CHEMICAL EQUILIBRIA

Concept of Equilibrium

Chemical Reactions generally do not reach completion but instead stop at some intermediate stage of equilibrium. In this equilibrium state, unreacted reactants are present along with products but no further net change occurs.

Equilibrium Constant

Ex 1  Write the equilibrium expression (K_c) for each of the following:

(a) \(2 \text{H}_2(g) + \text{O}_2(g) \leftrightharpoons 2 \text{H}_2\text{O}(g)\)

(b) \(2 \text{C}_6\text{H}_6(g) + 15 \text{O}_2(g) \leftrightharpoons 12 \text{CO}_2(g) + 6 \text{H}_2\text{O}(g)\)

Equilibrium Constants in Terms of Pressure
Ex 2 For the equilibrium \( 2 \text{SO}_3(g) \rightleftharpoons 2 \text{SO}_2(g) + \text{O}_2(g) \) at a temperature of 1000 K, \( K_c \) has the value \( 4.08 \times 10^{-3} \). Calculate the value for \( K_p \).

Magnitude of Equilibrium Constants

The equilibrium constant indicates the relative amounts of reactants and products present at equilibrium.

- Reactants \( \rightleftharpoons \) Products
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Ex 3 The equilibrium constant for the reaction \( \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \) varies with temperature in the following way: \( K_c = 794 \) @ 298 K; \( K_c = 54 \) @ 700 K. Is the formation of HI favored more at higher or lower temperatures?

Direction of the Chemical Equation and \( K \)

Heterogeneous Equilibria
Ex 4  Write the equilibrium expressions for $K_c$ and $K_p$ for the reaction

$$3 \text{ Fe}(s) + 4 \text{ H}_2\text{O}(g) \rightleftharpoons \text{ Fe}_3\text{O}_4(s) + 4 \text{ H}_2(g)$$

Calculating Equilibrium Constants

1. Tabulate the known initial and equilibrium concentrations of all species involved.
2. For those species for which both the initial and equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.
3. Use the stoichiometry of the reaction to calculate the changes in concentration for all the other species in the equilibrium.
4. From the initial concentrations and the changes in concentration, calculate the equilibrium concentrations. Use these to evaluate the equilibrium constant.

Ex 5  An experiment is run at 425°C to determine the equilibrium constant for the reaction

$$\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g)$$

at that temperature. $\text{H}_2(g)$ and $\text{I}_2(g)$, both at the same initial partial pressure of 5.73 atm, are mixed. When the reaction comes to equilibrium, the partial pressure of HI is measured to be 9.00 atm. Compute the equilibrium constant, assuming that no side reactions occur.
Applications of Equilibrium Constants

Predicting the Direction of Reaction

The Reaction Quotient (Q) — gives information about which direction the reaction will proceed. Q looks the same as the equilibrium expression except the partial pressures are not necessarily at equilibrium.
Ex 6  The reaction \( 2 \text{NO}(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{NOBr}(g) \)
has an equilibrium constant of 116.6 at 25°C. In each of the following mixtures, compute the reaction quotient \( Q \) and use it to decide the direction the reaction takes (right to left) to come to equilibrium. The initial partial pressures (all in atm) in the gas mixture are

(a) \( P_{\text{NO}} = 0.188; \quad P_{\text{Br}_2} = 0.300; \quad P_{\text{NOBr}} = 1.203 \)

(b) \( P_{\text{NO}} = 0.300; \quad P_{\text{Br}_2} = 0.188; \quad P_{\text{NOBr}} = 1.203 \)

Ex 7  The progress of the reaction \( \text{H}_2(g) + \text{Br}_2(g) \rightleftharpoons 2 \text{HBr}(g) \)
can be monitored visually by following changes in the color of the reaction mixture (\( \text{Br}_2 \) is reddish brown, and \( \text{H}_2 \) and \( \text{HBr} \) are colorless). A gas mixture is prepared at 700 K, in which 0.40 atm is the initial partial pressure of both \( \text{H}_2 \) and \( \text{Br}_2 \) and 0.90 atm is the initial partial pressure of \( \text{HBr} \). The color of this mixture fades as the reaction progresses toward equilibrium. What condition must \( K \) satisfy (for example, it must be greater than or smaller than a given number)?

Calculation of Equilibrium Concentrations
Consider the following equilibrium:

\[ 2 \text{BrCl}(g) \leftrightarrow \text{Br}_2(g) + \text{Cl}_2(g) \quad K = 32 \text{ @ 500K} \]

Calculate the partial pressure of BrCl that is in equilibrium with a mixture of 0.182 atm of bromine and 0.0876 atm of chlorine at 500K.

**Le Chatelier’s Principle**

When left to itself, a system at equilibrium remains constant and unchanging. However, if that system is put under some external stress (e.g. changing V, changing T, or adding or removing products or reactants) it will react in a way that will counteract (but not cancel) the stress.

**Change in Reactant or Product Concentrations**

**Effects of Volume and Pressure Changes**

**Effect of Temperature Changes**
Ex 9  Given the following exothermic reaction:

\[ 2 \text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{SO}_3(g) \]

Which direction will the equilibrium shift when the following changes are made?

(a) Add more \( \text{O}_2 \)?
(b) Remove some \( \text{SO}_3 \)?
(c) Remove some \( \text{SO}_2 \)?
(d) Increase the temperature?
(e) Decrease the volume (constant \( T \))? 

Some problems to try on your own:

1. The value of the equilibrium constant for the following reaction is \( K_1 \).

\[ 3 \text{H}_2(g) + \text{N}_2(g) \rightleftharpoons 2 \text{NH}_3(g) \]

How is \( K_1 \) related to the equilibrium constant \( K_2 \) for the related equilibrium?

\[ 2 \text{NH}_3(g) \rightleftharpoons 3 \text{H}_2(g) + \text{N}_2(g) \]

2. The equilibrium constant (\( K_p \)) for the reaction

\[ \text{Fe}_3(s) + 2 \text{H}_2\text{O}(g) \rightleftharpoons \text{Fe}_2\text{O}_3(s) + 2 \text{H}_2(g) \]

is 3.51 at 527°C. 5.42 g of Fe and 7.88 g of \( \text{H}_2\text{O} \) are placed in a closed, 5.0-L container and allowed to reach equilibrium. Calculate the pressure of \( \text{H}_2 \) at equilibrium.

3. Find the equilibrium partial pressure of \( \text{N}_2\text{O}_4(g) \) and \( \text{NO}_2(g) \) in the reaction

\[ \text{N}_2\text{O}_4(g) \rightleftharpoons 2 \text{NO}_2(g) \quad K = 0.98 \text{ @ 298K} \]

if a flask is charged with enough \( \text{N}_2\text{O}_4 \) to exert an initial partial pressure of 0.050 atm.

4. For the reaction

\[ \text{SO}_2\text{Cl}_2(g) \rightleftharpoons \text{SO}_2(g) + \text{Cl}_2(g) \quad K = 2.40 \text{ @ 100°C} \]

(a) Initial partial pressure of \( \text{SO}_2\text{Cl}_2 \) in a tank with rigid walls is 1.398 atm, no other species are present. Calculate the Q. Does total pressure increase or decrease as the rxn \( \rightarrow \) equilibrium?

(b) Calculate the partial pressures of \( \text{SO}_2\text{Cl}_2 \), \( \text{SO}_2 \), and \( \text{Cl}_2 \) after equilibrium is reached.

5. 0.500 atm of \( \text{H}_2 \) and 0.500 atm of \( \text{I}_2 \) are placed in a container. The reaction between the two to form HI is allowed to come to equilibrium. What are the equilibrium partial pressures of all compounds?

\[ \text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2 \text{HI}(g) \quad K = 54 \text{ @ 700K} \]

6. Given the following data:

\[ \begin{align*}
\text{N}_2(g) + 3 \text{H}_2(g) & \rightleftharpoons 2 \text{NH}_3(g) \quad K_{@25°C} = 3.5 \times 10^8 \\
\text{N}_2(g) + \text{O}_2(g) & \rightleftharpoons 2 \text{NO}(g) \quad K_{@25°C} = 1.7 \times 10^{-3} \\
2 \text{NO}_2(g) & \rightleftharpoons \text{N}_2\text{O}_4(g) \quad K_{@25°C} = 1.7 \times 10^2
\end{align*} \]

Arrange the following reactions in order from most reactant-favored to most product-favored.

(1) \[ 2 \text{NH}_3(g) \rightleftharpoons \text{N}_2(g) + 3 \text{H}_2(g) \]
(2) \[ 2 \text{NO}(g) \rightleftharpoons \text{N}_2(g) + \text{O}_2(g) \]
(3) \[ 2 \text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g) \]