Fundamental Equilibrium Concepts

Section 85 – Equilibrium Constants

1. Explain why there may be an infinite number of values for the reaction quotient of a reaction at a given temperature but there can be only one value for the equilibrium constant at that temperature.

   Solution

   For a general reaction of the type $mA + nB \rightleftharpoons xC + yD$, the reaction quotient Q_c is written as $Q_c = \frac{[C]^x[D]^y}{[A]^m[B]^n}$. When the reaction reaches equilibrium, the forward and reverse reactions are proceeding at the same rate. Each component's net concentration does not change with time; accordingly, the reaction quotient will take on one value, which is called the *equilibrium constant.* Prior to equilibrium being reached, the rates of the forward and reverse reactions are not equal and the concentration of each component will be different at different times prior to equilibrium being achieved. Because it is possible to have an infinite number of concentrations before equilibrium, it is possible to calculate an infinite number of values of Q_c.

2. Explain why an equilibrium between $Br_2(l)$ and $Br_2(g)$ would not be established if the container were not a closed vessel shown in Figure 85-3.

   Solution

   Equilibrium cannot be established between the liquid and the gas phase if the top is removed from the bottle because the system is not closed; one of the components of the equilibrium, the Br_2 vapor, would escape from the bottle until all liquid disappeared. Thus, more liquid would evaporate than can condense back from the gas phase to the liquid phase.

3. If you observe the following reaction at equilibrium, is it possible to tell whether the reaction started with pure NO_2 or with pure N_2O_4?

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

   Solution

   For the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, when equilibrium is achieved, the following relationship will be satisfied: $K_c = \frac{[N_2O_4]}{[NO_2]^2}$. Thus, at equilibrium, both reactants and products will be present. Because the same position of equilibrium will be achieved, no matter from which direction (either combination of NO_2 or decomposition of N_2O_4), it is not possible to tell in which direction the reaction took place to achieve the equilibrium position. Prior to achieving equilibrium, it is possible to tell in which direction the reaction is proceeding. For example, in this system, if the color of the reaction mixture were a deep reddish brown that became a lighter intensity with time, then it would be possible to recognize that equilibrium is being approached as a result of the brown NO_2 molecules combining to form the colorless N_2O_4 molecules.

4. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
   (a) $CH_4(g) + Cl_2(g) \rightleftharpoons CH_3Cl(g) + HCl(g)$
   (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
   (c) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$
   (d) $BaSO_3(s) \rightleftharpoons BaO(s) + SO_2(g)$
   (e) $P_4(g) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$
   (f) $Br_2(g) \rightleftharpoons 2Br(g)$
   (g) $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l)$
   (h) $CuSO_4 \cdot 5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$

   Solution

   (a) $Q_c = \frac{[CH_3Cl][HCl]}{[CH_4][Cl_2]}$; (b) $Q_c = \frac{[NO]^2}{[N_2][O_2]}$; (c) $Q_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$; (d) $Q_c = [SO_2]$; (e) $Q_c = \frac{1}{[P_4][O_2]^5}$; (f) $Q_c = \frac{[Br]^2}{[Br_2]}$; (g) $Q_c = \frac{[CO_2]}{[CH_4][O_2]^2}$; (h) $Q_c = [H_2O]^5$

5. Write the mathematical expression for the reaction quotient, Q_c, for each of the following reactions:
   (a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
   (b) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
   (c) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
   (d) $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$
   (e) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$
   (f) $2Pb(NO_3)_2(s) \rightleftharpoons 2PbO(s) + 4NO_2(g) + O_2(g)$
   (g) $2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(l)$
   (h) $S_8(g) \rightleftharpoons 8S(g)$

   Solution

   Answer: (a) $Q_c = \frac{[NH_3]^2}{[H_2]^3[N_2]}$; (b) $Q_c = \frac{[NO]^4[H_2O]^6}{[NH_3]^4[O_2]^5}$; (c) $Q_c = \frac{[NO_2]^2}{[N_2O_4]}$; (d) $Q_c = \frac{[CO][H_2O]}{[CO_2][H_2]}$; (e) $Q_c = [NH_3][HCl]$, (f) $Q_c = [NO_2]^4[O_2]$; (g) $Q_c = \frac{1}{[H_2]^2[O_2]}$; (h) $Q_c = \frac{[S]^8}{[S_8]}$

6. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.
   (a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3] = 0.20\ M$, $[N_2] = 1.00\ M$, $[H_2] = 1.00\ M$

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; NH_3 = 3.0 atm, N_2 = 2.0 atm, H_2 = 1.0 atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3]$ = 0.00 *M*, $[SO_2]$ = 1.00 *M*, $[O_2]$ = 1.00 *M*

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 16.5$; SO_3 = 1.00 atm, SO_2 = 1.00 atm, O_2 = 1.00 atm

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_c = 4.6 \times 10^4$; [NO] = 1.00 *M*, $[Cl_2]$ = 1.00 *M*, [NOCl] = 0 *M*

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_P = 0.050$; NO = 10.0 atm, $N_2 = O_2$ = 5 atm

Solution

(a) $Q_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(1.00)(1.00)^3}{(0.20)^2} = 25$

$Q_c > K_c$, proceeds left;

(b) $Q_P = \frac{P_{N_2}(P_{H_2})^3}{(P_{NH_3})^2} = \frac{(2.0)(1.0)^3}{(3.0)^2} = 0.22$

$Q_P < K_P$, proceeds right;

(c) $Q_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.00)^2(1.00)}{(0)} = \text{undefined}$

$Q_c > K_c$, proceeds left;

(d) $Q_P = \frac{(P_{SO_2})^2 P_{O_2}}{(P_{SO_3})^2} = \frac{(1.00)^2(1.00)}{(1.00)^2} = 1.00$

$Q_P < K_P$, proceeds right;

(e) $Q_P = \frac{(P_{NOCl})^2}{(P_{NO})^2 P_{Cl_2}} = \frac{(0)^2}{(1.00)^2(1.00)} = 0$

$Q_P < K_P$, proceeds right;

(f) $Q_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(10.0)^2}{(5.00)(5.00)} = 4$

$Q_c > K_c$, proceeds left

7. The initial concentrations or pressures of reactants and products are given for each of the following systems. Calculate the reaction quotient and determine the direction in which each system will proceed to reach equilibrium.

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_c = 17$; $[NH_3]$ = 0.50 *M*, $[N_2]$ = 0.15 *M*, $[H_2]$ = 0.12 *M*

(b) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ $K_P = 6.8 \times 10^4$; NH_3 = 2.00 atm, N_2 = 10.00 atm, H_2 = 10.00 atm

(c) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_c = 0.230$; $[SO_3]$ = 2.00 *M*, $[SO_2]$ = 2.00 *M*, $[O_2]$ = 2.00 *M*

(d) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $K_P = 6.5$ atm; SO_2 = 1.00 atm, O_2 = 1.130 atm, SO_3 = 0 atm

(e) $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl(g)$ $K_P = 2.5 \times 10^3$; NO = 1.00 atm, Cl_2 = 1.00 atm, NOCl = 0 atm

(f) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $K_c = 0.050$; $[N_2]$ = 0.100 *M*, $[O_2]$ = 0.200 *M*, [NO] = 1.00 *M*

Solution

(a) $Q_c = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(0.15)(0.12)^3}{(0.50)^2} = 1.0 \times 10^{-3}$; $Q_c < K_c$, proceeds right;

(b) $Q_P = \frac{P_{N_2}(P_{H_2})^3}{(P_{NH_3})^2} = \frac{(10.00)(10.00)^3}{(2.00)^2} = 2.50 \times 10^3$; $Q_P < K_P$, proceeds right;

(c) $Q_c = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(2.00)^2(2.00)}{(2.00)^2} = 2.00$; $Q_c > K_c$, proceeds left;

(d) $Q_P = \frac{(P_{SO_2})^2 P_{O_2}}{(P_{SO_3})^2} = \frac{(1.00)^2(1.130)}{(0)^2} = \text{undefined but very large}$; $Q_P > K_P$, proceeds left;

(e) $Q_P = \frac{P_{NOCl}}{(P_{NO})^2 P_{Cl_2}} = \frac{(0)^2}{(1.00)^2(1.00)} = 0$; $Q_P < K_P$, proceeds right;

(f) $Q_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(1.00)^2}{(0.100)(0.200)} = 50$; $Q_c > K_c$, proceeds left

8. Benzene is one of the compounds used as octane enhancers in unleaded gasoline. It is manufactured by the catalytic conversion of acetylene to benzene: $3C_2H_2(g) \rightleftharpoons C_6H_6(g)$. Which value of K_c would make this reaction most useful commercially? $K_c \approx 0.01$, $K_c \approx 1$, or $K_c \approx 10$. Explain your answer.

Solution

Since $K_c = \frac{[C_6H_6]}{[C_2H_2]^3}$, a value of $K_c \approx 10$ means that C_6H_6 predominates over C_2H_2. In such a case, the reaction would be commercially feasible if the rate to equilibrium is suitable.

9. The following reaction has $K_P = 4.50 \times 10^{-5}$ at 720 K.

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

If a reaction vessel is filled with each gas to the partial pressures listed, in which direction will it shift to reach equilibrium? $P(NH_3)$ = 93 atm, $P(N_2)$ = 48 atm, and $P(H_2)$ = 52 atm

Solution

The reaction quotient expression for this problem is $Q_p = \frac{(P_{\mathrm{NH_3}})^2}{(P_{\mathrm{N_2}})(P_{\mathrm{H_2}})^3}$. Plugging in the given values of partial pressures gives $\frac{(93)^2}{\left((48) \times (52)^3\right)}$, so $Q_p = 1.3 \times 10^{-3}$. Since this value is larger than K_P (4.50×10^{-5}), the system will shift toward the reactants to reach equilibrium.

10. Determine if the following system is at equilibrium. If not, in which direction will the system need to shift to reach equilibrium?

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

$[SO_2Cl_2] = 0.12\ M$, $[Cl_2] = 0.16\ M$ and $[SO_2] = 0.050\ M$. K_c for the reaction is 0.078.

Solution

The reaction quotient expression is $Q_c = \frac{[\mathrm{SO_2}][\mathrm{Cl_2}]}{[\mathrm{SO_2Cl_2}]}$. Plugging in the values provided gives $Q_c = \frac{(0.050)(0.16)}{(0.12)} = 0.067$. The value of Q_c is lower than the value of K_c, so this reaction will shift toward the products.

11. For a titration to be effective, the reaction must be rapid and the yield of the reaction must essentially be 100%. Is $K_c > 1$, < 1, or ≈ 1 for a titration reaction?

Solution

$K_c > 1$; the product must be formed in overwhelmingly large proportions.

12. Among the solubility rules previously discussed is the statement: All chlorides are soluble except Hg_2Cl_2, AgCl, $PbCl_2$, and CuCl.

    (a) Write the expression for the equilibrium constant for the reaction represented by the equation
    $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

    (b) Write the expression for the equilibrium constant for the reaction represented by the equation
    $Pb^{2+}(aq) + 2Cl^-(aq) \rightleftharpoons PbCl_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

Solution

(a) $K_c = [Ag^+][Cl^-] < 1$. AgCl is insoluble; thus, the concentrations of ions are much less than 1 *M*;

(b) $K_c = \frac{1}{\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^-\right]^2} > 1$ because $PbCl_2$ is insoluble and formation of the solid will reduce the concentration of ions to a low level (< 1 *M*).

13. Among the solubility rules previously discussed is the statement: Carbonates, phosphates, borates, and arsenates—except those of the ammonium ion and the alkali metals—are insoluble.

(a) Write the expression for the equilibrium constant for the reaction represented by the equation
$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3{}^{2-}(aq)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.
(b) Write the expression for the equilibrium constant for the reaction represented by the equation
$3Ba^{2+}(aq) + 2PO_4{}^{3-}(aq) \rightleftharpoons Ba_3(PO_4)_2(s)$. Is $K_c > 1$, < 1, or ≈ 1? Explain your answer.

Solution

(a) $K_c = \left[Ca^{2+}\right]\left[CO_3{}^{2-}\right] < 1$. $CaCO_3$ is insoluble in water, and the concentrations of the ions are much less than 1 *M*. (b) $K_c = \dfrac{1}{\left[Ba^{2+}\right]^3\left[PO_4{}^{3-}\right]^2} > 1$. $Ba_3(PO_4)_2$ is insoluble in water, and the concentrations of the ions are much less than 1 *M*. Division of small concentrations into 1 gives a number larger than 1.

14. For a precipitation reaction to be useful in a gravimetric analysis, the product of the reaction must be insoluble. Is $K_c > 1$, < 1, or ≈ 1 for a useful precipitation reaction?

Solution

K_c is the product of all reaction products divided by the product of the reactants, with all concentrations of reactants and products raised to their respective stoichiometric powers. As the precipitate is formed, the amount of its corresponding ions in solution declines to lower levels. Because the value of the numerator is 1 and the concentrations in the denominator are very small, the value of K_c will be much greater than 1 for a useful precipitation reaction.

15. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $K_c = 0.50$ at 400 °C
(b) $H_2 + I_2 \rightleftharpoons 2HI$ $K_c = 50.2$ at 448 °C
(c) $Na_2SO_4 \bullet 10H_2O(s) \rightleftharpoons Na_2SO_4(s) + 10H_2O(g)$ $K_P = 4.08 \times 10^{-25}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.122$ at 50 °C

Solution

$K_P = K_c(RT)^{\Delta n}$, where Δ*n* is the sum of gaseous products minus the sum of gaseous reactants.
(a) $\Delta n = (2) - (1 + 3) = -2$, $K_P = 0.50[0.08206 \times 673.15]^{-2} = 1.6 \times 10^{-4}$; (b) $\Delta n = (2) - (1 + 1) = 0$, $K_P = K_c(RT)^0 = K_c = 50.2$; (c) $\Delta n = (10) - (0) = 10$, $K_c = K_P(RT)^{-\Delta n}$, $K_c = 4.08 \times 10^{-25}[0.08206 \times 298.15]^{-10} = 5.31 \times 10^{-39}$; (d) $\Delta n = (1) - (0) = 1$, $K_c = 0.122(0.08206 \times 323.15)^{-1} = 4.60 \times 10^{-3}$

16. Convert the values of K_c to values of K_P or the values of K_P to values of K_c.
(a) $Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$ $K_c = 4.7 \times 10^{-2}$ at 25 °C
(b) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $K_P = 48.2$ at 500 °C
(c) $CaCl_2 \bullet 6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$ $K_P = 5.09 \times 10^{-44}$ at 25 °C
(d) $H_2O(l) \rightleftharpoons H_2O(g)$ $K_P = 0.196$ at 60 °C

Solution

$K_P = K_c(RT)^{\Delta n}$, where Δn is the sum of gaseous products minus the sum of gaseous reactants. (a) $\Delta n = (2) - (1 + 1) = 0$, $K_P = K_c(RT)^0 = K_c = 4.7 \times 10^{-2}$; (b) $\Delta n = (2) - (2 + 1) = -1$, $K_c = K_P(RT)^{-(-1)} = 48.2(0.08206)(773.15) = 3.06 \times 10^3$ (c) $\Delta n = (6) - (0 + 0) = 6$, $K_c = K_P(RT)^{-\Delta n} = 5.09 \times 10^{-44}(0.08206 \times 298.15)^{-6} = 2.37 \times 10^{-52}$; (d) $\Delta n = (1) - (0) - 1$, $K_c = K_P(RT)^{-1} = 0.196(0.08206 \times 3.3315)^{-1} = 7.17 \times 10^{-3}$