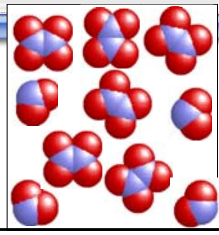
Chapter 13 - Chemical Equilibrium



The Equilibrium State

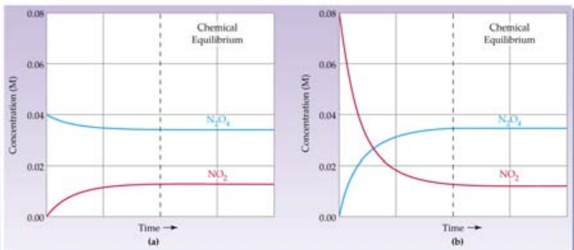
- Not all chemical reactions go to completion.
- When you hear “equilibrium”, what do you think of?
- Example: weather patterns: ocean water evaporates at the same rate that it rains. They are in equilibrium.

The Equilibrium State

- Equilibrium: The state reached when the **concentrations** of reactants and products remain constant over time.
- Most reactions are reversible.
  - A + B ↔ C + D
  - A and B react to make C and D
  - But C and D can also react to make A and B

The Equilibrium State

- Figure 13.1



The Equilibrium State

- We commonly use concentrations to describe equilibrium.
  - [ ] = M = moles/L
  - At equilibrium, the concentrations of substances remain constant.
  - The rate of the forward reaction is the same as the rate of the reverse reaction.
- Usually one side of the equation is favored (reactants or products).

The Equilibrium Constant, K_c

- The Equilibrium Constant, K_c, tells us which side of the reaction is favored.
- $2\ H_2\ (g) + O_2\ (g) \leftrightarrow 2\ H_2O\ (g)$
- $K_c = [H_2O]^2 / [H_2]^2[O_2]$
  - K_c is the equilibrium constant, a value
  - The fraction is the equilibrium constant expression
- K_c is constant at a particular T, K_c is unitless.

Equilibrium equation: $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ ← Products / ← Reactants

Equilibrium constant — Equilibrium constant expression

The Equilibrium Constant, K_c

- Write the equilibrium constant expressions (K_c) for the following equations. (Note: Expressions don't include solids or liquids!)
  - $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$
  - $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$
  - $2SO_2 (g) + O_2 (g) \leftrightarrow 2SO_3 (g)$
- $K_c = [CH_4][H_2O] / [CO][H_2]^3$
- $K_c = [N_2][H_2]^3 / [NH_3]^2$
- $K_c = [SO_3]^2 / [SO_2]^2[O_2]$

The Equilibrium Constant, K_c

- $2 H_2 (g) + O_2 (g) \leftrightarrow 2 H_2O (g)$
- If $K_c = 2.4 \times 10^{47}$ (e.g., a large number) what does this tell you about the **equilibrium** of the reaction?
  - A. There are more reactants than products
  - B. There are more products than reactants
  - C. More information is needed.
- How can you figure this out?

The Equilibrium Constant, K_c

- $2 HBr (g) \leftrightarrow H_2 (g) + Br_2 (g)$
- $K_c = 2 \times 10^{-19}$ (e.g., a small number), what does this tell you about the **equilibrium** of the reaction?
  - A. There are more reactants than products
  - B. There are more products than reactants
  - C. More information is needed.

Calculating K_c

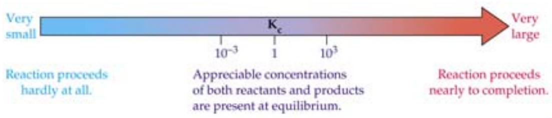
- $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$
- At 500 K, the following concentrations were measured: $[N_2] = 3.0 \times 10^{-2}$ M, $[H_2] = 3.7 \times 10^{-2}$ M, $[NH_3] = 1.6 \times 10^{-2}$ M. What is K_c?
- Are you writing an expression or solving for a number?
- Problems 13.1 - 13.4

Group Quiz #3

- $N_2O_4\ (g) \leftrightarrow 2NO_2\ (g)$
- At 100^{o}C, the following concentrations are measured: $[N_2O_4] = 0.0172$ M, $[NO_2] = 0.00140$ M. What is K_c at this temperature?

Interpreting the Equil. Constant

- If $K_c > 10^3$, products are favored over reactants; reaction goes nearly to completion.
- If $K_c < 10^{-3}$, reactants are favored over products; reaction hardly proceeds at all.
- If K_c is in the range 10^{-3} - 10^3, appreciable concentration of reactants and products are present.
- Problem 13.8



K_c versus K_p

- Can measure gas pressures instead of molar concentrations. Pressure is directly proportional to concentration.
- PV = nRT ⌫ P = (n/V) RT ⌫ n/V = M
- $2NH_3(g) \leftrightarrow N_2(g) + 3H_2(g)$
  - $K_c = [N_2][H_2]^3 / [NH_3]^2$
  - $K_p = (P_{N2})(P_{H2})^3 / (P_{NH3})^2$
- $K_p = K_c(RT)^{\Delta n}$
  - Δn = moles product - moles reactant
  - R = 0.08206 L·atm / mol·K

Worked Example 13.5

- CH_4 (g) + $2H_2S$ (g) ↔ CS_2 (g) + $4H_2$ (g)
- At 1000 K, CH_4 is 0.20 atm, H_2S is 0.25 atm, CS_2 is 0.52 atm, and H_2 is 0.10 atm. What is K_p?
- Ans: 4.2×10^{-3}

Heterogenous Equilibria

- Homogeneous equil.: all substances are in one phase (all gas, all solid, etc.)
- Heterogeneous equil.: substances in 2 or more different phases
- $CaCO_3$ (s) ↔ CaO (s) + CO_2 (g)
- Solids and liquids have constant concentrations. If you increase the amount of $CaCO_3$, you also increase its volume.

Heterogeneous Equilibria

- Write K_c and K_p for the following equations:
- $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$
- $2Cu_2S(s) + 3O_2(g) \leftrightarrow 2Cu_2O(s) + 2SO_2(g)$
- $Hg(l) + Hg^{2+}(aq) \leftrightarrow Hg_2^{2+}(aq)$

Using the Equil. Constant

- $2H_2\,(g) + O_2\,(g) \leftrightarrow 2H_2O\,(g)$
  - $K_c = 2.4 \times 10^{47}$ at 500K
  - What is the concentration of H_2 at equilibrium if $[H_2O] = 1.0$ M and $[O_2] = 1.0 \times 10^{-16}$ M?
- $3H_2\,(g) + N_2\,(g) \leftrightarrow 2NH_3\,(g)$
  - Calculate K_c: $[H_2] = 0.104$ M, $[N_2] = 0.554$ M, $[NH_3] = 0.418$ M
  - Calculate P_{NH3}: $P_{H2} = 1.24$ atm, $P_{N2} = 2.17$ atm

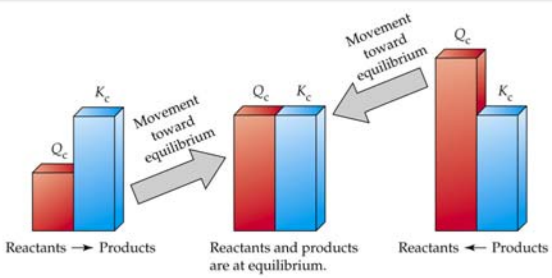
Reaction Quotient, Q

- Q is similar to K but may not be at equilibrium. Calculating Q tells us which direction a reaction must go to reach equilibrium.
- $H_2(g) + I_2(g) \leftrightarrow 2HI\,(g)$ $K_c = 57.0$ at 700 K
- If $[H_2] = 0.10$ M, $[I_2] = 0.20$ M, and $[HI] = 0.40$ M, is this system at equilibrium?
- What needs to happen to reach equilbrium?

Reaction Quotient, Q

- If $Q_c < K_c$, reaction shifts right (creates more products)
- If $Q_c > K_c$, reaction shifts left (creates more reactants)
- If $Q_c = K_c$, reaction is at equilibrium (no shifting)
- Figure 13.5
- Worked Ex 13.8, Problems 13.9 - 13.10

Reaction Quotient, Q



Direction of Shift

- $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$ K = 4.0
  2.0 M 1.0 M 0.50 M 0.50 M
- Is this system at equilibrium? In which direction will the reaction proceed to reach equilibrium?
- Group Quiz #4:
- $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$ K = 4.0
  0.20 M 0.10 M 1.0 M 1.0 M
- Is this system at equilibrium? In which direction will the reaction proceed to reach equilibrium?

Calculate Equil. Concentrations

- Given initial concentrations of reactants and K_c, we can calculate equilibrium concentrations.
- Use balanced equation and an ICE table.

K_c=2.5x10^{-5}	N_2 (g)	$3H_2$ (g)	$\leftrightarrow$	2 NH_3 (g)
Initial	1.00 M	1.00 M		0 M
Change	-x	-3x		+2x
Equilibrium	1.00 -x	1.00 - 3x		2x

Calculate Equil. Concentrations

- $N_2(g) + H_2(g) \leftrightarrow NH_3(g)$
- Is the equation balanced?
- $[N_2]_i$ = 1.00 M, $[H_2]_i$ = 1.00 M, $[NH_3]$ = 0 M
- What are equilibrium concentrations of all species?
- K_c = 2.5 x 10^{-5}
- Ans: $[N_2]_{eq}$ = 0.998 M, $[H_2]_{eq}$ = 0.993 M, $[NH_3]_{eq}$ = 5.00 x 10^{-3} M

PRACTICE!!!

- Worked examples 13.9 - 13.11
- Problems 13.11 - 13.15

Solving for Equil. Conc.

- Assumption that x is small isn't always valid!
- What to do?
- Quadratic formula!!!

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

- Gives two values of x; both won't always make sense

Solving for Equil. Conc.

- H_2 (g) + I_2 (g) $\leftrightarrow$ 2HI (g)

  1.00 M   2.00 M   0 M
- K_c = 50.5
- Calculate the equilibrium concentrations of all species.
- Check math by plugging concentrations in to equilibrium expression.

Group Quiz #5

- CO(g) + H_2O(g) $\leftrightarrow$ CO_2(g) + H_2(g)

  1.00 M   2.00 M   0 M   0 M
- K_c = 4.00
- What are the equilibrium concentrations?

Group Quiz #5 Answers

- $K_c = 4.00 = [CO_2][H_2] / [CO][H_2O]$
- $4.00 = x^2 / (1.00 - x)/(2.00 - x)$
- Assume $x << 1.00$, $x << 2.00$
- $x = 2.83$
- Assumption invalid; quadratic!
- $3.00x^2 - 12.00\ x + 8.00 = 0$
  - $[CO_2]_{eq} = [H_2]_{eq} = x = 0.845$ M
  - $[CO]_{eq} = 1.00 - x = 0.155$ M
  - $[H_2]_{eq} = 2.00 - x = 1.155$ M
- Check math by plugging in concentrations!

Factors Affecting Equil.

- Now we look at what factors can cause shifts in equilibrium. These can alter expenses in industrial settings where a shift toward creation of more products is often more economical.
  - Concentrations of reactants or products can be changed.
  - Pressure and volume of the system can be changed.
  - Temperature can be changed.
  - Addition of a catalyst.

Le Chatelier's Principle

- If a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress.
- "Stress" means a change in one of the factors mentioned on the previous screen.

Changes in Concentration

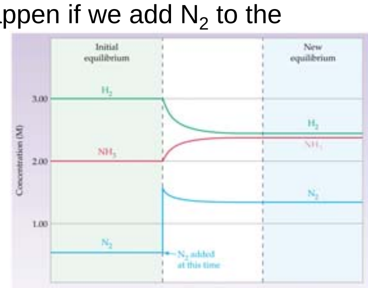
- $A \leftrightarrow B$ $K = 4$
- At equilibrium, [A] = 5 and [B] = 20
- I remove 5 B's. Is this still at equilibrium? If not, what is Q? Which way does this system need to shift? Can you figure this out non-mathematically?
- What happens if I add 5 A's?

Changes in Concentration

- $N_2\ (g) + 3\ H_2\ (g) \leftrightarrow 2\ NH_3\ (g)$
- $K_c = 0.296$ at 700 K
- At equilibrium, $[N_2] = 0.50$ M, $[H_2] = 3.00$ M, $[NH_3] = 2.00$ M
- Verify K_c

Adding Reactant, N_2

- What will happen if we add N_2 to the system?
- Figure 13.8



Changes in Concentration

- N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)

  1.50 M   3.00 M   2.00 M
- K_c = 0.296 at 700 K
- Calculate equilibrium concentrations

Changes in P and V

- Increase in volume: more space = more gases allowed. Shift to side with more **moles of gas**.
- Increase in pressure (same as decrease in volume): less volume = less gas allowed. Shift to side with fewer **moles of gas**.
- If same number of moles on both sides, P and V don't affect equilibrium.
- Adding an inert gas also won't change anything.

Changes in P and V

- N_2 (g) + 3 H_2 (g) ↔ 2 NH_3 (g)
- There are 4 moles of reactant and 2 moles of product.
- What will happen if we increase pressure?
- What will happen if we increase volume?
- Example 13.13 and Problem13.17

Changes in Temperature

- Changes in Conc., P, and V just shift equilibrium to maintain a constant K.
- Changes in Temperature usually affects the value of K.
- We can look at heat exchange (enthalpy) of a reaction to predict shift.
- Endothermic: heat is a "reactant"
- Exothermic: heat is a "product"

Changes in Temperature

- $2NO_2$ (g) $\leftrightarrow$ N_2O_4 (g) $\Delta H^o = +57.2$ kJ
- Endothermic, heat can be imagined to be a reactant, it must be put in to the system.
- Add heat, adds reactant
- Shifts right
- Figure 13.13

Low T High T

Adding a Catalyst

- Catalysts speed up a reaction so they reach equilibrium faster. Once at equilibrium, catalysts serve no purpose.
- If a system is already at equilibrium, adding a catalyst won't affect the system at all!

Le Chatelier's Principle

- Determine how the equilibrium will shift if the following changes are made:
- $2Cl_2(g) + 2H_2O(g) \leftrightarrow 4HCl(g) + O_2(g)$
  $\Delta H^o = +113$ kJ
- Temperature is increased
- Volume is increased
- Pressure is decreased
- HCl is added
- Ne (g) is added
- Cl_2 is added
- H_2O is removed

Le Chatelier's Principle

- Determine how the equilibrium will shift if the following changes are made:
- $2H_2 (g) + O_2 (g) \leftrightarrow 2H_2O (g)$ $\Delta H^o = -571$ kJ
- Temperature is increased
- Volume is decreased
- Pressure is decreased
- H_2 is added
- O_2 is removed
- H_2O is removed