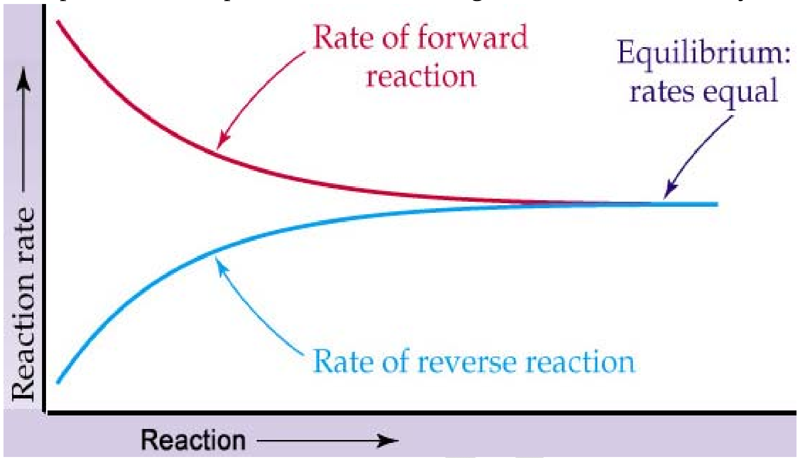
Name ___________________ Chemistry ___/___/___

Equilibrium & Reversible Reactions

So far this year we have assumed that reactions proceed to completion until the limiting reactant runs out. Many reactions do proceed to completion, but many others stop short, leaving both products and reactants. Even though it appears that a reaction may have stopped, the reaction has instead reached chemical equilibrium. **Chemical equilibrium is a dynamic state where the concentrations of the reactants and products remain constant**. Equilibrium is not static; the molecules are constantly moving and reacting in both directions. **At equilibrium, the rate of the forward reaction is equal to the rate of the reverse reaction**. Since the reactions proceed in both directions simultaneously, the chemical equation is written with a double half arrow which points in both directions. The reaction written to the right is a **reversible reaction**: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$



In the above reaction, nitrogen gas reacts with hydrogen gas to form ammonia and ammonia decomposes to form both nitrogen gas and hydrogen gas.

Mass-Action Expressions

Chemists use mass-action expressions to describe a system undergoing a chemical change. Mass action expressions are used for reversible reactions. **In a mass action expression, the concentration of the products is written over the concentration of the reactants**.

$$\frac{[\text{products}]}{[\text{reactants}]}$$

To denote concentration, scientists write a substance's formula in brackets. Concentration is measured in Molarity, moles/L or moles/dm^3; both are exactly the same. Example: Write the mass action expression for the following equation: $N_2(g) + 3H_2 \rightleftharpoons 2NH_3(g)$

$$\frac{[NH_3]^2}{[N_2]x[H_2]^3}$$

Notice that the concentration of each substance is raised to the power of its coefficient value in the balanced equation.

Equilibrium Constant

When numeric values are used for the concentrations of the substances in a mass action expression, scientists call the expression an **equilibrium expression**. The value calculated in an equilibrium expression is called the **equilibrium constant, K_{eq}**. Any substance that has a constant concentration during a reaction, including solids and all pure liquids, is not written as part of an equilibrium expression. **Only gases and aqueous ions are written in equilibrium expressions.**

Example: For the following equation: $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. At a particular temperature, a scientist determined the concentration of HI to be 1.3M, H_2 to be 0.3M & I_2 to be 0.3M. Calculate the equilibrium constant at this temperature.

$$\frac{[H_2] \text{ x } [I_2]}{[HI]^2} \longrightarrow \frac{[0.3] \text{ x } [0.3]}{[1.3]^2} \longrightarrow \mathbf{K_{eq} = 0.05}$$

When the K_{eq} value for an equilibrium expression is greater than one, there are more of the products than the reactants. When the K_{eq} value is less than one, there are more reactants than products.

In summary: **K_{eq} > 1 products favored; K_{eq} < 1 reactants favored**.

The value of the equilibrium constant is not affected by the initial concentrations of any of the substances involved in the reaction. Only temperature will cause the equilibrium constant to change.

Solubility Equilibrium

Salts differ in their solubilities. Even if a salt is said to be "insoluble" in water, it still dissolves to some extent. The **solubility product constant, K_{sp}**, is used to represent the equilibrium established between a solid and the ions it forms in solution. The equations used to determine solubility of a solid, have the solid written as a reactant and the aqueous ions as the products. The solubility of aluminum hydroxide would be written as: $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^{1-}(aq)$. As long as some undissolved (solid) salt is present in solution, the concentration of the solid salt is constant and it is not included in equilibrium expressions. In a solubility product expression only the aqueous ions are written. The solubility product expression of aluminum hydroxide would be written as: $K_{sp} = [Al^{3+}] \times [OH^{1-}]^3$.

Common Ion Effect

The **common ion effect** is a **decrease in the solubility of a compound when it is dissolved in a solution that already contains an ion in common with the salt being dissolved**. For example, barium sulfate is an insoluble salt which means very little dissolves in solution. Doctors use barium sulfate to take X-rays of the digestive tract. Barium sulfate is safe but barium ions are very poisonous. Doctors must be sure that there are no barium ions in the solution. To do so, they add sodium sulfate, a very soluble solid. When sodium sulfate dissolves in solution, a large amount of sulfate ions are added to solution. The excess of sulfate ions means that all the barium ions will be bonded to the sulfate ions and none will be free floating.

$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$ by adding $Na_2SO_4 \rightleftharpoons 2Na^{2+} + SO_4^{2-}$ there is an excess of SO_4^{2-}. This means all of the Ba^{2+} ions will be bonded to SO_4^{2-} ions, forming $BaSO_4$. SO_4^{2-} is the common ion because it appears in both compounds and it decreases the solubility of Ba^{2+} ion.

Homework:

1. What is chemical equilibrium?
2. At equilibrium, the rate of the forward reaction is equal to:
3. Draw a graph that shows the above concept.
4. What do scientists use in chemical equations to indicate that a reaction is reversible?
5. Write an example of a reversible chemical equation.
6. In a mass action expression, which concentration is written on top?
7. How do scientists denote concentration?
8. What are the two ways in which concentration is measured?

Write mass action expressions for the following reactions.

9. $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

10. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

11. $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$

12. $4NH_3(g) + 5O_2(g) \rightleftharpoons 6H_2O(g) + 4NO(g)$

13. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

14. $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

15. $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$

16. $NH_2COONH_4(g) \rightleftharpoons CO_2(g) + 2NH_3(g)$

17. $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

18. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

Calculate each of the following.

19. What is the K_{eq} of H_2SO_3 in water if the equilibrium concentrations are 3.0 M for $[H_2SO_3]$ and 0.219 M for both $[H_3O^+]$ and $[HSO_3^-]$? $H_2SO_3(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_3^-(aq)$

20. What is the K_{eq} if the $[N_2]$ is 2.95 M, $[H_2]$ is 7.68 M, and $[NH_3]$ is 5.78M? $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$

21. Calculate the equilibrium constant for the following reaction $4NH_3(g) + 5O_2(g) \rightleftharpoons 6H_2O(g) + 4NO(g)$ given the following concentrations $[NH_3]$ = 1.1 M, $[O_2]$ = 0.6 M, $[H_2O]$ = 0.02 M and [NO] = 0.012 M.

22. Calculate the concentration of OH^- if the equilibrium concentration of NH_2OH in water is 2.55 M.
$[OH^-] = [NH_3OH^+]$ $K_{eq} = 1.1 \times 10^{-8}$ $NH_2OH\,(aq) + H_2O\,(l) \rightleftharpoons NH_3OH^+\,(aq) + OH^-\,(aq)$

23. The K_{eq} for a reaction is 120 at a certain temperature. If the concentration of PCl_5 and PCl_3 are 0.12 moles/liter and 0.098 moles/liter respectively, what is the concentration of Cl_2? $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

24. What does K_{eq} represent?

25. What types of substances are not written in an equilibrium expression?

26. What is favored if a K_{eq} value is greater than one?

27. What is favored if a K_{eq} value is less than one?

28. What are the only factors that can change a K_{eq} value?

29. What does K_{sp} represent?

30. When is K_{sp} used?

31. What is not written in a solubility product expression?

Set up solubility product expressions for each of the following.

32. $Zn(OH)_2(s) \rightleftharpoons Zn^{2+}(aq) + 2OH^{1-}(aq)$

33. $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

34. $PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^{-}(aq)$

35. $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$

36. $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^{-}(aq)$

37. $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

Calculate each of the following.

38. What is the concentration of Ca^{2+} in a saturated solution of CaF_2 if $[F^-]$ is 2.2×10^{-3}? $K_{sp} = 5.3 \times 10^{-9}$

$CaF_2 (s) \rightleftharpoons Ca^{2+} (aq) + 2F^{-} (aq)$

39. What is the concentration of lead ions in a saturated lead(II) bromide solution at 298K? K_{sp} of $PbBr_2 = 2.1 \times 10^{-6}$

40. At 298 K the solubility product constant of silver sulfide is 8.00×10^{-51}. Calculate the silver ion concentration of a saturated solution of silver sulfide?

41. Calculate the concentration of barium ions in a saturated barium sulfate solution at 298 K. The solubility product constant for barium sulfate is 1.1×10^{-10}.

42. What is the common ion effect?

43. Give an example of the common ion effect.