

## 10.8: Study Points

- If two opposing chemical reactions proceed simultaneously *at the same rate*, the processes are said to be in **equilibrium**. The two opposing reactions are shown linked with a double arrow ( $\rightleftharpoons$ ). An example of opposing chemical reactions and their equilibrium expressions are:



and



The equilibrium would be written as:



- An equilibrium constant ( $K$ ) is a numerical value that relates the concentrations of the **products** and **reactants** for a chemical reaction that is at equilibrium. The numeric value of an equilibrium constant is **independent of the initial concentrations of reactants**, but is dependent on the **temperature**. Equilibrium constants are *generally* not written with units (although they may be).
- Because equilibrium constants are written as the concentrations (or partial pressures) of **products** divided by the concentrations (or partial pressures) of **reactants**, a *large* value of  $K$  means that there are more products in the equilibrium mixture than there are reactants. Likewise, a *small* value of  $K$  means that, at equilibrium, there are more reactants than products.
- Equilibrium constants that are based on **partial pressures** are often written as  $K_p$ , while equilibrium constants based on **molar concentrations** are written as  $K_c$ .
- An expression for an equilibrium constant can be written from a balanced chemical equation for the reaction. **The Law of Mass Action** states the following regarding equilibrium expressions:
  - Partial pressures (or molar concentrations) of **products** are written in the **numerator** of the expression and the partial pressures (or concentrations) of the **reactants** are written in the **denominator**.
  - If there is more than one reactant or more than one product, the partial pressures (or concentrations) are *multiplied* together.
  - The partial pressure (or concentration) of each reactant or product is then **raised to the power** that numerically equals the **stoichiometric coefficient** appearing with that term in the balanced chemical equation.
  - Reactants or products that are present as **solids** or **liquids** *do not appear* in the equilibrium expression.
- As an example of an equilibrium expression, consider the reaction of nitrogen and hydrogen to form ammonia. The partial pressure of ammonia will be in the numerator, and it will be *squared*. Because there are two reactants, the partial pressures for nitrogen and hydrogen will be *multiplied* in the denominator. The partial pressure of nitrogen will be raised to the "first power" (which is not shown) and the partial pressure of hydrogen will be *cubed*.



$$\frac{(P_{\text{NH}_3})^2}{P_{\text{N}_2}(P_{\text{H}_2})^3} = K$$

- If equilibrium values for a given reaction are known, the equilibrium constant can be calculated simply by substituting those values in the equilibrium expression. Quite often, however, initial and equilibrium values are only given for selected reactants and products. In these cases, *initial* and *equilibrium* values are arranged in an **ICE Table**, and the *changes* between initial and equilibrium states are calculated based on reaction stoichiometry.
- Because the **partial pressure** of a gas and the **molar concentration** of that gas are directly proportional, the ideal gas law can be rearranged as follows, to give an expression relating molarity and partial pressure of a gas.

$$P_{\text{gas}} V = nRT$$

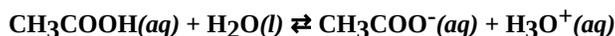
Dividing by the volume in **liters** gives the term ( $\frac{n}{V}$ ) which is equivalent to *molarity*,  $M$ .

$$P_{\text{gas}} = MRT$$

- Le Chatelier's Principle states that, if a "stress" is applied to a chemical reaction at equilibrium, the system will readjust in the direction that best reduces the stress imposed on the system. In this context, *stress* refers to a change in **concentration**, a change

in **pressure** or a change in **temperature**, although only concentration is considered here. If pressure or temperature are changed, the numeric value  $K$  will change; **if only concentration changes are involved,  $K$  does not change**. In a reaction at equilibrium, the introduction of more products will shift the mass balance towards more reactants, and the introduction of more reactants will lead to the formation of more products, but the *ratio of Products/Reactants* (as defined by the equilibrium expression) does *not* change, hence,  $K$  is unchanged.

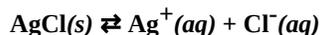
- For a **weak acid**, dissociating in water to form its **conjugate base** and **hydronium** ion, the equilibrium constant is referred to as  $K_a$ . Because a weak acid is only "partially dissociated", the concentration of BH in solution is large, thus  $K_a$  for a weak acid is "small" (in the range of  $10^{-3}$  to  $10^{-6}$ ). For example, acetic acid (the acidic component of vinegar), has an acid dissociation constant of  $K_a = 1.8 \times 10^{-5}$ .



- For a solution of a *weak acid* in water, the concentration of hydronium ion will be *very small*. If the concentration of the weak acid is fairly large (typically  $> 0.01$  M) the concentration of the undissociated acid will be much larger than  $[\text{H}_3\text{O}^+]$ . Because of this, the hydronium ion concentration (hence, the pH) can be fairly accurately estimated from the  $K_a$  of the weak acid and the initial concentration of the acid ( $C_0$ ), by the equation:

$$[\text{H}_3\text{O}^+] = \sqrt{K_a \times C_0}$$

- The equilibrium constant defining the solubility of an ionic compound with low solubility is defined as  $K_{sp}$ , where "sp" refers to "solubility product". Because reactants or products that are present as solids or liquids *do not appear* in equilibrium expressions, for silver chloride, the expression  $K_{sp}$  will be written as:



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

- For silver chloride, the **solubility** at 25 °C is  $1.67 \times 10^{-5}$  M. That means the concentrations of silver and chloride ions in solution are *each*  $1.67 \times 10^{-5}$  M, making the value of  $K_{sp}$  under these conditions:

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (1.67 \times 10^{-5})^2 = 2.79 \times 10^{-10}$$

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