Why?

When a reaction reaches equilibrium we can calculate the concentrations of all species, both reactants and products, by using information about starting concentrations or pressures and the numerical value of the equilibrium constant. Knowing how to set up and solve equilibrium problems for gas-phase systems is essential preparation for applying equilibrium concepts to more complicated systems, such as acid-base chemistry. The mixture of reactants and products can often be altered by applying a stress to the system (changing species concentrations, changing pressures, changing temperature, etc.), and the shift in the position of the equilibrium can be understood and predicted on the basis of LeChatelier's Principle.

Learning Objectives
- Understand how to incorporate stoichiometry into the set-up of an equilibrium problem
- Understand the concept of the reaction quotient, Q, as a means of determining whether or not a system is at equilibrium, and if not, how a system must proceed to reach equilibrium
- Understand how various stresses cause a shift in the position of equilibrium on the basis of LeChatelier's Principle

Success Criteria
- Be able to set up and solve for all species using K_c or K_p
- Be able to predict the direction of a reaction on the basis of Q
- Be able to check equilibrium calculation results, using a Q calculation
- Be able to apply LeChatelier's Principle to determine the direction a system at equilibrium must shift to reach a new equilibrium

Prerequisite

Have read all of Chapter 15

Key Question

1. Consider the following reaction

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
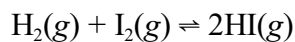
    At 425°C, an equilibrium mixture has the following concentrations

$$[HI] = 1.01 \text{ x } 10^{-2} \text{ mol/L}$$

$$[H_2] = 1.25 \text{ x } 10^{-3} \text{ mol/L}$$

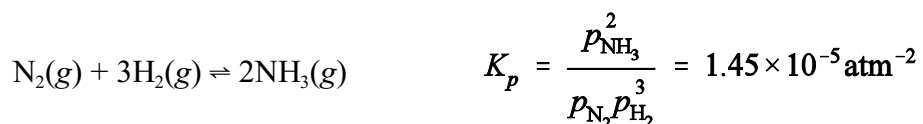$$[I_2] = 1.49 \text{ x } 10^{-3} \text{ mol/L}$$

    What is the value of K_c?

Information (Meaning of K)

The importance of the equilibrium constant for any system is that the reactant and product concentrations *at equilibrium* must be such that the ratio that defines the value of K_c or K_p is obtained. Hence, any combination of initial reactant and product concentrations in a reaction mixture will have adjusted so as to result in the K_c value when equilibrium is established. Likewise, for gas-phase reactions, any combination of initial reactant and product partial pressures will have adjusted so as to result in the K_p value when equilibrium is established. The magnitude of the K value indicates whether the reaction at equilibrium favors products or reactants. The ratio that defines K places product species in the numerator and reactant species in the denominator. Therefore, if the K for a reaction is greater than 1, at equilibrium products will predominate. The reaction is said to be product favored. Conversely, if K is less than 1, then at equilibrium reactants will predominate, and the reaction is said to be reactant-favored.

Key Question

2. At 500 °C, $K_p = 1.45 \text{ x } 10^{-5} \text{ atm}^{-2}$ for the Haber process:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_p = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3} = 1.45 \times 10^{-5} \text{atm}^{-2}$$

    When the reaction for the Haber process comes to equilibrium, does the equilibrium mixture contain mostly reactants or product?

Information (The Reaction Quotient, Q)

We can calculate the ratio of concentrations or pressures like K_c and K_p at any time in course of a reaction. When the system is *not at equilibrium*, the ratio of the product concentrations raised

to their stoichiometric coefficients to the reactant concentrations raised to their stoichiometric coefficients is called the *reaction quotient* and given the symbol Q. The form of Q is the same as the form of K_c or K_p, but the values for products and reactants are not presumed to be the values at equilibrium. The value of Q relative to K_c or K_p indicates the direction in which the reaction must run to achieve equilibrium. If $Q < K$, then the reactant concentrations or pressures are too high and the product concentrations or pressures are too low. To achieve equilibrium, the reaction must run in the forward direction (shift right), using up reactants and forming more products. Conversely, if $Q > K$, then the reactant concentrations are too low and the product concentrations are too high. To achieve equilibrium, the reaction must run in the reverse direction (shift left), using up products and reforming more reactants.

Key Question

3. Consider the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. A vessel is found to have the following concentrations at 425°C:

    $$[\text{HI}] = 2.50 \text{ mol/L}$$

    $$[H_2] = [I_2] = 0.360 \text{ mol/L}$$

    Given that $K = 54.8$ for the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at this temperature, is the system at equilibrium? If not at equilibrium, how can the system above achieve equilibrium?

Information (Calculating Amounts of All Species in an Equilibrium Mixture)

If a system comes to equilibrium, all reactant and product concentrations must be such that when their numerical values are substituted into the expression for K_c the calculated value of Q is equal to the value of K_c for the reaction. Likewise, for a gas-phase reaction in which pressures are used, the values of all partial pressures at equilibrium must be such that when their numerical values are substituted into the expression for K_p the calculated value of Q is equal to the value of K_p for the reaction.

Very often we know the initial concentrations or pressures of reactants and want to know the values that will be found once equilibrium is established. To calculate these amounts, we generally set the unknown variable x to represent the amount of a particular reactant that must be consumed to reach equilibrium. Then, using the stoichiometry of the reaction and knowledge of the direction the reaction will run (from Q, if inobvious), we write algebraic expressions involving x to represent the amounts that will be present at equilibrium. We then substitute these algebraic expressions into the concentration or pressure terms of the equilibrium constant expression. Solving for the numerical value of x then allows calculating the numerical values of concentration or pressure for all reactants and products. In setting up the problem, it is useful to write down under each species in the balanced equation the initial amount, the algebraic expression for how each amount will change, and the algebraic expressions for each final amount.

Key Questions

4.   For the reaction $(NH_3)B(CH_3)_3(g) \rightleftharpoons NH_3(g) + B(CH_3)_3(g)$ at 100 °C $K_p = 4.62$ atm. If the partial pressures of $NH_3(g)$ and $B(CH_3)_3(g)$ in an equilibrium mixture at 100 °C are both 1.52 atm, what is the partial pressure of $(NH_3)B(CH_3)_3(g)$ in the mixture?

5.   At 425°C, 1.00 mol of $H_2(g)$ and 1.00 mol of $I_2(g)$ are mixed in a one liter vessel. What will be the concentrations of $H_2(g)$, $I_2(g)$, and $HI(g)$ at equilibrium? At 425°C, $K_c = 54.8$.

Information (Using Q to Check Your Results)

Calculations of this sort involve a lot of mathematical manipulation, and it is easy to make a mistake. How can you know when you have gone astray? The best way is to substitute your found values into the expression for Q and compare the calculated value with the given K. Because of rounding, do not expect an exact match. However, if $Q \neq K$ by a wide margin, check your work. Q is also useful at the beginning of an equilibrium problem, when the direction in which the reaction will run is not obvious. Remember, if $Q < K$ the reaction will run in the forward directs, but if $Q > K$ it will run in the reverse direction.

Key Questions

6.   Check the values you found in Key Question 5 by calculating the value of Q. Does your value agree with $K = 54.8$?

7.   Suppose 0.800 mol $H_2(g)$, 0.900 mol $I_2(g)$, and 0.100 mol $HI(g)$ are mixed in a one liter vessel at 425°C. $K = 54.8$
   a.   In which direction must the reaction run (forward or backwards) to achieve equilibrium?

   b.   What are the concentrations of all species at equilibrium?

Information (LeChatelier's Principle)

   In 1884 Henri LeChatelier formulated the following principle:

   If a stress is applied to a system at equilibrium, the system will tend to adjust to a new equilibrium, which minimizes the stress, if possible.

The stresses are changes in concentration, pressure, and temperature. If the stress causes a change in the amounts of reactants and products present once equilibrium is reestablished, we say that a *shift in the position of the equilibrium* has occurred. If we think of a reaction equation in the usual way, with reactants on the left and products on the right, a stress to the system at equilibrium may cause either of the following:

Shift to the right   more reactant(s) consumed resulting in greater product and lesser reactant concentrations

Shift to the left   more product(s) consumed resulting in greater reactant and lesser product concentrations

Sometimes the stress cannot be alleviated by either kind of shift, in which case the original equilibrium is maintained. The effects of each kind of stress on a system at equilibrium are summarized below.

- Concentration change:
  - ✓ K_c or K_p remains the same.
  - ✓ Increasing reactant concentrations or decreasing product concentrations causes a shift right (more product forms).
  - ✓ Increasing product concentrations or decreasing reactant concentrations causes a shift left (more reactant forms).

- Pressure change:
  - ✓ K_c or K_p remains the same.
  - ✓ Only changes that affect the partial pressures of reactants and/or products can cause a change.
    > For example, adding an inert gas has no effect.
  - ✓ Increasing pressure causes a shift to the side with the lower sum of coefficients on gas species.
    > For example, increasing the pressure on an equilibrium mixture for the reaction, $N_2(g) + 3 H_2(g) \rightleftharpoons 2 NH_3(g)$, causes a shift right.
  - ✓ If the sum of coefficients on gas species is the same on the left and right, changing the pressure has no effect.
    > For example, for an equilibrium mixture for the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2 HI(g)$, changing the pressure has no effect on the position of the equilibrium.

- Temperature change:
  - ✓ K_c and K_p change values!
  - ✓ Raising the temperature drives the endothermic process.
    > For example, for the reaction, $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, $\Delta H° = +58.0$ kJ/mol. Therefore, raising the temperature on an equilibrium mixture will favor formation of more $NO_2(g)$
  - ✓ Lowering the temperature drives the exothermic process.
    > For example, for the reaction, $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$, $\Delta H° = +58.0$ kJ/mol. Therefore, lowering the temperature on an equilibrium mixture will favor formation of more $N_2O_4(g)$, because the reverse reaction is exothermic.

- Adding a catalyst
  - ✓ A catalyst has no effect on the position of the equilibrium, just how fast it gets there.

Key Questions

8. For each of the following reactions at equilibrium, predict the effect (if any) the indicated stress would have on the position of the equilibrium. Note whether or not the value of the equilibrium constant changes.

a. $H_2(g) + I_2(g) \rightleftharpoons 2\ HI(g)$ More $HI(g)$ is added.

b. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ $NH_3(g)$ is removed as it forms.

c. $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$ Overall pressure is increased.

d. $2\ NO(g) + Cl_2(g) \rightleftharpoons 2\ NOCl(g)$ $\Delta H^\circ = -75.5$ kJ/mol
                                                              Temperature is increased.

e. $H_2O(g) + C(s) \rightleftharpoons H_2(g) + CO(g)$ Overall pressure is increased.

f. $C(s) + O_2(g) \rightleftharpoons CO_2(g)$ Overall pressure is decreased.

g. $N_2O_4(g) \rightleftharpoons 2\ NO_2(g)$ $N_2(g)$ is added, increasing overall pressure.

h. $N_2(g) + 3\ H_2(g) \rightleftharpoons 2\ NH_3(g)$ Iron powder is added as a catalyst.