CH 223 Chapter Thirteen Concept Guide

1. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ OH^-(aq)$

(b) $Cu(NH_3)_4^{2+}(aq) \rightleftharpoons Cu^{2+}(aq) + 4\ NH_3(aq)$

(c) $CH_3CO_2H(aq) + H_2O(\ell) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$

Solution

(a) $K_c = [Cu^{2+}]\ [OH^-]^2$

(b) $$K_c = \frac{[Cu^{2+}][NH_3]^4}{[Cu(NH_3)_4^{2+}]}$$

(c) $$K_c = \frac{[CH_3CO_2^-][H_3O^+]}{[CH_3CO_2H]}$$

2. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $$CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$$

(b) $C(s) + CO_2(g) \rightleftharpoons 2\ CO(g)$

(c) $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$

Solution

(a) $$K_c = \frac{[CO_2]}{[CO][O_2]^{1/2}}$$

(b) $$K_c = \frac{[CO]^2}{[CO_2]}$$

(c) $$K_c = \frac{[CO_2]}{[CO]}$$

3. Writing Equilibrium Constant Expressions

Problem

Write the equilibrium constant (K_c) expressions for each of the following reactions:

(a) $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$

(b) $2\ NO(g) + Br_2(g) \rightleftharpoons 2\ NOBr(g)$

(c) $2\ HF(g) \rightleftharpoons H_2(g) + F_2(g)$

Solution

(a) $$K_c = \frac{[NO]^2}{[N_2][O_2]}$$

(b) $$K_c = \frac{[NOBr]^2}{[NO]^2[Br_2]}$$

(c) $$K_c = \frac{[H_2][F_2]}{[HF]^2}$$

4. Interpreting the Value of K

Question

A student's task was to remove silver ion for an aqueous solution as completely as possible by causing it to form a precipitate. Given the following information, which would be the better method: to add a solution containing sulfate ion or one containing an equivalent amount of sulfide ion?

$Ag_2SO_4(s) \rightleftharpoons 2\ Ag^+ + SO_4^{2-}$ $\quad K = 1.5 \times 10^{-5}$

$Ag_2S(s) \rightleftharpoons 2\ Ag^+ + S^{2-}$ $\quad K = 7.1 \times 10^{-50}$

Solution

The precipitates formed would be silver sulfate and silver sulfide upon addition of sulfate ion or sulfide ion, respectively. Comparison of the equilibria that would result after precipitate formation using the two K values shows that the sulfide would leave a far lower concentration of Ag^+ in solution after the precipitation reaction went to completion. Thus, the student should choose the silver and sulfide reaction:

$Ag_2S(s) \rightleftharpoons 2\ Ag^+ + S^{2-}$

5. Manipulation of Equilibrium Expressions

Question

Consider the following equilibria involving $SO_2(g)$ and their corresponding equilibrium constants.

(1) $SO_2(g) + {}^1/_2\, O_2(g) \rightleftharpoons SO_3(g) \quad K_1$

(2) $2\, SO_3(g) \rightleftharpoons 2\, SO_2(g) + O_2(g) \quad K_2$

Which of the following expressions relates K_1 to K_2?

(a) $K_2 = K_1^2$

(b) $K_2^2 = K_1$

(c) $K_2 = \dfrac{1}{K_1}$

(d) $K_2 = \dfrac{1}{K_1^2}$

Solution

Reaction 2 is the inverse of reaction 1, and squared. Thus, (d) is the correct answer. K_2 is related to K_1 by:

$$K_2 = \frac{1}{K_1^2}$$

6. Writing Equilibrium Constant Expressions

Problem

Calculate K for the reaction

$SnO_2(s) + 2\, CO(g) \rightleftharpoons Sn(s) + 2\, CO_2(g)$

given that:

$SnO_2(s) + 2\, H_2(g) \rightleftharpoons Sn(s) + 2\, H_2O(g) \quad K = 8.12$

$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g) \quad K = 0.771$

Solution

In general, when two or more equations are added to produce a net equation, the equilibrium constant for the net equation is the product of the equilibrium constants for the added equations. In this case, we need to reverse and double the second reaction to add to the first reaction.

$$SnO_2(s) + 2\,H_2(g) \rightleftharpoons Sn(s) + 2\,H_2O(g) \qquad K = 8.12$$
$$2\,CO(g) + 2\,H_2O(g) \rightleftharpoons 2\,H_2(g) + 2\,CO_2(g) \qquad K = \frac{1}{(0.771)^2}$$
$$SnO_2(s) + 2\,CO(g) \rightleftharpoons Sn(s) + 2\,CO_2(g) \qquad K = (8.12)\left(\frac{1}{(0.771)^2}\right)$$

For this reaction, K=13.7

7. Evaluation of the Value of K

Question

The equilibrium constant for the formation of gaseous lithium iodide by combination of the elements in the gas phase at 3000 K is given as:

$Li(g) + {}^1/_2\,I_2(g) \rightleftharpoons LiI(g) \quad K_p = 644$

(a) What is the equilibrium constant value for this reaction if it is represented by the equation given above multiplied by a factor of 2?

(b) What is the equilibrium constant value for the reverse of the reaction as written above?

Solution

(a) Multiplying the reaction by a factor of 2 requires that the given value of K_p be squared:

$K_p = (644)^2 = 4.15 \times 10^5$

$2\,Li(g) + {}^1/_2\,I_2(g) \rightleftharpoons 2\,LiI(g) \quad K_p = (644)^2$

(b) When the equation is reversed, K_p becomes the reciprocal of the original value:

$$K_p = \frac{1}{644} = 1.55 \times 10^{-3}$$

$LiI(g) \rightleftharpoons Li(g) + {}^1/_2\,I_2(g) \qquad K_p = \frac{1}{644}$

8. Reaction Quotient

Problem

The concentration equilibrium constant (K_c) for the reaction

$ClF_3(g) \rightleftharpoons ClF(g) + F_2(g)$

is 8.77×10^{-14} at 25 °C. Describe what happens quantitatively when a solution is prepared so that it is 17.50 M in ClF_3,1.3×10^{-6} M in ClF,and 4.72×10^{-7} M in F_2.

Approach
Calculate the reaction quotient, Q, and compare it to K.

Solution
The reaction quotient for the solution is:

$$Q = \frac{[ClF][F_2]}{[ClF_3]} = (1.3 \times 10^{-6}\ M)\frac{(4.72 \times 10^{-7}\ M)}{(17.50\ M)} = 3.5 \times 10^{-14}$$

$Q < K_c$, therefore the concentrations of the reactants will decrease and those of the products will increase, and the reaction will proceed toward equilibrium in the forward direction. In this case, ClF_3 will decompose until equilibrium is reached.

9. Equilibrium Concentrations

Question
Chlorine gas, Cl_2, dissociates into chlorine atoms in a reversible reaction for which K = 0.37 at 3000 K. What is the concentration of chlorine atoms in a vessel that originally contained 1.0 M of molecular chlorine?

Approach
First, write the balanced equation. Then write the corresponding equilibrium expression and identify what is unknown. Make a table to include the chemical equation, initial concentrations, changes in concentration, and equilibrium concentrations. Substitute the equilibrium concentrations from the table into the equilibrium expression and solve for the unknown (x). If an approximation was made, remember to check for validity. Finally, answer the question in the problem using some form of the value of x.

Solution
The reaction is $Cl_2(g) \rightleftharpoons 2\,Cl(g)$. The unknown is [Cl] at equilibrium, and we choose the concentration of Cl_2 that dissociates into Cl as x. The algebraic expression that must be solved for is found by arranging the known and the unknown as shown in this lesson.

	Cl_2	$\rightleftharpoons$	**2 Cl(g)**
Initial	1.0 M		0 M
Change	- x		+ 2x
Equilibrium	1.0 - x		2x

The equilibrium constant is represented as:

$$K = \frac{[Cl]^2}{[Cl_2]} = \frac{(2x)^2}{(1.0 - x)} = 0.37$$

Inspection shows that the values of K and the known concentration are similar in magnitude, therefore this problem should be solved using the quadratic equation.

$4x^2 = (0.37)(1.0 - x)$

$4x^2 + 0.37x - 0.37 = 0$

With a = 4, b = 0.37, and c = -0.37, the quadratic equation is:

$$\frac{-0.37 \pm \sqrt{(0.37)^2 - (4)(4)(-0.37)}}{(2)(4)}$$

$$\frac{-0.37 \pm 2.5}{8}$$

x = 0.27 M or -0.36 M

Therefore, $[Cl]_2 = 2x = (2)(0.27\ M) = 0.54\ M$.

Finally, check this answer by substituting all concentrations into the equilibrium expressions and compare.

$$K = \frac{[Cl]^2}{[Cl_2]} = \frac{(0.54)^2}{(1.0 - 0.27)} = 0.40$$

10. Le Chatelier's Principle: Factors That Influence Equilibria - Concentration

Problem

A reaction of potassium chromate and hydrochloric acid was allowed to come to equilibrium:

$$\underset{\substack{\text{chromate ion}\\\text{yellow}}}{2\,CrO_4^{2-}} + H^+ \rightleftharpoons \underset{\substack{\text{dichromate ion}\\\text{orange}}}{Cr_2O_7^{2-}} + H_2O(\ell)$$

Describe the changes that will occur in the equilibrium system when:

(a) additional acid is added

(b) additional potassium chromate is added

(c) zinc is added (note that $ZnCrO_4$ is highly insoluble and $ZnCr_2O_7$ is very soluble)

(d) NaOH is added

Solution

(a) Some of the additional H^+ will react with the remaining chromate ion to produce more dichromate ion and water. $[CrO_4^{2-}]$ will decrease and $[Cr_2O_7^{2-}]$ will increase.

(b) Some of the additional chromate ion will react with some of the H^+ to produce more dichromate ion. Water and $[H^+]$ will decrease.

(c) Addition of Zn^{2+} will remove some of the chromate ion as $ZnCrO_4$. This will lower the concentration of chromate ion. Thus, some of the dichromate ion will react to form additional chromate ion and H^+.

(d) Addition of NaOH will remove some of the H^+ as a result of an acid-base reaction. The decrease in $[H^+]$ will yield a reaction of additional $Cr_2O_7^{2-}$ with H_2O. $[Cr_2O_7^{2-}]$ will decrease and $[CrO_4^{2-}]$ will increase.

11. Le Chatelier's Principle: Factors That Influence Equilibria -Temperature and Pressure

Question

For the reaction

$2\ Hg(\ell) + O_2(g) \rightleftharpoons 2\ HgO(s)$

$\Delta H° = -180.7$ kJ over a temperature range of 298 K to 500 K. $K_p = 3.2 \times 10^{20}$ at 298 K.

(a) Is the value of K_p at 500 K expected to be greater or less than the value of K_p at 298 K?

(b) Will a decrease in the partial pressure of O_2 cause the reaction to shift to the left or to the right?

Solution

(a) This is an exothermic reaction, thus heat can be considered a "product."

$2\ Hg(\ell) + O_2(g) \rightleftharpoons 2\ HgO(s) + 180.7$ kJ

Increasing the temperature favors the endothermic reaction, or the reverse reaction in this case. Therefore, the equilibrium will be shifted toward the reactant side (left) as the temperature is increased. The value of K_p is expected to be less than 3.2×10^{20}. (The value of K_p at 500 K is 5.1×10^{-7}.)

(b) Decreasing the pressure favors an increase in the amount of gas present. In this case, the reverse reaction (shift to the left) would be favored.

12. Le Chatelier's Principle: Factors That Influence Equilibria - Concentration, Temperature, and Volume

Problem The value of K_p for the following reaction is 0.16 at 25 °C. The enthalpy change for the reaction at standard conditions is +16.1 kJ.

$2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

To which direction will the equilibrium shift (left, right, or no change) and how will K change when each of the following changes to the system is made?

(a) Adding more $Br_2(g)$

(b) Removing some NOBr(g)

(c) Decreasing the temperature

(d) Increasing the container volume

Approach

This is an endothermic reaction, thus heat is considered a "reactant."

$+\ 16.1\ kJ + 2\ NOBr(g) \rightleftharpoons 2\ NO(g) + Br_2(g)$

Solution

(a) Left. Some of the added "product" will be consumed, thus the equilibrium will shift to the left. There will be no change in K.

(b) Left. Here, a "reactant" is being depleted. The equilibrium will shift to the left. K will not change.

(c) Left. When the temperature decreases, the system responds by shifting in the direction that leads to generation of thermal energy. The equilibrium shifts left and the value of K decreases.

(d) Right. Increasing the volume of the flask will result in a shift to the side of the equilibrium with more gas molecules. There are three moles of gas on the right and only two on the left. K will not change.