QUESTIONS AND PROBLEMS

A

1. (a) What kind of a unit is always in the denominator of a rate expression? (b) A man runs 16 kilometres in 4 hours. What is his average rate of travel? (c) A process generates 0.5 mole of CO_2 in 10 minutes. What is the rate of the CO_2 formation process? Show units.
2. Express the rate of the reaction $2HI(g) \longrightarrow H_2(g) + I_2(g)$ in terms of H_2 concentration buildup.
3. Gaseous NH_3 reacts very slowly with O_2. A catalyst is needed to get a reasonable rate at workable temperatures. The somewhat related compound PH_3 (see periodic table) reacts quite rapidly with oxygen at room temperature. What causes the difference?
4. Several processes are listed below. Some are fast and some are slow. Indicate *why* you would expect each process to be fast or slow at room temperature.

   (a) $5C_2O_4^{--} + 2MnO_4^- + 16H^+ \longrightarrow 10CO_2 + 2Mn^{++} + 8H_2O$ SLOW

   (b) $2C_2H_6 + 7O_2 \longrightarrow 4CO_2 + 6H_2O$ SLOW

   (c) $Ag^+ + Cl^- \longrightarrow AgCl$ FAST

   (d) $Ce^{++++} + Fe^{++} \longrightarrow Fe^{+++} + Ce^{+++}$ FAST

   (e) $H^+ + OH^- \longrightarrow H_2O$ FAST

   (f) $2NH_3 + 2\frac{1}{2}O_2 \longrightarrow 2NO + 3H_2O$ SLOW

5. Explain, in terms of the kinetic theory, why an increase in concentration of reactants should increase the rate of a reaction.
6. In recovering copper from a solution obtained by passing water through mine dumps, iron scrap is used. The equation is

   $$Fe(s) + Cu^{++}(aq) \longrightarrow Fe^{++}(s) + Cu(s)$$

   How might you *increase* the rate of the process?
7. A wooden splint that glows in air will burst into flames if it is plunged into a tube full of O_2 gas. Why?
8. (a) A reaction mechanism that involves the simultaneous collision of just 4 molecules is not normally proposed. Why?
   (b) Explain why the following equation does not represent the *mechanism* for the oxidation of HBr by O_2:

   $$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

   (c) Write the suggested reaction mechanism for the reaction given in (b) above. What piece of experimental information suggests this mechanism? Refer to page 396.
9. (a) Why does milk keep better in a refrigerator than it does if allowed to stand on the cupboard shelf? Explain. Consider the energetics of the process. (b) Why does a match ignite a mixture of propane and oxygen?
10. Why is lump sugar satisfactory for use in hot chocolate but granulated sugar preferable for use in iced tea?
11. Examine Figures 15-5 and 15-6. Which "pie slice" contains the *slowest*-moving tin atoms?
12. Refer to Figure 15-7. Describe the shape of the plot obtained at a third temperature T_3, where T_3 is *lower* than the original temperature, T_1.
13. Figure 15-8 is a "road map" for the trip from city R to city P via mountain pass A. Assuming such a trip is similar to a chemical reaction, what is represented by city R, city P, and mountain pass A?
14. Consider the reaction A + B → C + D + 70 kcal. The activation energy for the process between A and B is 22 kcal. (a) Sketch the potential energy diagram for the process between C and D. Label both axes. (b) Sketch the potential energy diagram for the reverse process. (c) Sketch the potential energy diagram for the forward process in the presence of a good catalyst.
15. Write the equation for the decomposition of formic acid (HCOOH). What is the catalyst for this process?
16. Refer to Figure 15-9. Where does the activated complex form? What two possible "futures" exist for the activated complex?

B

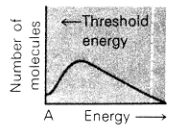
17. An aircraft flies between Toronto and Windsor, Canada, (a distance of 200 miles) in an hour and 10 minutes (gate to gate). (a) What is the effective overall *rate of travel* of the airplane? Give units. (b) Was the airplane going faster than the overall rate at some point on its trip? Explain. (c) What is frequently the rate-determining step when the airport is very busy or is closed by a storm?
18. A mixture of isooctane (C_8H_{18}) and oxygen in an automobile cylinder explodes in accordance with the equation

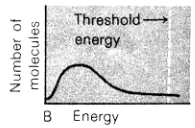
    $$C_8H_{18}(g) + 12\tfrac{1}{2}O_2(g) \longrightarrow 8CO_2(g) + 9H_2O(g)$$

    What *units* might be used to describe the reaction? Refer to page 391.
19. (a) The reaction of a gaseous chlorine atom with a hydrogen molecule (H_2) is very fast. Knowing this fact, explain why ultraviolet light will initiate the reaction of a mixture of H_2 and Cl_2. (b) Refer to the reaction between H_2 and I_2 on page 398. Would you expect ultraviolet light to be as effective in initiating this reaction as it is in the $H_2 + Cl_2$ reaction? Explain.
20. What is the function of the pilot light in a gas stove? Explain by drawing the approximate potential energy diagram for the reaction

    $$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$$

    and indicating with an arrow the function of the pilot light.
21. A manufacturer of flashcubes containing magnesium powder and oxygen gas wants to achieve a somewhat longer duration for the flash period. Can you suggest a possible way to do this?
22. An old rule of thumb states that, for many common reactions, an increase in temperature of 10 °C doubles the rate of the reaction. Does this mean that an increase of 10 °C doubles the average kinetic energy of the molecules? Explain, using a curve like that shown in Figure 15-7.





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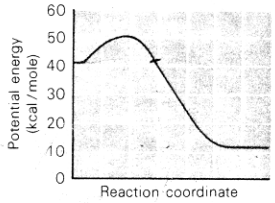
23. Explain why a *mechanism* for ammonia formation such as

$$3H_2 + N_2 \longrightarrow 2NH_3$$

is highly unlikely.

24. Given the kinetic energy distribution curves and the threshold energies for reactions A and B, ** Which reaction will be faster at room temperature? (b) Which reaction will show the greater rate increase if the temperature is raised 10 °C?

25. Given the potential energy diagram at right: (a) Is this reaction exothermic or endothermic? (b) Would you expect this reaction to occur rapidly at room temperature? Why or why not? (c) What is ΔH for this reaction? (d) What is the activation energy for the forward reaction? (e) At what point on the graph might an activated complex exist? (f) Which of the following reactions could this diagram most likely represent?

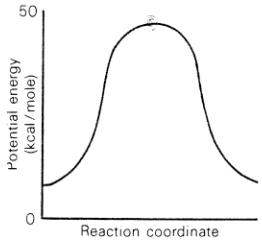


(1) $H_2SO_4(l) \xrightarrow{H_2O} 2H^+(aq) + SO_4^{--}(aq)$

(2) $NH_4NO_3(s) \xrightarrow{H_2O} NH_4^+(aq) + NO_3^-(aq)$

(3) $(NH_4)_2Cr_2O_7(s) \xrightarrow{\text{heat}} N_2(g) + Cr_2O_3(s) + 4H_2O(g)$

Explain your reasoning in each case.



26. Consider the potential energy diagram at left. (a) Is this reaction exothermic, endothermic, or neither? (b) Would you expect this reaction to occur rapidly at room temperature? Explain your answer. (c) Of the following reactions, which one might this diagram represent?

(1) $H_2SO_4(l) \longrightarrow 2H^+(aq) + SO_4^{--}(aq)$
(2) $NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$
(3) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$
(4) $C(graphite) \longrightarrow C(diamond)$, where $\Delta H = +0.45$ kcal

Reaction (4) takes place only at high temperatures and pressures.

27. For a particular reaction, ΔH is -60 kcal, and the activation energy for the forward reaction is $+30$ kcal. (a) Draw the potential energy curve for the reaction. Be sure to label the axes and include a scale on the potential energy axis. (b) Label the parts of the curve representing (1) the reactants, (2) the products, (3) the activation energy of the forward reaction, (4) the activated complex, and (5) the net energy absorbed or released (give the amount of energy, and note whether it is absorbed or released).

C

28. In Experiment 10, hydrogen gas is produced by the reaction of magnesium ribbon with 15 ml of 3 *M* hydrochloric acid added to about 40 ml of water:

$$Mg(s) + 2H^+(aq) + 2Cl^-(aq) \longrightarrow Mg^{++}(aq) + 2Cl^-(aq) + H_2(g)$$

(a) How can you express the rate of the reaction? (b) What units, if any, should be used? (c) What effect on rate would you expect to result from using 15 ml of 6 *M* HCl in 40 ml of water? (d) Is your answer qualitative or quantitative? Why?

29. Black powder is a mixture of charcoal, sulfur, and the compound saltpeter, or potassium nitrate. A laboratory mixture of the powdered ingredients may not ignite when touched with the flame of a match, but, after processing through a powder mill, it explodes violently when ignited by a match. Can you suggest why?

30. One of the important processes in the formation of photochemical smog is

$$2NO(g) + O_2 \xrightarrow{\text{light}} 2NO_2(g)$$

NO comes from automobile exhaust products. The rate of NO_2 formation is studied at constant O_2 concentration and variable NO concentration. Data are shown below:

Relative initial concentration of NO	*Relative initial rate of process*
1	1
2	4
3	9

What would the relative initial rate of the process be at an NO concentration of 5? Write a generalized expression for the rate of NO_2 formation when NO concentration is a variable. Would these data be consistent with the following mechanism? Explain your answer.

$$NO + NO \longrightarrow N_2O_2 \quad \text{FAST}$$
$$N_2O_2 + O_2 \longrightarrow 2NO_2 \quad \text{SLOW}$$

Explain your answer.

31. The rate law for the reaction

$$NO + O_3 \longrightarrow NO_2 + O_2$$

is rate $= k[NO][O_3]$. Which of the following mechanisms is consistent with this rate law? Explain your answer.

(a) $NO \longrightarrow N + O$ SLOW
$N + O_3 \longrightarrow NO_2 + O$ FAST
$O + O \longrightarrow O_2$ FAST
$NO + O_3 \longrightarrow NO_2 + O_2$ OVERALL

(b) $NO + O_3 \longrightarrow NO_2 + O_2$ SLOW

(c) $O_3 \longrightarrow O_2 + O$ SLOW
$O + NO \longrightarrow NO_2$ FAST
$O_3 + NO \longrightarrow NO_2 + O_2$ OVERALL

32. Suppose the disks on the apparatus in Figure 15-5 are 1.0 cm apart and rotating at a rate of 1,200 revolutions per minute to yield the "pie-slice" distribution shown in Figure 15-6. Suppose the rate of rotation of the disks is increased to 2,400 revolutions per minute. What are the velocities of the tin atoms that arrive on pie slices 1 and 2? Refer to the footnote on page 402.

33. For the reaction

$$H_2 + Cl_2 \longrightarrow 2HCl + 44 \text{ kcal}$$

the energy of activation for the process as written is 37 kcal. What is the energy of activation for the decomposition of HCl to give H_2 and Cl_2?