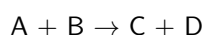# 1 Equilibrium

Equilibrium Constant. Que? The nature of the equilibrium state:

- Reactions are reversible.

- dynamic - $\rightleftharpoons$ indicates that the reaction is proceeding in both the forward and reverse directions.

- Equilibrium does not mean nothing is happening.

- Once equilibrium is established, the rate of reaction in each direction is equal.

- This keeps the concentration of reactants and products constant.

$$A + B \rightarrow C + D$$

- The nature and properties of the equilibrium state are the same, no matter what the direction of approach.

- Initially, since there is only A and B present, they react very quickly.

- As A and B react, there are less and less of unreacted A and B molecules and so the rate of this reaction slows down.

- As the concentrations of C and D build up, they start to react to form A and B.

- And eventually the rate at which A and B react equals the rate at which C and D react. At this point equilibrium is established.

Note the concentrations of A, B, C, and D are not necessarily equal at equilibrium, but the concentrations are constant at equilibrium.

The equilibrium constant is used to determine equilibrium conditions. It is always temperature dependent.

For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$
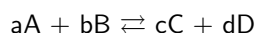
The equilibrium constant expression is

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

The product concentrations appear in the numerator and the reactant concentration in the denominator. Each concentration is raised to the power of its stoichiometric coefficient in the balanced equation.

indicate concentration

- K_c is for concentration

- K_p is for partial pressure

In equilibrium constant expressions:

- Pure solids do not appear in the expression

- Pure liquids do not appear in the expression

- Water as a liquid or gas does not appear in the expression

If you know the concentration of things, just plug them into the K expression and solve.

Changing coefficients:

- When the stoichiometric coefficients of a balanced equation are multiplied by some factor, the K value is raised to the power of the multiplication factor.

- For the reverse reaction, take the reciprocal of K

- When adding reactions to produce another, multiply the respective K's to determine the K of the final reaction.

K_p only applies when all reactants and products are gases. Pressure must be units of atmospheres.

K_c and K_p are not interchangeable!

$$K_p = K_c(RT)^n$$

where n is the change in the number of moles of gas from the reactant to product side of the arrow.

Use a RICE table if you are not given all the concentrations.

External factors affecting equilibria:

Le Chatelier's Principle - If you disrupt a system in equilibrium, shifts in direction occur to reestablish equilibrium positions.

Temperature:

- Exothermic reactions - heat is a product

- Endothermic reactions - heat is a reactant

- The value of K is a constant only at constant T

- If you change T, the value of K changes

Changing reagent and product amounts:

- Adding reagent - shift tries to consume additional material by favoring forward reaction

- Removing a reagent - shift tries to replace material by favoring reverse reaction

- Adding product - shift tries to consume the product by favoring reverse reaction

- Removing product - shift tries to replace the product by favoring forward reaction

- Has no effect on the value of K

Pressure:

- An increase in pressure favors the side with the least # of gas moles

- A decrease in pressure favors the side with the most # of gas moles

- Has no effect on solids and liquids

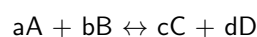- Has no effect on the value of K

Catalysts:

- No effect on the value of K

- But the reaction gets to equilibrium faster!

Weak acids only dissociate partly. There is an equilibrium constant associated with weak acid dissociation, K_a. It works just like K_c.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} < 1$$

The reaction quotient, Q.

For a general reaction

$$aA + bB \leftrightarrow cC + dD$$

the reaction quotient is

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

Q has the appearance of K but the concentrations are not necessarily at equilibrium.

If $K > Q$, the system is not at equilibrium.

- Products are too small and the reactants are too big.

- The system will move towards equilibrium by making products and consuming reactants.

If K = Q, the system is at equilibrium.

If $K < Q$, the system is not at equilibrium.

- Reactants are too small and the products are too big.

- The system will move towards equilibrium by making reactants and consuming products.

Chapter Problems

1. K_{eq} for the reaction $2A + B \rightleftarrows 2C$ is 8.0 Find the concentration of C when the concentration of A is 5.00×10^{-4} M and the concentration of B is 2.50×10^{-4} M.

2. For the reaction

$$4NH_3 \text{ (g)} + 3O_2 \text{ (g)} \leftrightharpoons 2N_2 \text{ (g)} + 6H_2O \text{ (l)}$$
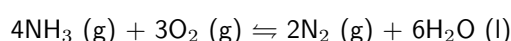
How will the concentration of each chemical be affected byd ecreasing the volume of the container?

3. Bromine and chlorine react to produce bromine monochloride according to the equation below. $K_c = 36.0$ under the conditions of the experiment.

$$Br_2 \text{ (g)} + Cl_2 \text{ (g)} \leftrightarrow 2BrCl \text{ (g)}$$
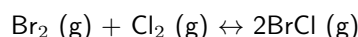
If 0.180 moles of bromine gas and 0.180 moles of chlorine gas are introduced into a 3.0 Liter flask and allowed to come to equilibrium, what is the equilibrium concentration of the bromine monochloride? How many moles of bromine monochloride are produced?

4. When 2.0 mol of carbon disulfide and 4.0 mol of chlorine are placed in a 1.0 Liter flask, the following equilibrium system results. At equilibrium, the flask is found to contain 0.30 mol of carbon tetrachloride. What quantities of the other components are present in this equilibrium mixture? What is the equilibrium constant at this temperature?

$$CS_2 \text{ (g)} + 3Cl_2 \text{ (g)} \leftrightharpoons S_2Cl_2 \text{ (g)} + CCl_4 \text{ (g)}$$
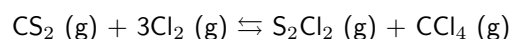
5. Suppose you dissolved benzoic acid, C_6H_5COOH, in water to make a 0.15 M solution. K_a for benzoic acid $= 6.3 \times 10^{-5}$ at $25°$ C. Solve for the concentration of benzoic acid, the concentration of hydronium ion, the concentration of benzoate anion, and the pH.

6. Calculate the hydronium ion concentration and the pH of a 0.50 M solution of HNO_2. For HNO_2, $K_a = 4.5 \times 10^{-4}$.

7. At $60.2°$ C, the equilibrium constant for the reaction, N_2O_4 (g) $\leftrightarrow$ $2NO_2$ (g), is 8.75×10^2. At this temperature, a vessel contains dinitrogen tetroxide at a concentration of 1.72×10^{-2} M at equilibrium. What concentration of nitrogen dioxide does it contain?

8. If you wished to maximize the products in the following reaction, would you run the reaction at a high pressure or at a low pressure?

$$CaCO_3 \text{ (s)} \leftrightharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$$
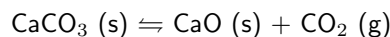
9. At $500°$ C, the equilibrium constant for the following reaction is 0.080. What is the value of Q if $[NH_3]$ = 0.059 M, $[N_2]$ = 0.59 M and $[H_2]$ = 0.42 M? How will this reaction proceed?

$$N_2 \text{ (g)} + 3H_2 \text{ (g)} \leftrightharpoons 2NH_3 \text{ (g)}$$
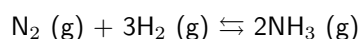
10. When 54.0 grams of ammonia is placed in an evacuated 3.50 liter rigid container and heated to 550. K, 12.75% of the gas has dissociated. What is the K_p value?

11. Write the equilibrium expression for the following reaction: Dinitrogen pentoxide gas decomposes into nitrogen dioxide gas and oxygen gas.

12. For the chemical equilibrium $A + 2B \leftrightharpoons 2C$, the value of the equilibrium constant, K, is 10. What is the value of the equilibrium constant for the following reaction: $4C \leftrightharpoons 2A + 4B$?