10.2: The Equilibrium Constant

The constant in the equation in section 10.1 is called the **equilibrium constant** for the reaction. What the equilibrium constant for this reaction tells us is that, regardless of pressures (or concentrations), a mixture of the two gasses will undergo reaction such that the ratios of the partial pressures reach a constant value, given by the equilibrium constant, *K*. Once this constant ratio has been reached does this mean the reactions stop? Of course not. In the region of the plot where the concentrations of N_2O_4 and NO_2 are constant (the lines are level) N_2O_4 is still decomposing to form two molecules of NO_2 and two molecules of NO_2 are still reacting to synthesize a molecule of N_2O_4, but the lines are level because the **rates** of the two chemical reactions have become constant; N_2O_4 is decomposing at the same *rate* as two molecules of NO_2 are reacting to form N_2O_4.

In theory, *all* chemical reactions are equilibria. In practice, however, most reactions are so slow in the reverse direction that they are considered “irreversible”. When a reaction evolves a gas, forms a precipitate or proceeds with the generation of a large amount of heat or light (for example, combustion) the reaction is essentially irreversible. Many chemical reactions are, however, readily reversible and for these reactions the mathematical expression for the equilibrium constant can be written using a simple set of rules.

1. 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.
2. If there is more that one reactant or more that one product, the partial pressures (or concentrations) are multiplied together.
3. 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.
4. Reactants or products that are present as solids or liquids or solvents *have a defined activity of 1*. Therefore, although their activity **does** formally appear in the equilibrium expression, they do not affect the value of the equilibrium constant, and so are often not written in the expression.

Thus, for the reaction of nitrogen with hydrogen gas to form ammonia:

$$N_2\ (g) + 3\ H_2\ (g) \rightleftarrows 2\ NH_3\ (g)$$

The expression for the equilibrium constant will have the partial pressure of ammonia in the numerator, and it will be *squared*, corresponding to the coefficient “2” in the balanced equation; $(P_{NH_3})^2$. 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*, corresponding to the coefficient “3”; $(P_{N_2})(P_{H_2})^3$. The final expression for the equilibrium constant is given in the equation below:

$$\frac{(P_{NH_3})^2}{PN_2(P_{H_2})^3} = K$$

Exercise 10.2.1

For the chemical reactions shown below, write an expression for the equilibrium constant in terms of the partial pressures of the reactants and products.

1. PCl_5 *(g)* ⇄ PCl_3 *(g)* + Cl_2 *(g)*
2. 2 NOCl *(g)* ⇄ 2 NO *(g)* + Cl_2 *(g)*
3. PCl_3 *(g)* + 3 NH_3 *(g)* ⇄ $P(NH_2)_3$ *(g)* + 3 HCl *(g)*

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