

Answers to Chapter 6 Review Questions pg. 392-7

1. d 2. b 3. c 4. a 5. e 6. d 7. d 8. b 9. d 10. e 11. a 12. d 13. c 14. d

15. Rate of reaction is equal to the change in the quantity of a reactant or a product divided by the time during which the change occurs.

16. Sample answers: a. mL/s b. kPa/s c. pH/s

17. a. The rate will increase since at a higher total pressure the particles are forced closer together and they will collide more often, resulting in a higher frequency of successful collisions.

b. The rate will not be affected because the particles in an aqueous solution cannot be forced any closer together and cannot be made to collide more often by increasing the pressure.

18. The reactant particles have strong bonds that require a high energy collision to break; the reactant particles have a shape that requires an exact orientation before a collision can be effective.

19. a. The initial rate of reaction occurs when the reactants are first mixed together and have just begun to react.

b. The initial rate of reaction can be determined graphically by determining the slope of the tangent to the reaction curve (concentration vs. time) at $t = 0$.

c. It is possible for the instantaneous rate to have the same value as the average rate of reaction. This would happen when a tangent to the reaction curve has the same slope as a line drawn between two points on the reaction curve. It occurs when the shape of the curve is straight between two points.

20. a. A catalyst speeds up a reaction by providing an alternate path with a lower activation energy so that a greater percentage of the collisions occur with enough energy to get over the activation energy barrier.

b. A catalyst would not be expected to speed up this reaction. This reaction is between two oppositely charged ions in solution, and is therefore already a fast reaction. No simpler two-particle process is likely.

21. The partial pressure of a gas is increased by adding more of that gas to the container, thus increasing its concentration. There will be more collisions between reactant particles as a result, and the rate will increase.

22. Without stirring, the solid solute becomes surrounded by more and more concentrated solution as it dissolves, eventually becoming surrounded by a zone of saturated solution. This dissipates slowly by diffusion. By stirring, the solution is kept as dilute as possible, ensuring that many water molecules are available to surround solute particles. The effect is the same as increasing the surface area of a reactant. Stirring would have to be very vigorous to substantially increase the kinetic energy of the particles and this is not the major reason that stirring increases the rate of dissolving.

23. The activation energy is the minimum energy that colliding reactant particles must have to allow them to reach a transitional state where they may break up into products. The activated complex is an unstable association of reactant particles formed temporarily at the transition state that will break apart either to re-form the reactants or to form products.

24. To determine the initial rates of reactions at different concentrations, several experiments are carried out, each with a different concentration of reactant.

Data for each experiment is plotted as graphs of concentration vs. time.

From these curves, the initial rates are determined for each experiment by measuring the slope of the tangent lines at time zero on each graph. These initial rates are plotted and the resulting graph of initial rate vs. initial concentration of reactant shows the relationship between reaction rate and concentration.

25. For an effective collision to occur, particles must collide with sufficient energy to get over the activation energy barrier and at a favourable orientation. There is a relatively good probability of a collision between two particles meeting these criteria. For three or more particles to collide in this manner is much less probable.

26. (i) For a solid catalyst, the more surface area exposed, the better the ability of the substance to catalyze the reaction.

(ii) The state of the reactants compared to the state of the catalyst affects how the substance can catalyze the reaction. For reactions between gases, the catalyst is most often in the solid state since the gases can be easily passed over a solid. If the catalyst for a reaction between gases is also a gas, continual intimate mixing of the gases would be required.

(iii) The purity of the catalyst is also a factor. Contaminants in the catalyst would result in less contact between particles that are involved in the reaction. Also, an impurity could interfere with the reaction.

(iv) Temperature would be a factor for a biological catalyst (called an enzyme). At higher temperatures, this type of catalyst is destroyed because its action depends on its shape, and because it is a protein, it becomes denatured at high temperatures.

27. a. The straight line represents a direct relationship between rate and concentration.

b. The slope of the graph represents the rate constant, k .

c. The reaction is first order and has the form $\text{rate} = k[A]$.

28. a. The rate constant, k , will not be affected by a change in the concentration of the reactants.

b. NO_3 is a reaction intermediate because it is produced in step 1 and used up in step 2.

29. $+5.0 \times 10^2 \text{ kJ}$ 30. $+3.1 \times 10^2 \text{ kJ}$

31. The catalyzed reaction is faster because it has a lower activation energy.

32. $+7 \times 10^2 \text{ kJ}$ 33. $+4.7 \times 10^2 \text{ kJ}$ 34. $-1.7 \times 10^2 \text{ kJ}$ 35. $+1.7 \times 10^2 \text{ kJ}$

$$\begin{aligned} 36. \text{ rate of formation of } A_2 &= \Delta \text{concentration} / \Delta t = (c_f - c_i) / (t_f - t_i) \\ &= (0.68 \text{ mol/L} - 0.52 \text{ mol/L}) / (5.6 \text{ min} - 4.4 \text{ min}) \\ &= 0.16 \text{ mol/L} / 1.2 \text{ min} \\ &= 0.13 \text{ mol/L} \cdot \text{min} \end{aligned}$$

The mole ratio $\text{AB}:A_2$ is 2:1. For every 2 mol of AB that decompose, 1 mol of A_2 is produced.

rate of decomposition of AB = $0.13 \text{ mol } A_2/\text{L} \cdot \text{min}$ ($2 \text{ mol AB}/1 \text{ mol } A_2$) = $0.26 \text{ mol/L} \cdot \text{min}$

37. change in amount of $\text{HNO}_3(\text{aq})$ is 0.10 mol

rate of change of Cu = $0.10 \text{ mol HNO}_3 \times (1 \text{ mol Cu}/4 \text{ mol HNO}_3) = 0.025 \times 0.10 \text{ mol} = 0.025 \text{ mol}$

mass of copper used in this time = $0.025 \text{ mol} \times 63.55 \text{ g/mol} = 1.6 \text{ g}$

rate of change in mass of copper = $1.6 \text{ g}/90.0 \text{ s} = 0.018 \text{ g/s}$

38. a. III b. IV c. III d. II

39. The coefficients in the chemical equation indicate the mole ratios for the components of the reaction. For every 4 mol of $\text{HBr}_{(\text{g})}$ that decompose, 2 mol of $\text{Br}_{2(\text{g})}$ is formed. In other words, there is a 2:1 ratio of $\text{HBr}_{(\text{g})}$ decomposition to $\text{Br}_{2(\text{g})}$ formation.

rate of decomposition HBr = rate of formation of $\text{Br}_2 \times (4 \text{ mol HBr}/2 \text{ mol Br}_2)$

40. rate in mol/s = $0.48 \text{ g}/5.8 \text{ min} \times 1 \text{ mol}/84.32 \text{ g} \times 1 \text{ min}/60 \text{ s} = 1.6 \times 10^{-5} \text{ mol/s}$

41. Potential energy diagram A most accurately shows the catalytic action on the mechanism. Step 1 has the highest activation energy, and it will be the slowest or rate-determining step. The catalyst would be used to lower the activation energy of the rate-determining step 1.

42. a. +20 kJ

b. No; the reverse reaction would have a greater activation energy than in (a).

$$E_a(\text{rev}) = E_a(\text{fwd}) - \Delta H = +45 \text{ kJ} - (-25 \text{ kJ}) = 70 \text{ kJ}$$

43. a. There are two steps in the reaction.

b. $C + D$ = overall activation energy

c. The overall reaction is exothermic.

d. Quantity B represents the activation energy for step 1.

e. Quantity E represents the difference between potential energy of the product(s) of step 1 and the potential energy of the final product(s).

44. a. Both reactions are second order.

b. If the molar concentration of R is doubled, the rate of reaction A will quadruple (2^2) and the rate of reaction B will double (2^1).

45. a. catalyst b. intermediate c. intermediate d. reactant

46. When the volume is reduced to half the original volume, the concentration of the reactants will each be doubled. Since the rate law is first order only in gas $X_2(g)$, the rate of the reaction would be expected to double.

47. a. Step 2 is the rate-determining step since it is identified as a slow step.

b. Intermediates are formed in one step and consumed in a subsequent step. The intermediates are $AlBr_4^-$, $C_2H_5^+$, and $C_6H_6C_2H_5^+$.

c. $AlBr_3$ is a catalyst because it is part of the reaction as a reactant in step 1 and is regenerated in step 3.

61. The mole ratio $Na_3AlF_6(l) : F_2(g)$ is 1 : 3. For every 1 mol of $Na_3AlF_6(l)$ that decomposes, 3 mol of $F_2(g)$ is produced.

$$\text{rate of decomposition } Na_3AlF_6(l) = 0.85 \text{ mol/s} \times (1 \text{ mol } Na_3AlF_6 / 3 \text{ mol } F_2(g)) = 0.28 \text{ mol/s}$$

$$m \text{ } Na_3AlF_6(l) = 0.28 \text{ mol} \times 209.95 \text{ g/mol} = 58.786 \text{ g}$$

$$\text{average rate of decomposition of } Na_3AlF_6(l) = 59 \text{ g/s}$$

$$63. n(N_2O_5) = 5.00 \times 10^5 \text{ g} / 108.02 \text{ g/mol} = 4.628 \times 10^4 \text{ mol}$$

$$N_2O_5(g) \text{ is used up at a rate of } 4.628 \times 10^4 \text{ mol/h} = 4.628 \times 10^4 \text{ mol} / 60 \text{ min} = 7.715 \times 10^1 \text{ mol/min}$$

The mole ratio of $NO_2(g) : N_2O_5(g)$ is 4:2. For every 4 mol of $NO_2(g)$ produced, 2 mol of $N_2O_5(g)$ is consumed.

$$\text{rate of formation } NO_2 = 7.715 \times 10^1 \text{ mol } N_2O_5 / \text{min} \times (4 \text{ mol } NO_2 / 2 \text{ mol } N_2O_5) = 1.54 \times 10^2 \text{ mol/min}$$