Module 9. Principles of Chemical Equilibrium Lecture 1

Learning Objective	Openstax 2e Chapter
Equilibrium	**13.1**
Activities	*
Equilibrium Constant (K)	**13.2**

*See:
- General Chemistry by Petrucci , 11th edition, Chapter 15-2
- First Year General Chemistry by Mombourquette, Chapter 12.2.1

Suggested Practice Problems

Chapter 13 Exercises – Questions: 3, 5, 15, 23, 25

Answers can be found in the Chapter 13 Answer Key

Differences between Physical and Chemical Equilibrium

Physical equilibrium	**Chemical equilibrium**
The equilibrium of a substance between two or more physical phases.	The equilibrium between reactants and products in a reversible reaction.

$$NH_3 \ (aq) + H_2O \ (aq) \ \rightleftarrows \ NH_4^+(aq) + HO^-(aq)$$

$$Br_2 \ (l) \ \rightleftarrows \ Br_2 \ (g)$$

At room temp.

Ammonium Hydroxide
氨水

$$Ag^+(aq) + \ I^-(aq) \ \rightleftarrows \ AgI(s)$$

$$H_2O \ (l) \ \rightleftarrows \ H_2O \ (s)$$

At 273 K

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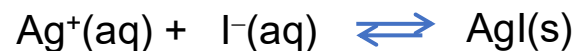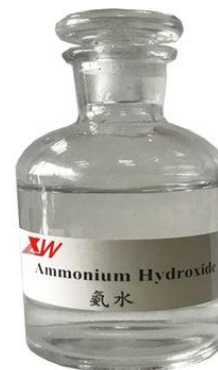
Reactions don't always go completely to products

- In first term, we did stoichiometric calculations where we assumed that reactions went to completion (*at least one reactant was completely used up*).

$$C_xH_y(s) + xO_2 \xrightarrow[\text{combustion}]{\textit{100\% completion}} CO_{2(g)} + H_2O_{(g)}$$
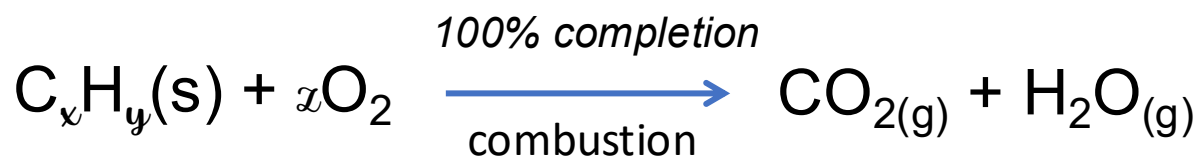
- Now, we explore what happens if the reactions don't go to completion.

$$NH_3(aq) + H_2O \underset{}{\overset{\textit{reaches equilibrium}}{\rightleftharpoons}} NH_4^+(aq) + HO^-(aq)$$
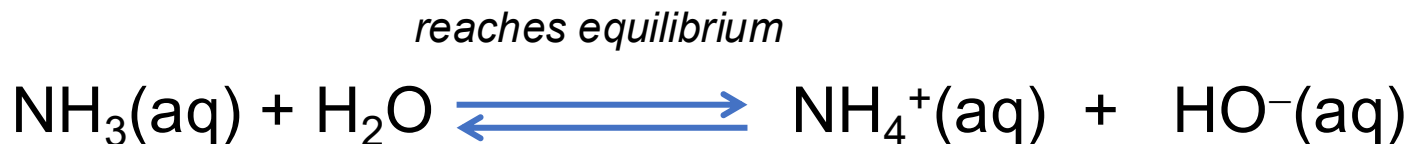
What is an equilibrium?

- Equilibrium is the state of a reaction system whereby the forward reaction rate (to produce products) is equal to the reverse reaction rate (to reconstitute reactants).

$$NH_3 \text{ (aq)} + H_2O \underset{reverse}{\overset{forward}{\rightleftarrows}} NH_4^+ \text{ (aq)} + HO^-\text{(aq)}$$
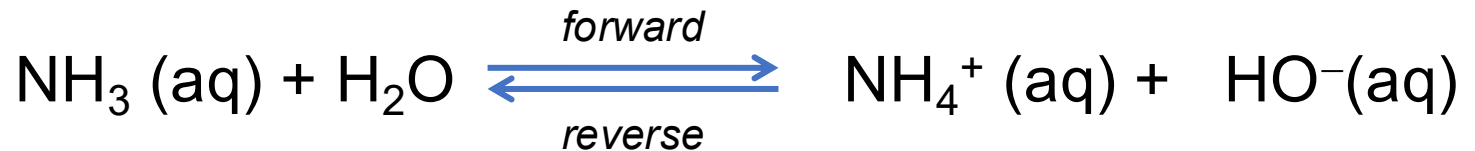
- The concentrations of reactants and products remain constant at equilibrium.

- Although this sounds like a "static" state, it is dynamic!

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Equilibrium – It is *Dynamic*!
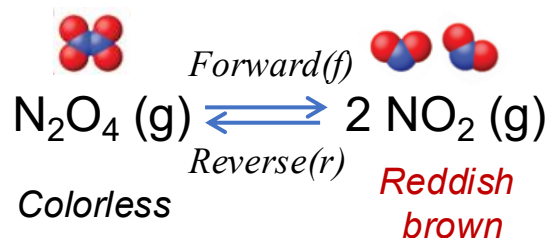
A+B $\rightleftharpoons$ C+D

Initially there is only **A** and **B**, so no reverse reaction.
As **A + B** is used up, forward reaction slows ($\downarrow$ [A] [B], fewer collisions)
As **C + D** is produced, reverse reaction speeds up ($\uparrow$ [C] [D], more collisions)

Eventually, they reach the same speed and no further change in amounts occurs.
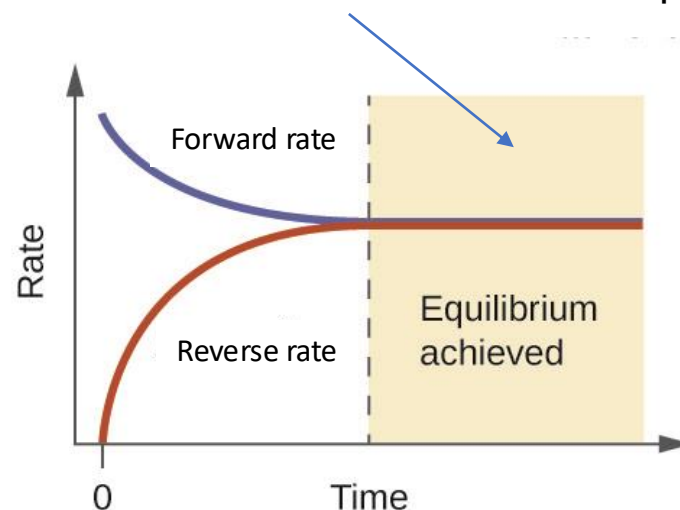The equilibrium doesn't stop, it is dynamic!

Approaching Equilibrium

$$N_2O_4 \text{ (g)} \underset{\textit{Reverse(r)}}{\overset{\textit{Forward(f)}}{\rightleftharpoons}} 2\,NO_2 \text{ (g)}$$

Colorless   Reddish brown

Concentrations of N_2O_4 and NO_2 become constant (but not necessarily equal).
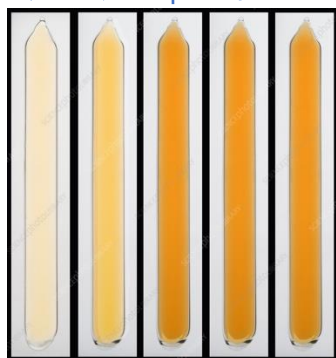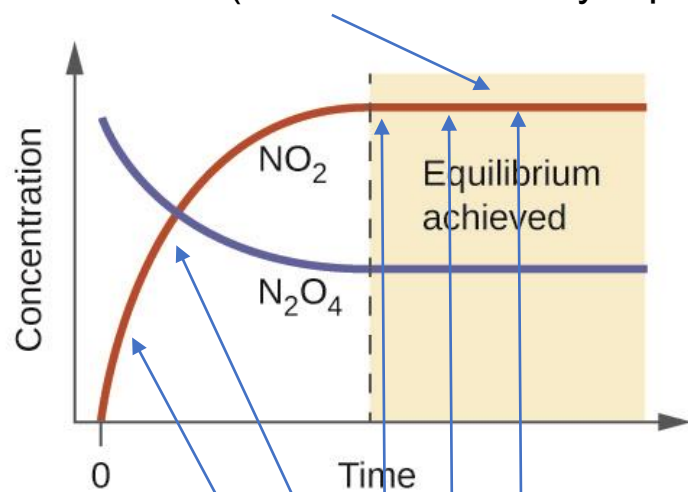
Forward and reverse RATES are equal.

Equilibrium Definition & Mathematical Expression

Definition:

In a closed reaction vessel at constant temperature, a reaction proceeds spontaneously toward equilibrium. At equilibrium, the amounts of starting materials and products remain constant, so their ratio (reaction quotient **Q**) is also a constant value (the equilibrium constant, **K**).

Consider the reaction: $mA + nB \rightleftharpoons yC + zD$

At <u>any point</u> in a reaction $\mathbf{Q} = \dfrac{[C]^y \, [D]^z}{[A]^m \, [B]^n}$

Q is called the **Reaction Quotient** and is used to describe the nature of the reaction mixture.

At <u>equilibrium</u> $\mathbf{Q} = \mathbf{K}$

K is called the **Equilibrium Constant**

Equilibrium Constant: Concentration & Pressure

$$m\mathbf{A} + n\mathbf{B} \rightleftharpoons y\mathbf{C} + z\mathbf{D}$$

If we've measured solution concentrations:
$$K_c = \frac{[C]^y\,[D]^z}{[A]^m\,[B]^n}$$
We describe K_c in terms of molar concentrations of starting materials and products.

If we've measured gas pressures:
$$K_p = \frac{P(C)^y\,P(D)^z}{P(A)^m\,P(B)^n}$$
We describe K_P in terms of partial pressures of starting materials and products.

Practice Problems – Calculating K_C

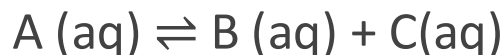Q1. Determine K_c for the following reaction given the equilibrium concentrations at 400 °C.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
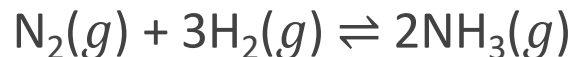
$[N_2]$ = 0.516 M
$[H_2]$ = 1.550 M
$[NH_3]$ = 0.980 M

$$K_c = \frac{[NH_3]^2}{[N_2]\,[H_2]^3} = \frac{[0.980\ M]^2}{[0.516\ M][1.550\ M]^3} = 0.500\ M^{-2}$$

Q2. Determine K_c for the following reaction given the equilibrium concentrations.

$$A\ (aq) \rightleftharpoons B\ (aq) + C(aq)$$

$[A]$ = 0.55 M
$[B]$ = 0.33 M
$[C]$ = 0.43 M

$$K_c = \frac{[B][C]}{[A]} = \frac{0.33\ M\ \times\ 0.43\ M}{0.55\ M} = 0.26\ M$$

Note that K_c may have different units for different reactions.

Relationship between K_c and K_p for ideal gas

For gas-phase solutions, the equilibrium constant may be expressed in terms of either the molar concentrations (K_c) or partial pressures (K_p) of the reactants and products. A relation between these two K values can be derived as:

$$m\mathbf{A} + n\mathbf{B} \rightleftarrows y\mathbf{C} + z\mathbf{D}$$

$$K_P = K_c(RT)^{\Delta n}$$

Recall that R can be expressed in many different Units!

TABLE 6.3 Five Common Values* of R
0.082057338 atm L mol^{-1} K^{-1}
0.083144598 bar L mol^{-1} K^{-1}
8.3144598 kPa L mol^{-1} K^{-1}
8.3144598 Pa m^3 mol^{-1} K^{-1}
8.3144598 J mol^{-1} K^{-1}
* Based on the CODATA recommended 2014 values of the fundamental physical constants (www.physics.nist.gov/cuu/Constants/).

where:

K_P = pressure equilibrium constant

K_c = concentration equilibrium constant

R = ideal gas constant ($8.3145 \frac{kPa \cdot L}{mol \cdot K}$)

T = the temperature (in kelvin)

$\Delta n = y+z - (m+n)$, the change in molar amounts of product and reactant gases

Note: A full derivation of this relationship can be found in section 13.2 of OpenStax Chemistry 2e

Exercise: K_c versus K_p

For the following reaction, we calculated that K_c = 0.500 M^{-2} at 400°C. What is K_P at 400°C?

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
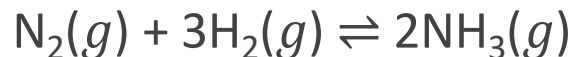
$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^{2-(1+3)} = K_c(RT)^{-2} = 0.500\ M^{-2} \times (R \times 673.15\ K)^{-2}$$

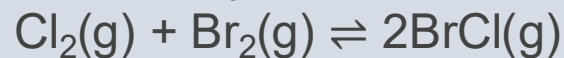$$K_p = 0.500\ M^{-2} \times (8.314\ kPa\ L\ mol^{-1}K^{-1} \times 673.15\ K)^{-2}$$

$$= 0.500\ \times (8.314\ \times 673.15)^{-2}\ kPa^{-2}$$

$$= \mathbf{1.60\ \times 10^{-8}\ kPa^{-2}}$$

Exercise: K_c versus K_p

A Special Case

For the following reaction, $K_c = 4.7 \times 10^{-2}$ at 25°C. What is its K_P ?

$$Cl_2(g) + Br_2(g) \rightleftharpoons 2BrCl(g)$$

In this case, $\Delta n = 2 - (1 + 1) = 0$, So

$$K_p = K_c(RT)^{\Delta n} = K_c(RT)^0 = K_c$$

In this case, both K_c and K_p are dimensionless!

K expression in Relative Activities

- Many reactions involve **mixed phases**, so it's not always possible to use either K_C or K_P

$$m\mathbf{A}(aq) \rightleftharpoons n\mathbf{B}(g) \qquad K = \frac{P(B)^n \; (kPa)}{[A]^m \; (mol/L)} \quad \Bigg] \quad \textit{Mixed units!}$$

- A better option is to use a measure that is independent of phase. This measure the "**relative activity**", expressed as ***a***.

| ① If we've measured solution concentrations:	② If we've measured gas pressure:
$$a = \frac{\text{Concentration}}{\text{Standard Concentration}}$$	$$a = \frac{\text{Pressure}}{\text{Standard Pressure}}$$
Standard Concentration, C° = 1 mol/L.	Standard Pressure, P° = 1 bar (100 kPa)

③ For any pure liquid or pure solid, ***a*** = 1. This means that the *K* value is independent of the amount of pure liquid/or pure solid present in the system.

$$m\mathbf{A}(aq) \rightleftharpoons n\mathbf{B}(g) \qquad K = \frac{a(B)^n}{a(A)^m} \quad \Bigg] \quad \textit{unitless!}$$

Example: The Haber Process

$$3 H_2 (g) + N_2 (g) \rightleftharpoons 2 NH_3 (g)$$
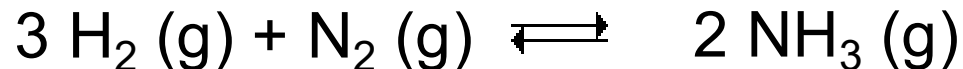
Central Learning Outcome in Chemistry:
Chemicals have benefits and hazards, and these must be considered together.

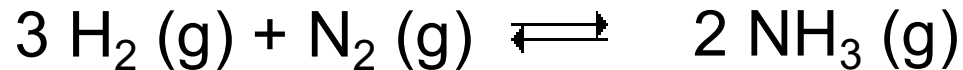https://cen.acs.org/articles/86/i33/Haber-Bosch-Reaction-Early-Chemical.html

Benefit: *Fertilizer, modern agriculture*

Hazard: *Explosives in WWII*

Example: The Haber Process

$$3\ H_2\ (g) + N_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$$

The following conditions are found for this reaction at equilibrium. What are the values of K_P and K (expressed in activities) ?

$p(NH_3) = 103$ kPa
$p(N_2) = 2840$ kPa
$p(H_2) = 10.3$ kPa

$$K_P = \frac{P(NH_3)^2}{P(H_2)^3 \times P(N_2)} = \frac{(103\ \text{kPa})^2}{(10.3\ \text{kPa})^3 \times (2840\ \text{kPa})} = 3.42 \times 10^{-3}\ \text{kPa}^{-2}$$

$a(NH_3) = 103$ kPa /100 kPa = 1.03
$a(N_2) = 2840$ kPa /100 kPa = 28.4
$a(H_2) = 10.3$ kPa /100 kPa = 0.103

$$K = \frac{a(NH_3)^2}{a(H_2)^3 \times a(N_2)} = \frac{(1.03)^2}{(0.103)^3 \times (28.40)} = 34.2$$

K_P and K have very different values!