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Chapter 17: Basic Review Worksheet

1. Explain the *collision model* for chemical reactions. What "collides"?

2. Define *activation energy.*

3. Define *catalyst.* What do we call a biological catalyst?

4. Explain what it means when a reaction "has reached a state of chemical equilibrium."

5. What do we mean by an *equilibrium position*? Is the equilibrium position always the same for a reaction, regardless of the amounts of reactants initially present?

6. Compare *homogeneous* and *heterogeneous* equilibria.

7. Give Le Chatelier's principle in your own words,

8. Explain what is meant by *solubility product constant.*

9. Write the equilibrium constant expressions for each of the following reactions.
   a. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$
   b. $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$
   c. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

10. Write expressions for K_{sp} for each of the following sparingly soluble salts.
    a. ZnS
    b. $HgCl_2$
    c. LaF_3

11. Copper(II) sulfide (CuS) dissolves in water to give a solution that is 9.2×10^{-23} *M* at 25°C. Calculate K_{sp} for CuS at this temperature.

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Chapter 17: Review Worksheet

1. Do all collisions between molecules result in the breaking of bonds and the formation of products? Why?

2. How does the collision model account for the observation that higher concentrations and higher temperatures tend to make reactions occur faster?

3. Sketch a graph for the progress of a reaction illustrating the *activation energy* for the reaction.

4. Explain how an increase in temperature for a reaction affects the number of collisions that possess energy greater than E_a.

5. How does a *catalyst* speed up a reaction? Does a catalyst change E_a for the reaction?

6. Explain why equilibrium is a *dynamic* state.

7. What happens to the *rates* of the forward and reverse reactions as a system proceeds to equilibrium from a starting point where only reactants are present?

8. Although the equilibrium constant for a given reaction always has the same value at the same temperature, the actual *concentrations* present at equilibrium may differ from one experiment to another. Explain.

9. How does the fact that an equilibrium is *heterogeneous* influence the expression we write for the equilibrium constant for the reaction?

10. Suppose the reaction system

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

has already reached equilibrium. Predict the effect of each of the following changes on the position of the equilibrium:
   a. Additional $SO_2(g)$ is added to the system.
   b. The $SO_3(g)$ is liquefied and removed from the system.
   c. A very efficient catalyst is used.
   d. The volume of the container is drastically reduced.

11. Explain how dissolving a slightly soluble salt to form a saturated solution is an *equilibrium* process.

12. When writing expressions for K_{sp}, why is the concentration of the sparingly soluble salt itself not included in the expression?

13. Given the value for the solubility product for a slightly soluble salt, explain how the molar solubility, and the solubility in g/L, may be calculated.

14. Write the equilibrium constant expressions for each of the following reactions.
   a. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
   b. $N_2H_4(l) + O_2(g) \rightleftharpoons N_2(g) + 2H_2O(g)$
   c. $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$

15. For the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

at a particular temperature the equilibrium system contains $[SO_3(g)] = 0.42\ M$, $[SO_2(g)] = 1.4 \times 10^{-3}\ M$, and $[O_2(g)] = 4.5 \times 10^{-4}\ M$. Calculate K for the process at this temperature.

16. Write expressions for K_{sp} for each of the following slightly soluble salts.
   a. $Fe(OH)_3$
   b. $Cd(OH)_2$
   c. $Ba_3(PO_4)_2$

17. Silver chloride (AgCl) dissolves in water to give a solution containing 9.0×10^{-4} g solute per liter at 10°C. Calculate K_{sp} for AgCl at this temperature.

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Chapter 17: Challenge Review Worksheet

1. Explain why, once a chemical system has reached equilibrium, the concentrations of all reacts and products remain *constant* with time. Why does this *constancy* of concentration not contradict our picture of equilibrium as being *dynamic*?

2. Describe how we write the equilibrium expression for a reaction. Give three examples of balanced chemical equations and the corresponding expressions for their equilibrium constants.

3. Give balanced chemical equations and write the corresponding equilibrium constant expressions for examples of both homogeneous and heterogeneous equilibria.

4. Give an example (including a balanced chemical equation) of how each of the following changes can affect the position of equilibrium in favor of additional products for a system:
   a. The concentration of one of the reactants is increased.
   b. One of the products is selectively removed from the system.
   c. The reaction system is compressed to a smaller volume.
   d. The temperature is increased for an endothermic reaction.
   e. The temperature is decreased for an exothermic process.

5. Give three balanced chemical equations for solubility processes and write the expressions for K_{sp} corresponding to the reactions you have chosen.

6. Magnesium fluoride dissolves in water to give a solution containing 8.0×10^{-2} g solute per liter at 25°C. Calculate K_{sp} for magnesium fluoride at this temperature.

$$\text{mol HCl} = 11.6\ \text{mL} \times \frac{0.10\ \text{mol HCl}}{1000\ \text{mL}} = 0.00116\ \text{mol HCl}$$

$$0.00906\ \text{mol (base)} = \text{mol } HNO_3 + 0.00116\ \text{mol (HCl)}$$

$$\text{mol } HNO_3 = 0.0079\ \text{mol } HNO_3$$

$$\frac{0.0079\ \text{mol } HNO_3}{0.0500\ \text{L}} = 0.158\ \text{M } HNO_3$$

Chapter 17: Basic Review Worksheet

1. Chemists envision that a reaction can only take place between molecules if the molecules physically collide with each other.

2. The activation energy for a reaction represents the minimum energy the reactant molecules must possess for a reaction to occur when the molecules collide.

3. A catalyst is a substance that speeds up a reaction without being consumed. Biological catalysts are called enzymes.

4. Chemists define equilibrium as the balancing of two exactly opposing processes. When a chemical reaction is started by combining pure reactants, the only process possible initially is

   reactants → products

   However as the concentration of product molecules increases, it becomes more and more likely that product molecules will collide and react with each other

   products → reactants

   giving back molecules of the original reactants. At some point in the process the rates of the forward and reverse reactions become equal, and the system attains chemical equilibrium.

5. Consider this example: suppose we have a reaction for which K = 4, and we begin this reaction with 100 reactant molecules. At the point of equilibrium, there should be 80 molecules of product and 20 molecules of reactant remaining (80/20 = 4). Suppose we perform another experiment involving the same reaction, only this time we begin the experiment with 500 molecules of reactant. This time, at the point of equilibrium, there will be 400 molecules of product present and 100 molecules of reactant remaining (400/100 = 4). Since we began the two experiments with different numbers of reactant molecules, it's not troubling that there are different absolute numbers of product and reactant molecules present at equilibrium: however, the ratio, K, is the same for both experiments. We say that these two experiments represent two different positions of equilibrium: an equilibrium position corresponds to a particular set of equilibrium concentrations that fulfill the value of the equilibrium constant. Any experiment that is performed with a different amount of starting material will come to its one unique equilibrium position, but the equilibrium constant ratio, K, will be the same for a given reaction regardless of the starting amounts taken.

6. In a homogeneous equilibrium, all the reactants and products are in the same phase and have the same physical state (solid, liquid, or gas). For a heterogeneous equilibrium, however, one or more of the reactants or products exists in a phase or physical state different from the other substances.

7. Answers will vary, but a paraphrase of Le Chatelier's principle should go something like this: "when you make any change to a system at equilibrium, this throws the system temporarily out of equilibrium, and the system responds by reacting in whichever direction is necessary to reach a new position of equilibrium".

8. The solubility product constant is the constant for the equilibrium expression representing the dissolving of an ionic solid in water.

9. a. $K = [HBr(g)]^2 / [H_2(g)][Br_2(g)]$
   b. $K = [SO_2(g)][Cl_2(g)] / [SO_2Cl_2(g)]$
   c. $K = [CO_2(g)]$

10. a. $K_{sp} = [Zn^{2+}][S^{2-}]$
    b. $K_{sp} = [Hg^{2+}][Cl^-]^2$
    c. $K_{sp} = [La^{3+}][F^-]^3$

11. $K_{sp} = [Cu^{2+}][S^{2-}] = (9.2 \times 10^{-23})(9.2 \times 10^{-23}) = 8.5 \times 10^{-45}$

Chapter 17: Review Worksheet

1. No. When molecules collide, the molecules must collide with enough force for the reaction to be successful (there must be enough energy to break bonds in the reactants), and the colliding molecules must be positioned with the correct relative orientation for the products (or intermediates) to form.

2. Reactions are faster if higher concentrations are used for the reaction, because if there are more molecules present per unit volume there will be more collisions between molecules in a given time period. Reactions are faster at higher temperatures because at higher temperatures the reactant molecules have higher average kinetic energy, and the number of molecules that will collide with sufficient force to break bonds increases.

3. A graph illustrating the activation energy barrier for a reaction is given as Figure 17.4 in the text.

4. Although an increase in temperature does not change the activation energy for a reaction itself, at higher temperatures, the reactant molecules have higher energies and more collisions are effective. Recall that in the kinetic-molecular theory, temperature is a direct measure of average kinetic energy.

5. A catalyst speeds up a reaction by providing an alternate mechanism (pathway) having a lower activation energy than the original pathway.

6. To an outside observer, the system appears to have stopped reacting. On a microscopic basis, though, both the forward and reverse processes are still going on: every time additional molecules of the product form, somewhere else in the system molecules of product react to give back molecules of reactant.

7. A graph showing how the rates of the forward and reverse reactions change with time is given in the text as Figure 17.8. At the start of the reaction, the rate of the forward reaction is at its maximum, while the rate of the reverse reaction is zero. As the reaction proceeds, the rate of the forward reaction gradually decreases as the concentrations of reactants decrease, whereas the rate of the reverse reaction increases as the concentrations of products increase. Once the two rates have become equal, the reaction has reached a state of equilibrium.

8. The equilibrium constant for a reaction is a special ratio of the concentration of products present at the point of equilibrium to the concentration of reactants still present. A ratio means that we have one number divided by another number. Since the equilibrium constant is a ratio, there are an infinite number of sets of data that can give the same ratio: for example, the ratios 8/4, 6/3, 100/50 all have the same value, 2. The actual concentrations of products and reactants will differ from one experiment to another involving a particular chemical reaction, but the ratio of the amount of product to reactant at equilibrium should be the same for each experiment.

9. For a heterogeneous equilibrium, the concentrations of solids and pure liquids are left out of the expression for the equilibrium constant for the reaction: the concentration of a solid or pure liquid is constant.

10. a. The equilibrium position is shifted to the right.
    b. The equilibrium position is shifted to the right.
    c. The equilibrium position is not shifted.
    d. The equilibrium position is shifted to the right.

11. When a slightly soluble salt is placed in water, ions begin to leave the crystals of salt and enter the solvent to form a solution. As the concentration of ions in solution increases, eventually ions from the solution are attracted to and rejoin the crystals of undissolved salt. Eventually things get to the point that every time ions leave the crystals to enter the solution in one place in the system, somewhere else ions are leaving the solution to rejoin the solid. At the point where dissolving and "undissolving" are going on at the same rate, we arrive at a state of dynamic equilibrium.

12. We write the equilibrium constant (the solubility product), K_{sp}, for the dissolving of a slightly soluble salt in the usual manner: since the concentration of the solid material is constant, we do not include it in the expression for K_{sp}.

13. If the solubility product constant for a slightly soluble salt is known, the solubility of the salt in mol/L or g/L can be calculated. For example, for $BaSO_4$, $K_{sp} = 1.5 \times 10^{-9}$ at 25°C. Suppose x moles of $BaSO_4$ dissolve per liter; since the stoichiometric coefficients for the dissolving of $BaSO_4$ are all one, this means that x moles of $Ba^{2+}(aq)$ and x moles of $SO_4^{2-}(aq)$ will be produced per liter when $BaSO_4$ dissolves.

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = [x][x] = 1.5 \times 10^{-9}$$

$$x^2 = 1.5 \times 10^{-9} \text{ and therefore } x = 3.9 \times 10^{-5}\text{ M}$$

So the molar solubility of $BaSO_4$ is 3.9×10^{-5} M. This could be converted to the number of grams of $BaSO_4$ (233.4 g/mol):

$$(3.9 \times 10^{-5}\text{ mol/L})(233.4\text{ g/mol}) = 9.10 \times 10^{-3}\text{ g/L}$$

14. a. $K = [NO_2(g)]^2 / [NO(g)]^2 [O_2(g)]$
    b. $K = [N_2(g)] [H_2O(g)]^2 / [O_2(g)]$
    c. $K = [CO_2(g)] [NO(g)] / [CO(g)] [NO_2(g)]$

15. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$$K = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0.42]^2}{[1.4\times10^{-3}]^2[4.5\times10^{-4}]} = 2.0 \times 10^8$$

16. a. $K_{sp} = [Fe^{3+}][OH^-]^3$
    b. $K_{sp} = [Cd^{2+}][OH^-]^2$
    c. $K_{sp} = [Ba^{2+}]^3[PO_4^{3-}]^2$

17. $9.0 \times 10^{-4}\text{g} \times \dfrac{1\text{ mol}}{143.35\text{g AgCl}} = 6.3 \times 10^{-6}\text{ mol}$

$$K_{sp} = [Ag^+][Cl^-] = (6.3 \times 10^{-6})(6.3 \times 10^{-6}) = 4.0 \times 10^{-11} \text{ at } 10°C$$

Chapter 17: Challenge Review Worksheet

1. Once the point is reached that product molecules are reacting at the same speed at which they are forming, there is no further net change in concentration. However, the constancy of concentration is a macroscopic property. Microscopically, both the forward and reverse reactions are occurring and the system is dynamic.

2. The expression for the equilibrium constant for a reaction has as its numerator the concentrations of the products (raised to the powers of their stoichiometric coefficients in the balanced chemical equation for the reaction), and as its denominator the concentrations of the reactants (also raised to the powers of their stoichiometric coefficients). In general terms, for a reaction

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant expression has the form

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

in which the square brackets [] indicate molar concentration. For example, here are three simple reactions and the expression for their equilibrium constants:

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K = [NO]^2/[N_2]\,[O_2]$

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K = [SO_3]^2/[SO_2]^2\,[O_2]$

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K = [NH_3]^2/[N_2]\,[H_2]^3$

3. Answers will vary. Examples include

$C(s) + O_2(g) \rightleftharpoons CO_2(g)$ heterogeneous (solid, gases)
$K = [CO_2] / [O_2]$

$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ homogeneous (all gases)
$K = [CO_2]^2 / [CO]^2\,[O_2]$

4. There are various changes that can be made to a system in equilibrium. Here are examples of some of them.

   a. the concentration of one of the reactants is increased.

   Consider the reaction: $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

   Suppose the reactants have already reacted and a position of equilibrium has been reached which fulfills the value of K for the reaction At this point there will be present particular amounts of each reactant and of the product. Suppose 1 additional mole of O_2 is added to the system from outside. At the instant the additional O_2 is added, the system will not be in equilibrium: there will be too much O_2 present in the system to be compatible with the amount of SO_2 and SO_3 present. The system will respond by reacting to get rid of some of he excess O_2 until the value of the ratio K is again fulfilled. As the system reacts to reduce the excess of O_2, additional SO_3 will form. The net result is more SO_3 produced than if the change had not been made.

   b. the concentration of one of the products is decreased by selectively removing it from the system

   Consider the reaction: $CH_3COOH + CH_3OH \rightleftharpoons H_2O + CH_3COOCH_3$

   This reaction is typical of reactions involving organic chemical substances, in which two organic molecules react to form a larger molecule, with a molecule of water split out during the combination. This type of reaction on its own tends to come to equilibrium with only part of the starting materials being converted to the desired organic product (which effectively would leave the experimenter with a mixture of materials). A technique that is used by organic chemists to increase the effective yield of the desired organic product is to separate the two products. If the products are separated, they cannot react to give back the reactants. One method used is to add a drying agent to the mixture that chemically or physically absorbs the water from the system, removing it from the equilibrium. If the water is removed, the reverse reaction cannot take place and the reaction proceeds to a greater extent in the forward direction than if the drying agent had not been added. In other situations, an experimenter may separate the products of the reaction by distillation (if the boiling points make this possible). Again, if the products have been separated, then the reverse reaction will not be possible, and the forward reaction will occur to a greater extent.

c. The reaction system is compressed to a smaller volume

Consider the example: $3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$

For equilibria involving gases, when the volume of the reaction system is decreased suddenly, the pressure in the system increases. However, if the reacting system can relieve some of this increased pressure by reacting, it will do so. This will happen by the reaction occurring in whichever direction will give the smaller number of moles of gas (if the number of moles of gas is decreased in a particular volume, the pressure will decrease).

For the reaction above, there are two moles of the gas on the right side, but there is a total of four moles on the left side. If this system at equilibrium were to be suddenly compressed to a smaller volume, the reaction would proceed further to the right (in favor of more ammonia being produced).

d. the temperature is increased for an endothermic reaction

Consider the reaction: $2NaHCO_3 + \text{heat} \rightleftharpoons Na_2CO_3 + H_2O + CO_2$

Although a change in temperature actually does change the value of the equilibrium constant, we can simplify reactions involving temperature changes by treating heat energy as if it were a chemical substance. For this endothermic reaction, assume heat is one of the reactants. As we saw in the example in part (a) of this question, increasing the concentration of one of the reactants for a system at equilibrium causes the reaction to proceed further to the right, forming additional product. Similarly for the endothermic reaction given above, increasing the temperature causes the reaction to proceed further in the direction of products than if no change had been made. It is as if there were too much "heat" to be compatible with the amount of substances present. The substances react in a direction to consume some of the energy.

e. the temperature is decreased for an exothermic process.

Consider the reaction: $PCl_3 + Cl_2 \rightleftharpoons PCl_5 + \text{heat}$

As discussed in part (d) above, although changing the temperature at which a reaction is performed does change the numerical value of K, we can simplify our discussion of this situation by treating heat energy as if it were a chemical substance. Heat is a product of this reaction. If we are going to lower the temperature of this reaction system, the only way to accomplish this is to remove energy from the system. Lowering the temperature of the system "encourages" the system to produce more heat. So lowering the temperature will favor the product.

5. Examples will vary. Consider the following:

$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ $\quad K_{sp} = [Ag^+][Cl^-]$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$ $\quad K_{sp} = [Pb^{2+}][Cl^-]^2$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$ $\quad K_{sp} = [Ba^{2+}][SO_4^{2-}]$

6. $8.0 \times 10^{-2} g \times \frac{1\,mol}{62.31\,g\,MgF_2} = 1.3 \times 10^{-3}\,mol$

$$K_{sp} = [Mg^{2+}]\,[F^-]^2 = (1.3 \times 10^{-3})(2.6 \times 10^{-3})^2 = 8.8 \times 10^{-9}$$

Chapter 18: Basic Review Worksheet

1. Oxidation may be defined as the loss of electrons by an atom or as an increase in the oxidation state of the atom. Reduction may be defined as the gain of electrons by an atom or as a decrease in the oxidation state of the atom.

2. a. Cr = +3, O = +2
   b. Fe = +2, Cl = -1
   c. Na = +1, P = +5, O = -2

3. An oxidizing agent is a molecule, atom, or ion that causes the oxidation of some other species; it does so by accepting one or more electrons. A reducing agent is a molecule, atom, or ion that causes reduction of some other species; it does so by giving up one or more electrons. Therefore, an oxidizing agent, by taking electrons, is reduced. A reducing agent, by giving electrons, is oxidized.

4. A half-reaction is the partial equation of an overall oxidation-reduction equation which represents either oxidation or reduction. We use them because they make it easier to balance oxidation-reduction equations.

5. a. When a half-reaction is reversed, the cell potential is reversed.
   b. When the coefficients of a half-reaction are multiplied by a factor, the cell potential is unchanged.

6. Like those covered in Chapter 7, oxidation-reduction equations must be balanced by atoms (the total number of each type of atom on each side of the equation must be the same). With oxidation-reduction equations, we must also balance the charge (the number of electrons gained by one species must be lost by another; there are no "free" electrons).

7. a. $Mg(s) + 2Hg^{2+}(aq) \rightarrow Mg^{2+}(aq) + Hg_2^{2+}(aq)$
   b. $Zn(s) + 2Ag^+(aq) \rightarrow Zn^{2+}(aq) + 2Ag(s)$

8. The anode is the electrode where oxidation occurs in a galvanic cell; the cathode is the electrode where reduction occurs in a galvanic cell.