***Chemistry***

**13: Fundamental Equilibrium Concepts**

**13.3: Shifting Equilibria: Le Châtelier’s Principle**

31. The following equation represents a reversible decomposition:



Under what conditions will decomposition in a closed container proceed to completion so that no CaCO3 remains?

Solution

The amount of CaCO3 must be so small that is less than *KP* when the CaCO3 has completely decomposed. In other words, the starting amount of CaCO3 cannot completely generate the full required for equilibrium.

33. 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.

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



Is an equilibrium among CH4, O2, CO2, and H2O 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.

37. Suggest four ways in which the concentration of hydrazine, N2H4, could be increased in an equilibrium described by the following equation:



Solution

Add N2; add H2; decrease the container volume; heat the mixture.

39. 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) 

(b) 

(c) 

(d) 

Solution

(a) Δ*T* increase = shift right, Δ*P* increase = shift left; (b) Δ*T* increase = shift right, Δ*P* increase = no effect; (c) Δ*T* increase = shift left, Δ*P* increase = shift left; (d) Δ*T* increase = shift left, Δ*P* increase = shift right.

41. Water gas is a 1:1 mixture of carbon monoxide and hydrogen gas and is called water gas because it is formed from steam and hot carbon in the following reaction: . Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and hydrogen at high temperature and pressure in the presence of a suitable catalyst.

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



(b) What will happen to the concentrations of H2, CO, and CH3OH at equilibrium if more H2 is added?

(c) What will happen to the concentrations of H2, CO, and CH3OH at equilibrium if CO is removed?

(d) What will happen to the concentrations of H2, CO, and CH3OH at equilibrium if CH3OH is added?

(e) What will happen to the concentrations of H2, CO, and CH3OH at equilibrium if the temperature of the system is increased?

(f) What will happen to the concentrations of H2, CO, and CH3OH at equilibrium if more catalyst is added?

Solution

(a) ; (b) [H2] increases, [CO] decreases, [CH3OH] increases; (c) [H2] increases, [CO] decreases, [CH3OH] decreases; (d) [H2] increases, [CO] increases, [CH3OH] increases; (e) [H2] increases, [CO] increases, [CH3OH] decreases; (f) no changes.

43. Water gas, a mixture of H2 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



(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 H2O 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) ; (b) [H2O] no change, [CO] no change, [H2] no change; (c) [H2O] decreases, [CO] decreases, [H2] decreases; (d) [H2O] increases, [CO] increases, [H2] decreases; (f) [H2O] decreases, [CO] increases, [H2] increases. In (b), (c), (d), and (e), the mass of carbon will change, but its concentration (activity) will not change.

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



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 NH4Cl

Solution

Only (b). In (a), addition of a strong base forces the equilibrium toward forming more NH3(*aq*). In (b), the addition of HCl causes a reaction with NH3 to form more  by removing OH– as it reacts with the acid to form water. In (c),  ion causes the equilibrium to shift to the left, forming more NH3(*aq*).

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





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*).

49. Additional solid silver sulfate, a slightly soluble solid, is added to a solution of silver ion and sulfate ion at equilibrium with solid silver sulfate.



Which of the following will occur?

(a) Ag+ or concentrations will not change.

(b) The added silver sulfate will dissolve.

(c) Additional silver sulfate will form and precipitate from solution as Ag+ ions and  ions combine.

(d) The Ag+ ion concentration will increase and the  ion concentration will decrease.

Solution

(a) The solution already holds as many ions as it can.

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