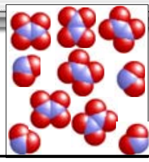
Chapter 13 - Chemical Equilibrium



The Equilibrium State

- Predict products: $CaCO_3$(s) + heat →
- Not all chemical reactions go to completion; most of them exist in a state made up of products and reactants.
- When you hear "equilibrium", what do you think of?
- Examples: weather patterns - ocean water evaporates at the same rate that it rains; water from faucet down the drain.
- They are in equilibrium - activity.

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

- We commonly use concentrations to describe equilibrium (but can also use gas pressure).
  - [ ] = M = mol/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).

Equilibrium Activity

- Copy the table below on your own paper. In each round, ½ of A's move and ¼ of B's move (round up when moving an odd #).

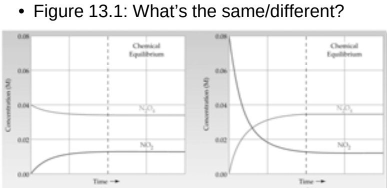
Round	A	B	# A to move	# B to move
1	32	0		
2				
3				
4				
5				

Equilibrium Activity

- What do you notice about the reactant and product "concentrations" over time?
  - Are they equal to each other?
- Did you always move the exact same toothpicks?
- Why is equilibrium referred to as a dynamic process?
  What was constant and what was different in rounds 4 and 5? Would these be the same if you continued to round 100?

The Equilibrium State

- Figure 13.1: What's the same/different?



The Equilibrium Constant, K_c

- Section 13.11: general reversible rxn
- A + B ⇆ C + D
- Forward, $rate_f = k_f[A][B]$
- Reverse, $rate_r = k_r[C][D]$
- Since forward and reverse rates are the same at equilibrium, $rate_f = rate_r$
- $k_f[A][B] = k_r[C][D]$
- k_f/k_r = **[C][D]/[A][B] = K_c** (equil. cons.)

The Equilibrium Constant, K_c

- The Equilibrium Constant, K_c, tells us which side of the reaction is favored.
- *a*A + *b*B ⇆ *c*C + *d*D
  - K_c is the equilibrium constant, a value
  - The fraction is the equilibrium constant expression

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

- Write K_c for: $2H_2$ (g) + O_2 (g) ⇆ $2H_2O$ (g)
- K_c is constant at a particular T, K_c is unitless.

The Equilibrium Constant, K_c

- Write the equilibrium constant expressions (K_c) for the following equations. (Note: Expressions don't include solids or liquids, but coefficients **ARE** used as exponents)
  - $CO(g) + 3H_2(g) \leftrightarrows CH_4(g) + H_2O(g)$
  - $2NH_3(g) \leftrightarrows N_2(g) + 3H_2(g)$
  - $2SO_2(g) + O_2(g) \leftrightarrows 2SO_3(g)$
- Worked Example 13.1; Problems 13.1

Calculating K_c

- $2NH_3(g) \leftrightarrows N_2(g) + 3H_2(g)$
- 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?
- Worked Example 13.2, Problems 13.2, 13.4

Group Work

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

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
- $2NH_3(g) \leftrightarrows N_2(g) + 3H_2(g)$
  - $K_c = [N_2][H_2]^3 / [NH_3]^2$
  - $K_p = (P_{N2})(P_{H2})^3 / (P_{NH3})^2$
- $K_p = K_c(RT)^{\Delta n}$
  - Δn = moles product - moles reactant
  - R = 0.08206 L·atm / mol·K

Worked Example 13.5

- $CH_4\ (g) + 2H_2S\ (g) \leftrightarrows CS_2\ (g) + 4H_2\ (g)$
- 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?
- Worked Example 13.6; Problems 13.5, 13.6

Heterogenous Equilibria

- Homogeneous equil.: all substances are in one phase (all gas, all solid, etc.)
- Heterogeneous equil.: substances in 2 or more different phases
- $CaCO_3\ (s) \leftrightarrows CaO\ (s) + CO_2\ (g)$
- 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 expressions for the following equations:
- $CaCO_3(s) \leftrightarrows CaO(s) + CO_2(g)$
- $2Cu_2S(s) + 3O_2(g) \leftrightarrows 2Cu_2O(s) + 2SO_2(g)$
- $Hg(l) + Hg^{2+}(aq) \leftrightarrows Hg_2^{2+}(aq)$
- Worked Example 13.7, Problem 13.7

The Equilibrium Constant, K_c

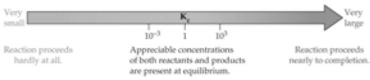
- $2\ H_2\ (g) + O_2\ (g) \leftrightarrows 2\ H_2O\ (g)$
- If $K_c = 2.4 \times 10^{47}$ (e.g., a large number) what does this tell you about the **equilibrium** of the reaction?
  - A. There are more reactants than products
  - B. There are more products than reactants
  - C. More information is needed.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

The Equilibrium Constant, K_c

- $2\ HBr\ (g) \leftrightarrows H_2\ (g) + Br_2\ (g)$
- $K_c = 2 \times 10^{-19}$ (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.

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



Using the Equil. Constant

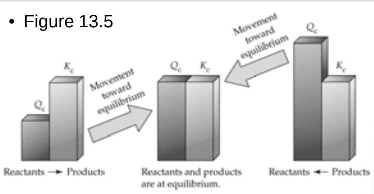
- $2H_2$ (g) + O_2 (g) ⇆ $2H_2O$ (g)
  - $K_c = 2.4 \times 10^{47}$ at 500K
  - What is the concentration of H_2 at equilibrium if $[O_2] = 1.0 \times 10^{-16}$ M and $[H_2O] = 1.0$ M ?
  - $[H_2] = 2.0 \times 10^{-16}$
- $3H_2$ (g) + N_2 (g) ⇆ $2NH_3$ (g)
  - Calculate K_c: $[H_2] = 0.104$ M, $[N_2] = 0.554$ M, $[NH_3] = 0.418$ M, at 500K
  - Calculate P_{NH3} if $P_{H2} = 1.24$ atm, $P_{N2} = 2.17$ atm

Reaction Quotient, Q

- Q is similar to K but may not be at equilibrium. Calculating Q tells us in which direction a reaction must go to reach equilibrium.
- H_2(g) + I_2(g) ⇆ 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 equilibrium?

Reaction Quotient, Q

- Figure 13.5



Reaction Quotient, Q

- If $Q_c < K_c$, reaction shifts right (creates more products)
- If $O_c > K_c$, reaction shifts left (creates more reactants)
- If $Q_c = K_c$, reaction is at equilibrium (no shifting)

- Worked Ex 13.8, Problems 13.9 - 13.10

Direction of Shift

- CO(g) + $3H_2$(g) ⇆ 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 Work:
- CO(g) + $3H_2$(g) ⇆ 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.
- N_2(g) + H_2(g) ⇆ NH_3(g)
- Use balanced equation and an ICE table.

K_c	N_2 (g)	H_2 (g)	⇆	NH_3 (g)
Initial				
Change				
Equilibrium				

Calculate Equil. Concentrations

- N_2(g) + H_2(g) ⇆ NH_3(g)
  1.00 M   1.00 M   0 M
- Is the equation balanced?
- Fill in the ICE table:

$K_c = 2.5 \times 10^{-5}$	N_2 (g)	H_2 (g)	⇆	NH_3 (g)
Initial				
Change				
Equilibrium				

Solving for Equil. Conc.

- 3 methods for solving equilibrium concentrations:
  - Use perfect squares ($H_2 + I_2$ ⇆ 2HI)
    - $K_c = (2x)^2 / (0.100 - x)^2 = 50.5$
  - Assume x is much smaller than initial concentration; **General** rule: if $K < 10^{-3}$, assume x is small
    - $K_c = x^2 / (0.100 - x) = 5.6 \times 10^{-10}$
  - Use quadratic if K_c is too small to make assumption. $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$
    - Gives two values of x; one is usually negative and incorrect.

Equil. Conc. - Perfect Squares

- H_2 (g) + I_2 (g) ⇆ 2HI (g)
  1.00 M   1.00 M   0 M
- K_c = 50.5
- Calculate the equilibrium concentrations of all species.

Equil. Conc. - Assume small x

- N_2(g) + O_2(g) ⇆ 2 NO(g)
  0.80 M   0.20 M   0.00 M
- $K_c = [NO]^2 / [N_2][O_2] = 1.0 \times 10^{-5}$
- $K_c = (2x)^2/(0.80 – x)(0.20 – x) = 1.0 \times 10^{-5}$
- Assume x is small (much smaller than 0.80 or 0.20) because K_c is small (less than 10^{-3})
- Check assumption
- Check math by plugging in concentrations!

Equil. Conc. - Quadratic Eqn.

- PCl_5(g) ⇆ PCl_3(g) + Cl_2(g)
  0.160 M   0 M   0 M

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

- $K_c = [PCl_3][Cl_2] / [PCl_5] = 5.8 \times 10^{-2}$.
- Not perfect squares and K_c isn't very small. Have to use quadratic.
- $K_c = x^2 / (0.160 - x) = 5.8 \times 10^{-2}$
- $x^2 + 5.8 \times 10^{-2}x - 9.28 \times 10^{-3} = 0$
- x = 0.0716 (other answer is negative!)

PRACTICE!!!

- Worked examples 13.9 - 13.11
- Problems 13.11 - 13.15

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 (increased or decreased).
  - Pressure and volume of the system can be changed.
  - Temperature can be changed.
  - A catalyst or inert gas (noble gas) can be added.

Le Chatelier's Principle

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

Water Tanks

Changes in Concentration

- A ⇆ 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? What is Q?

Changes in Concentration

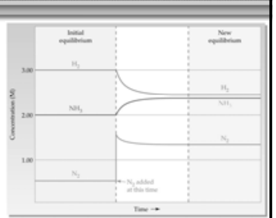
- N_2 (g) + 3 H_2 (g) ⇆ 2 NH_3 (g)
- K_c = 0.296 at 700 K
- At equilibrium,
  - $[N_2]$ = 0.50 M
  - $[H_2]$ = 3.00 M
  - $[NH_3]$ = 1.98 M
- Verify K_c

Adding Reactant, N_2

- What will happen if we add N_2 to the system?
- N_2 (g) + 3 H_2 (g) ⇆ 2 NH_3 (g)
  1.50 M   3.00 M   1.98 M
- Calculate Q
- $[NH_3]^2 / [N_2][H_2]^3 = 0.0968 < K_c$
- New equilibrium concentrations:
- $[N_2]$ = 1.31 M; $[H_2]$ = 2.43 M; $[NH_3]$ = 2.36 M

Changes in Concentration

- Figure 13.8



Changes in P and V

- Increase in volume: more space = more gases allowed. Shift to side with more **moles of gas** (look at total of coefficients).
- 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 a catalyst or an inert gas also won't cause a shift in equilibrium.

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?
- Worked examples 13.12, 13.13; Problems 13.16, 13.17

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) ⇆ 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:
- $2Cl_2(g) + 2H_2O(g)$ ⇆ $4HCl(g) + O_2(g)$ $\Delta H^o = +113$ kJ
- Temperature is increased
- Volume is increased
- Pressure is increased
- HCl is added
- Ne (g) is added
- Cl_2 is added
- H_2O is removed