Equilibrium Constant Expressions

Reactions don't stop when they come to equilibrium. But the forward and reverse reactions are in balance at equilibrium, so there is no net change in the concentrations of the reactants or products, and the reaction appears to stop on the macroscopic scale. Chemical equilibrium is an example of a *dynamic* balance between opposing forces — the forward and reverse reactions — not a static balance.

Let's look at the logical consequences of the assumption that the reaction between $ClNO_2$ and NO eventually reaches equilibrium.

$$ClNO_2(g) + NO(g) \rightleftharpoons NO_2(g) + ClNO(g)$$

The rates of the forward and reverse reactions are the same when this system is at equilibrium.

$$\text{At equilibrium:} \quad \text{rate}_{\text{forward}} = \text{rate}_{\text{reverse}}$$

Substituting the rate laws for the forward and reverse reactions into this equality gives the following result.

$$\text{At equilibrium:} \quad k_f(ClNO_2)(NO) = k_r(NO_2)(ClNO)$$

But this equation is only valid when the system is at equilibrium, so we should replace the ($ClNO_2$), (NO), (NO_2), and (ClNO) terms with symbols that indicate that the reaction is at equilibrium. By convention, we use square brackets for this purpose. The equation describing the balance between the forward and reverse reactions when the system is at equilibrium should therefore be written as follows.

$$\text{At equilibrium:} \quad k_f[ClNO_2][NO] = k_r[NO_2][ClNO]$$

Rearranging this equation gives the following result.

$$\frac{k_f}{k_r} = \frac{[NO_2][ClNO]}{[ClNO_2][NO]}$$

Since k_f and k_r are constants, the ratio of k_f divided by k_r must also be a constant. This ratio is the **equilibrium constant** for the reaction, K_c. The ratio of the concentrations of the reactants and products is known as the **equilibrium constant expression**.

$$K_c = \frac{k_f}{k_r} = \frac{[NO_2][ClNO]}{[ClNO_2][NO]}$$

No matter what combination of concentrations of reactants and products we start with, the reaction will reach equilibrium when the ratio of the concentrations defined by the equilibrium constant expression is equal to the equilibrium constant for the reaction. We can start with a lot of $ClNO_2$ and very little NO, or a lot of NO and very little $ClNO_2$. It doesn't matter. When the reaction reaches equilibrium, the relationship between the concentrations of the reactants and products described by the equilibrium constant expression will always be the same. At 25^{o}C, this reaction always reaches equilibrium when the ratio of these concentrations is 1.3 x 10^4.

$$K_c = \frac{k_f}{k_r} = \frac{[NO_2][ClNO]}{[ClNO_2][NO]} = 1.3 \times 10^4$$

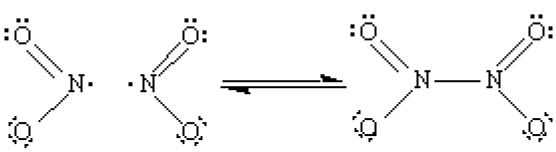
The procedure used in this section to derive the equilibrium constant expression only works with reactions that occur in a single step, such as the transfer of a chlorine atom from $ClNO_2$ to NO. Many reactions take a number of steps to convert reactants into products. But any reaction that reaches equilibrium, no matter how simple or complex, has an equilibrium constant expression that satisfies the rules in the following section.

Rules for Writing Equilibrium Constant Expressions

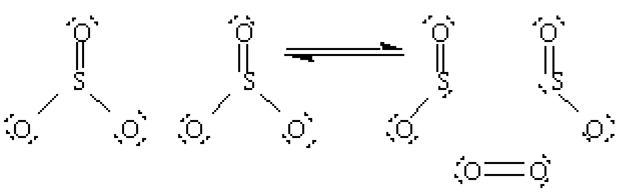
- Even though chemical reactions that reach equilibrium occur in both directions, the reagents on the right side of the equation are assumed to be the "products" of the reaction and the reagents on the left side of the equation are assumed to be the "reactants."
- The products of the reaction are always written above the line — in the numerator.
- The reactants are always written below the line — in the denominator.
- For homogeneous systems, the equilibrium constant expression contains a term for every reactant and every product of the reaction.
- The numerator of the equilibrium constant expression is the product of the concentrations of the "products" of the reaction raised to a power equal to the coefficient for this component in the balanced equation for the reaction.
- The denominator of the equilibrium constant expression is the product of the concentrations of the "reactants" raised to a power equal to the coefficient for this component in the balanced equation for the reaction.

Write equilibrium constant expressions for the following reactions.

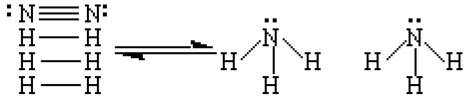
(a) $2\ NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$



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



(c) $N_2(g)\ +\ 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$



Gas-phase reactions were chosen for this introduction to kinetics and equilibrium because they are among the simplest chemical reactions. Some might question, however, why the equilibrium constant expressions in the preceding exercise are expressed in terms of the concentrations of the gases in units of moles per liter. Units of concentration were used to emphasize the relationship between chemical equilibria and the rates of chemical reactions, which are reported in terms of the concentrations of the reactants and products. This choice of units is indicated by adding a subscript "*c*" to the symbols for the equilibrium constants, to show that they were calculated from the concentrations of the components of the reaction.