



# Law of Chemical Equilibrium

# Equilibrium Analysis

- The reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$  is at equilibrium.
- Nitrogen and hydrogen are added to the reaction container:
  - What happens to the concentration of ammonia?  
It increases.
  - How do the concentrations of reactants and products at the new equilibrium compare to those at the original equilibrium? They're both higher.
  - How does the ratio of the concentrations of the reactants to products at the new equilibrium compare to those at the original equilibrium?  
It is the same. (This is predicted by Le Chatelier's principle .)

# Law of Equilibrium



- For the reaction:  $aA + bB = cC + dD$

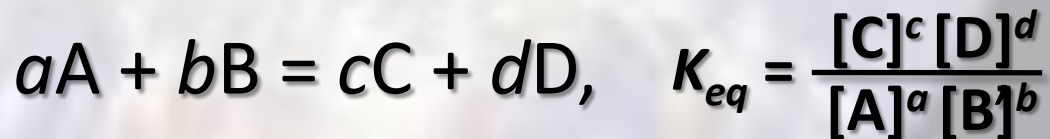
$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[ X ] = concentration of X

- This law can be explained by the relationship between concentration and the probability of effective collisions:
  - Recall that the probability of two independent events is the product of their individual probabilities. (If the probability of tossing heads is 0.5, the probability of tossing two heads is 0.25,  $0.5 \times 0.5$ )
  - **Concentration:** If the concentration of each of two reactants is doubled, the probability of effective collisions is quadrupled (the product of the probabilities)
  - **Coefficients:** If the coefficient for a reactant is 2 and its concentration is doubled, the probability of those two reactant particles colliding is quadrupled.

# The Nature of Equilibrium Expressions

- In the equilibrium expression for the reaction



note the location of:

- The products: **The numerator**
  - The reactants: **The denominator**
- Keep in mind that the products are in the numerator and the reactants are in the denominator of the equilibrium expression. This affects the meaning of  $K_{eq}$ :
    - $K_{eq} < 1$ ? **The reverse reaction is favored.**
    - $K_{eq} > 1$ ? **The forward reaction is favored.**



# Writing Equilibrium Expressions



- What is the equilibrium expression for the reaction  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = 2\text{NH}_3(\text{g})$ ?
  - **Step 1:** Write the product in the numerator raised to its coefficient and the reactants in the denominator raised to their coefficients.

$$K_{eq} = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

- **Step 2:** Look up and substitute the equilibrium constant into the equilibrium expression.

$$6.7 \times 10^5 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

# Solving Equilibrium Expressions

A reaction vessel contains 0.10 M nitrogen gas and 0.10 M hydrogen gas in equilibrium with ammonia? What is the concentration of the ammonia?



- **Step 1:** Write a balanced equation.



- **Step 2:** Write the equilibrium expression.

$$6.7 \times 10^5 = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

- **Step 3:** Substitute values into the equilibrium expression and solve.

$$6.7 \times 10^5 = \frac{[\text{NH}_3]^2}{(0.10\text{M})(0.10\text{M})^3}$$

$$67 = [\text{NH}_3]^2$$

$$[\text{NH}_3] = 8.2\text{M}$$

# Solution Equilibrium

- Recall that, for a saturated solution, the dissolved solute is in equilibrium with the undissolved solute.
- Consider what happens when lithium carbonate dissolves to form a saturated solution:



- What would you expect the equilibrium expression to be?

$$K_{eq} = \frac{[\text{Li}^+]^2 [\text{CO}_3^{2-}]}{[\text{Li}_2\text{CO}_3]}$$

# Solubility Expression Problems

- For the solution equilibrium,  
 $\text{Li}_2\text{CO}_3(s) = 2\text{Li}^+(aq) + \text{CO}_3^{2-}(aq)$ ,  
the equilibrium expression  $K_{eq} = \frac{[\text{Li}^+]^2 [\text{CO}_3^{2-}]}{[\text{Li}_2\text{CO}_3]}$ ,  
has some problems:
  - Concentration is meaningless for  $\text{Li}_2\text{CO}_3$  because it is a pure solid. Concentration describes the amount of one substance in another.
  - If a solution is saturated, no more solid will dissolve no matter how much you add, so the  $\text{Li}_2\text{CO}_3$  does not affect the equilibrium.



# Solubility Product

- The solution to the equilibrium expression problem is simple.
- Get rid of the solid:  $K_{eq} = \frac{[\text{Li}^+]^2 [\text{CO}_3^{2-}]}{[\text{Li}_2\text{CO}_3]}$ 
  - The new expression is called a solubility product.
  - The equilibrium constant is called  $K_{sp}$  instead of  $K_{eq}$ .
- $K_{sp} = [\text{Li}^+]^2 [\text{CO}_3^{2-}]$ 
  - Using the value from the reference table  
 $2.5 \times 10^{-2} = [\text{Li}^+]^2 [\text{CO}_3^{2-}]$

# Solubility Product Summary



- For the solution equilibrium  
 $A_xB_y(s) = xA^+(aq) + yB^-(aq),$

$$K_{sp} = [A^+]^x[B^-]^y$$