Fundamental Equilibrium Concepts

Section 86 – Shifting Equilibria: Le Chatelier's Principle

1. The following equation represents a reversible decomposition:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Under what conditions will decomposition in a closed container proceed to completion so that no $CaCO_3$ remains?

Solution

The amount of $CaCO_3$ must be so small that P_{CO_2} is less than K_P when the $CaCO_3$ has completely decomposed. In other words, the starting amount of $CaCO_3$ cannot completely generate the full P_{CO_2} required for equilibrium.

2. Explain how to recognize the conditions under which changes in volume will affect gas-phase systems at equilibrium.

Solution

An effect arises only when the number of moles of gaseous reactants in the equation that describes the equilibrium reaction differs from the number of moles of gaseous products. As the volume of a gaseous system decreases, the gases become compressed and the total number of molecules per unit volume increases, producing greater molar concentrations. This change in concentration represents a stress on the system, and the system will act to remove the stress, if possible. The pressure change will have an effect on the equilibrium only if the number of moles of gaseous reactants differs from the number of moles of gaseous products, shifting the condition of equilibrium to the side with the fewer number of moles.

3. What property of a reaction can we use to predict the effect of a change in temperature on the value of an equilibrium constant?

Solution

The change in enthalpy may be used. If the reaction is exothermic, the heat produced can be thought of as a product. If the reaction is endothermic the heat added can be thought of as a reactant. Additional heat would shift an exothermic reaction back to the reactants but would shift an endothermic reaction to the products. Cooling an exothermic reaction causes the reaction to shift toward the product side; cooling an endothermic reaction would cause it to shift to the reactants' side.

4. The following reaction occurs when a burner on a gas stove is lit:

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(g)$$

Is an equilibrium among CH_4, O_2, CO_2, and H_2O established under these conditions? Explain your answer.

Solution

No, it is not at equilibrium. Because the system is not confined, products continuously escape from the region of the flame; reactants are also added continuously from the burner and surrounding atmosphere.

5. A necessary step in the manufacture of sulfuric acid is the formation of sulfur trioxide, SO_3, from sulfur dioxide, SO_2, and oxygen, O_2, shown here. At high temperatures, the rate of formation of SO_3 is higher, but the equilibrium amount (concentration or partial pressure) of SO_3 is lower than it would be at lower temperatures.

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

(a) Does the equilibrium constant for the reaction increase, decrease, or remain about the same as the temperature increases?

(b) Is the reaction endothermic or exothermic?

Solution

(a) For the yield to decrease from that obtained at a lower temperature, the value of *K* must decrease with an increase in temperature.

(b) The observation that *K* decreases with an increase in temperature indicates the reaction is exothermic.

6. Suggest four ways in which the concentration of hydrazine, N_2H_4, could be increased in an equilibrium described by the following equation:

$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \Delta H = 95 \text{ kJ}$$

Solution

Add N_2; add H_2; decrease the container volume; heat the mixture.

7. Suggest four ways in which the concentration of PH_3 could be increased in an equilibrium described by the following equation:

$$P_4(g) + 6H_2(g) \rightleftharpoons 4PH_3(g) \qquad \Delta H = 110.5 \text{ kJ}$$

Solution

Add P_4; add H_2; decrease the container volume; heat the mixture.

8. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g) \qquad \Delta H = 92 \text{ kJ}$

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181 \text{ kJ}$

(c) $2O_3(g) \rightleftharpoons 3O_2(g) \qquad \Delta H = -285 \text{ kJ}$

(d) $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) \qquad \Delta H = -176 \text{ kJ}$

Solution

(a) *T* increase = shift right, *V* decrease = shift left;

(b) *T* increase = shift right, *V* decrease = no effect;

(c) *T* increase = shift left, *V* decrease = shift left;

(d) *T* increase = shift left, *V* decrease = shift right.

9. How will an increase in temperature affect each of the following equilibria? How will a decrease in the volume of the reaction vessel affect each?

(a) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ ΔH = 484 kJ

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta H = -92.2$ kJ

(c) $2Br(g) \rightleftharpoons Br_2(g)$ $\Delta H = -224$ kJ

(d) $H_2(g) + I_2(s) \rightleftharpoons 2HI(g)$ $\Delta H = 53$ kJ

Solution

(a) *T* increase = shift right, *V* decrease = shift left;

(b) *T* increase = shift left, *V* decrease = shift right;

(c) *T* increase = shift left, *V* decrease = shift right;

(d) *T* increase = shift right, *V* decrease = shift left.

10. Methanol can be prepared from carbon monoxide and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g) \qquad \Delta H = -90.2 \text{ kJ}$$

(b) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more H_2 is added?

(c) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if CH_3OH is added?

(e) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if the temperature of the system is increased?

(f) What will happen to the concentrations of H_2, CO, and CH_3OH at equilibrium if more catalyst is added?

Solution

(a) $K_c = \dfrac{[CH_3OH]}{[H_2]^2[CO]}$;

(b) $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ increases;

(c) $[H_2]$ increases, [CO] decreases, $[CH_3OH]$ decreases;

(d) $[H_2]$ increases, [CO] increases, $[CH_3OH]$ increases;

(e) $[H_2]$ increases, [CO] increases, $[CH_3OH]$ decreases;

(f) no changes.

11. Nitrogen and oxygen react at high temperatures.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad \Delta H = 181 \text{ kJ}$$

(b) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if more O_2 is added?

(c) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if N_2 is removed?

(d) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if NO is

added?

(e) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if the temperature of the system is increased?

(g) What will happen to the concentrations of N_2, O_2, and NO at equilibrium if a catalyst is added?

Solution

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

(b) [N_2] decreases, [O_2] increases, [NO] increases;

(c) [N_2] decreases, [O_2] increases, [NO] decreases;

(d) [N_2] increases, [O_2] increases, [NO] increases;

(e) [N_2] increases, [O_2] increases, [NO] increases(same moles in decreased volume);

(f) [N_2] decreases, [O_2] decreases, [NO] increases; (g) no changes occur.

12. Water gas, a mixture of H_2 and CO, is an important industrial fuel produced by the reaction of steam with red hot coke, essentially pure carbon.

(a) Write the expression for the equilibrium constant for the reversible reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \qquad \Delta H = 131.30 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more C is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if CO is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Solution

(a) $K_c = \frac{[CO][H_2]}{[H_2O]}$; (b) [$H_2O$] no change, [CO] no change, [H_2] no change; (c) [H_2O] decreases, [CO] decreases, [H_2] decreases; (d) [H_2O] increases, [CO] increases, [H_2] decreases; (e) [H_2O] decreases, [CO] increases, [H_2] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

13. Pure iron metal can be produced by the reduction of iron(III) oxide with hydrogen gas.

(a) Write the expression for the equilibrium constant (K_c) for the reversible reaction

$$Fe_2O_3(s) + 3H_2(g) \rightleftharpoons 2Fe(s) + 3H_2O(g) \qquad \Delta H = 98.7 \text{ kJ}$$

(b) What will happen to the concentration of each reactant and product at equilibrium if more Fe is added?

(c) What will happen to the concentration of each reactant and product at equilibrium if H_2O is removed?

(d) What will happen to the concentration of each reactant and product at equilibrium if H_2

is added?

(e) What will happen to the concentration of each reactant and product at equilibrium if the volume of the reaction vessel is decreased?

(f) What will happen to the concentration of each reactant and product at equilibrium if the temperature of the system is increased?

Solution

(a) $K_c = \frac{[H_2O]^3}{[H_2]^3}$; (b) no changes occur; (c) $[H_2]$ decreases, $[H_2O]$ decreases; (d) $[H_2]$ increases, $[H_2O]$ increases; (e) $[H_2]$ increases, $[H_2O]$ increases (concentrations rise due to decreased volume, but there is no shift in the equilibrium); (f) $[H_2]$ decreases, $[H_2O]$ increases. In (b), (c), (d), (e), and (f), the mass of Fe will change, but its concentration (activity) will not change.

14. Ammonia is a weak base that reacts with water according to this equation:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH

(b) Addition of HCl

(c) Addition of NH_4Cl

Solution

Only (b). In (a), addition of a strong base forces the equilibrium toward forming more $NH_3(aq)$. In (b), the addition of HCl consumes OH^-, shifting the equilibrium right and increasing the conversion of NH_3 to NH_4^+. In (c), NH_4^+ ion causes the equilibrium to shift to the left, forming more $NH_3(aq)$.

15. Acetic acid is a weak acid that reacts with water according to this equation:

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

Will any of the following increase the percent of acetic acid that reacts and produces $CH_3CO_2^-$ ion?

(a) Addition of HCl

(b) Addition of NaOH

(c) Addition of $NaCH_3CO_2$

Solution

Only (b). In (a), the addition of HCl increase the H_3O^+ concentration and shifts the equilibrium to the left, decreasing the acetate ion concentration and increasing the acetic acid concentration. In (b), the addition of a strong base consumes H_3O^+ and shifts the equilibrium to the right, forming acetate ion. In (c), addition of the acetate ion shifts the equilibrium left, increasing the concentration of acetic acid.

16. Suggest two ways in which the equilibrium concentration of Ag^+ can be reduced in a solution of Na^+, Cl^-, Ag^+, and NO_3^-, in contact with solid AgCl.

$$Na^+(aq) + Cl^-(aq) + Ag^+(aq) + NO_3^-(aq) \rightleftharpoons AgCl(s) + Na^+(aq) + NO_3^-(aq)$$

$\Delta H = -65.9\ \text{kJ}$

Solution

Add NaCl or some other salt that produces Cl^- to the solution. Cooling the solution forces the equilibrium to the right, precipitating more AgCl(*s*).

17. How can the pressure of water vapor be increased in the following equilibrium?

$$H_2O(l) \rightleftharpoons H_2O(g) \qquad \Delta H = 41\ \text{kJ}$$

Solution

Add heat or reduce the pressure.

18. A solution is saturated with silver sulfate and contains excess solid silver sulfate:

$$Ag_2SO_4(s) \rightleftharpoons 2Ag^+(aq) + SO_4^{2-}(aq)$$

A small amount of solid silver sulfate containing a radioactive isotope of silver is added to this solution. Within a few minutes, a portion of the solution phase is sampled and tests positive for radioactive Ag^+ ions. Explain this observation.

Solution

Though the solution is saturated, the dynamic nature of the solubility equilibrium means the opposing processes of solid dissolution and precipitation continue to occur (just at equal rates, meaning the dissolved ion concentrations and the amount of undissolved solid remain constant). The radioactive Ag^+ ions detected in the solution phase come from dissolution of the added solid, and their presence is countered by precipitation of nonradioactive Ag^+.

19. When equal molar amounts of HCl and HOCl are dissolved separately in equal amounts of water, the solution of HCl freezes at a lower temperature. Which compound has the larger equilibrium constant for acid ionization?

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

Solution

The freezing point depression is proportional to the molal concentration of solute particles in a solution, $\Delta T = ik_f m$ (see Chapter 11 on solutions). Both HCl and HOCl are acids, and thus act as covalent electrolytes when dissolved in water, reacting with water molecules to yield ions as shown in the simplified equilibrium equations above. The ionization reactions above each yield two moles of product species for each mole of acid dissolved. Since both solutions are of equal molal concentration, observing a lower freezing point for the HCl solution indicates its van't Hoff factor is greater than that for HOCl ($i_{HCl} > i_{HOCl}$). This results from the essentially complete ionization of HCl (a "strong acid") and the relatively slight ionization of HOCl (a "weak acid"), that is, $K_{HCl} > K_{HOCl}$.