} = 0.004$ mol/(L•s)

Instantaneous rate, $r_{ins(c = 0.23)} = \frac{\Delta c}{\Delta t}$

$r_{ins(c = 0.23)} = 0.001$ mol/(L•s)

(d) As $[NO_2]$ was halved, the rate was multiplied by 1/4, roughly.

(e) The reaction is second order or rate is proportional to $[NO_2]^2$.

15. (a) When we compare Trials 1 and 2, we see that as [W] is doubled, rate is unchanged; therefore, rate depends on $[W]^0$.
When we compare Trials 1 and 3, we see that as [X] is doubled, rate is multiplied by 2; therefore, rate depends on $[X]^1$.
When we compare Trials 1 and 4, we see that as [Y] is doubled, rate is multiplied by 4; therefore, rate depends on $[Y]^2$.
Overall, $r = k\,[X]^1\,[Y]^2$.

(b) The rate-determining step is $X + 2Y \rightarrow$ products.

(c) A possible mechanism might be:

$X + 2Y \rightarrow XY_2$ (slow)
$XY_2 + W \rightarrow WXY_2$ (fast)
$WXY_2 + X \rightarrow Z$ (fast)

Making Connections

16. (a) When we compare Trials 1 and 2, we see that as [Hbn] is doubled, rate is multiplied by 2; therefore, rate depends on $[Hbn]^1$.
When we compare Trials 2 and 3, we see that as [CO] is tripled, rate is multiplied by 3; therefore, rate depends on $[CO]^1$.

(b) The overall order is two.

(c) Overall, $r = k\,[Hbn]^1\,[CO]^1$.

(d) The carbon monoxide rate constant might be expected to be larger than the oxygen rate constant because it seems to bind so quickly to hemoglobin. On the other hand, as will be discovered in the next unit, the more significant factor is the equilibrium constant for the binding reaction, which is much larger for carbon monoxide than for oxygen.

UNIT 3 PERFORMANCE TASK: ENERGY AND RATES ANALYSIS OF CHEMICAL REACTIONS

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Prediction/Hypothesis

(a) $Mg_{(s)} + 2\ HCl_{(aq)} \rightarrow H_{2(g)} + MgCl_{2(aq)}$

$Mg_{(s)} + H_2SO_{4(aq)} \rightarrow H_{2(g)} + MgSO_{4(aq)}$

$Mg_{(s)} + 2\ HC_2H_3O_{2\ (aq)} \rightarrow H_{2(g)} + Mg(C_2H_3O_2)_{2(aq)}$

(b) The molar enthalpy should be about the same for all three acids, since it is expressed "per mole" of magnesium. The largest rate should be with a dibasic strong acid (sulfuric acid) which yields 2 mol of hydrogen ion for each mole of acid, and the smallest with a weak acid (acetic acid) which yields a fraction of a mole of hydrogen ion for each mole of acid.

Experimental Design

(c) (Answers will vary.) Variables such as temperature and concentrations must be controlled. In the thermochemistry part, maximum temperature of the solution would be measured. In the kinetics part, time for the magnesium ribbon to be consumed might be a possibility, but a better method would be to measure the volume of hydrogen gas trapped in a gas measuring tube, over time.

Materials

(d) (Answers will vary.)
Styrofoam cups (for calorimetry)
stopwatches (for kinetics)

Procedure

(e) (Answers will vary. This is a student-designed experiment and considerable opportunity should be provided students to come up with their own procedures, in particular in the measurements of changes of gas production over time. The following is only one possible minimal design.)

1. Place 50 mL of 0.50 mol/L hydrochloric acid in a Styrofoam cup calorimeter. Measure the initial temperature of the acid. Add a measured mass of magnesium to the acid. Record the maximum temperature.
2. Repeat the previous step for separate samples of the other acids.
3. Place 50 mL of hydrochloric acid in an Erlenmeyer flask, stoppered with a one-hole rubber stopper and delivery tube leading to an inverted water-filled graduated cylinder. Measure the time taken for 20 mL of gas to be produced.
4. Repeat the previous step for separate samples of the other acids.

Evidence

(f) (Sample answers)

Thermochemistry				
Acid	**Initial *T* (°C)**	**Final *T* (°C)**	**Volume of Acid (mL)**	**Mass of Mg (g)**
HCl	24.2	31.0	50	0.075
H_2SO_4	22.0	28.5	50	0.079
HAc	21.2	27.0	50	0.076

Kinetics	
Acid	**Time for 20 mL of Gas to Form (s)**
HCl	31
H_2SO_4	15
HAc	160