Chem 30: Acid & Base

Notes

Defining Equilibrium

What are Equilibrium Reactions?
- Equilibrium reactions are reactions that do not go to completion. They appear to stop even though there is still reactant available that could react.

What is happening at Equilibrium?
- Macroscopic properties (such as colour, pressure/volume, pH, temperature) remain constant. At this macroscopic level, everything appears to have stopped.
- At the molecular level, forward and reverse reactions are still taking place, and they occur at the **same** rate.
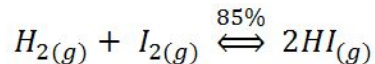
KEY NOTES about Equilibrium:
- MUST occur in a **closed system** (so reactants/products cannot escape the system).
- **rate** $_{forward}$ **= rate** $_{reverse}$
- We use double arrows to represent an equilibrium reaction: ⇌

Interpreting Equilibrium Reactions

Reactions that proceed > 50%: **favours products.**
Reactions that proceed < 50%: **favours reactants**.

For example,

$$H_{2(g)} + I_{2(g)} \overset{85\%}{\Longleftrightarrow} 2HI_{(g)}$$

- This reaction proceeds 85%. At equilibrium, our yield of product will be 85% of the stoichiometrically predicted amount.
- This reaction **favours products**.

Le Chatelier's principle

Le Chatelier's principle says that when an equilibrium system is stressed (through changes in temperature, volume, pressure, and concentration), it will shift to restore the original balance.

Concentration change
If the concentration of reactants increases, then the equilibrium shifts towards products, and vice versa.
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<u>Temperature change</u>
- ● Temperature can be thought of as a reactant in endothermic reactions and a product in exothermic reactions.
- ● Heating an exothermic reaction (adding to the product side) would cause the equilibrium to shift to the left (reactant side).
- ● Note that temperature is usually a gradual change, so concentration graphs will be sloped rather than show vertical lines.

<u>Pressure change</u>
- ● We can think of an increase in pressure as a decrease in volume (e.g. squeezing a balloon), and pressure decrease as an increase in volume.
- ● Decreasing volume increases the concentration of a gas and vice versa, so equilibrium shifts for pressure change are the same as concentration changes. A way to think about this is when pressure increases and volume decreases, there is less space for gas molecules, so the side (either reactant or product) with fewer gas molecules would be favoured.
- ● **Only gases are affected by pressure changes!**

<u>Volume change</u>
- ● Only gases and solutions are affected by volume change.
- ● For both gases and solutions, a decrease in volume would increase concentration, and vice versa. This allows us to predict the Le Chatelier shift according to concentration change.

* **Catalysts do not cause a le chatelier shift** because they increase the rates of both the forward and backward reactions by the same amount.

Equilibrium Constant, K_c

What is "K_c"?

- ● K_c is called the **equilibrium constant**. It provides us information about the **extent of reaction** at equilibrium.

How do we calculate "K_c"?

$$aA + bB \Longleftrightarrow cC + dD$$

- ● If we are given a chemical reaction like the one above, the equation for K_c is:

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

- ● [A], [B], [C], [D] represent the concentrations of the reactants/products in **mol/L at equilibrium.**
- ● The exponents "a, b, c, d" are **equal to the molar coefficients** of the chemical reaction.

KEY NOTES about K_c constant:
- If $K_c > 1$, the reaction **favours products.**
- If $0 < K_c < 1$, the reaction **favours reactants.**
- DO NOT include **solids** or **liquids** in the equilibrium constant equation.
- K_c is very **temperature dependent.**
- K_c tells us **nothing** about reaction rate. (i.e. how quickly this reaction will reach equilibrium.)

I.C.E Tables and Calculating Equilibrium Concentrations

ICE Tables are a simple way to calculate equilibrium reaction amounts.

For example: 1.00 mol of $H_{2(g)}$ reacts with 2.00 mol of $I_{2(g)}$ in a 1.00L container. At equilibrium $[H_{2(g)}] =$ 0.22 mol/L, calculate all equilibrium concentrations.

| (mol/L)	$H_{2(g)}$	+	$I_{2(g)}$	⇌	$2HI_{(g)}$
Initial (I)	1.00		2.00		0.00
Change (C)	-0.78		-0.78		+1.56
Equilibrium (E)	0.22		1.22		1.56

KEY Notes about ICE Tables:
- ★ **Only the "Change" row can be used to relate substances.**
- Factor in the mole ratio. (E.g. 2(0.78) = 1.56).
- Polarity changes when you go across the ⇌. (E.g. -0.78 → +1.56)
- Do **NOT** include **solids** or **liquids**.

Brønsted-Lowry Acids and Bases

Brønsted-Lowry acids donate a proton (i.e. an H^+) in a chemical reaction.
Brønsted-Lowry bases accept a proton (i.e. an H^+) in a chemical reaction.

For example,

$$CH_3COOH_{(aq)} + H_2O_{(l)} \Longleftrightarrow CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$
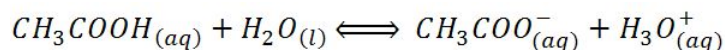
- The "$CH_3COOH_{(aq)}$" becomes "$CH_3COO^-_{(aq)}$". **It loses an H^+.** Therefore, it is a **B-L acid.**
- The "$H_2O_{(l)}$" becomes "$H_3O^+_{(aq)}$". **It gains an H^+.** Therefore, it is a **B-L base.**

Difference between Brønsted-Lowry and Arrhenius Theory?
  ● B-L theory removes the requirement for aqueous solution.
  ● E.g. Certain gases, in some chemical equations, can be classified as a B-L acid or base.

*Substances can only be classified as a B-L acid or base in the **context of the reaction** (i.e. Some compounds may act as a B-L acid in one reaction and a B-L base in a different reaction.).

Strong Acids and Strong Bases:

  ● Strong acids (and bases) are the first **6 compounds at the top of the list** in the "Relative Strengths of Acids and Bases" table of the Alberta Chemistry Data Booklet.
  ● Strong acids **quantitatively** ionize $H_2O_{(l)}$ to produce $H_3O^+_{(aq)}$, and their K_A values are classified as "very high". Strong bases are soluble compounds that contain $OH^-_{(aq)}$.

5 Step Method for Predicting Brønsted-Lowry Acid-Base Reactions:

*CONCEPT: In an acid-base reaction, the strongest acid will react with the strongest base.

Step 1: List all ions/molecules that are present in the solution.

  A) Dissociate soluble ionic compounds. (e.g. $KNO_{3(aq)} \rightarrow K^+_{(aq)} + NO_3^-{}_{(aq)}$)
  B) Ionize strong acids. (e.g. $HNO_{3(aq)} \rightarrow H_3O^+_{(aq)} + NO_3^-{}_{(aq)}$)
  C) Leave weak acids as is. (e.g. $CH_3COOH_{(aq)} \rightarrow CH_3COOH_{(aq)}$)
  D) Don't forget to list $H_2O_{(l)}$. (Since this is a solution.)

Step 2: Identify (and label) substances in the solution as acid or base.

Step 3: Identify the strongest acid (SA) and the strongest base (SB).

Step 4: React the strongest acid with the strongest base by moving exactly **one H^+** from the acid to the base.

Step 5: Predict the equilibrium position (does it favour reactants or products?).
  A) If SA is **above** the SB in the data table, reaction **favours products.**
  B) If SA is **below** the SB in the data table, reaction **favours reactants.**

Conjugate Acid-Base Pairs:

  ● Compounds that differ by exactly **one H^+.** (E.g. HCl and Cl^-, HCO_3^- and CO_3^{2-}, CH_3COOH and CH_3COO^-).

* Every acid-base reaction has **two** pairs of conjugate acid-base pairs.

Amphiprotic Substances:
- Ions that can function as an **acid or a base**. They can give away an H^+ or they can also receive an H^+. (Eg. HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, HSO_4^-, $HOOCCOO^-$).

*Don't try and memorize. Instead, look for compounds of the form H____ with a negative charge.

Polyprotic Acid and Bases
- Polyprotic acids can donate **more than one H^+** in an acid-base reaction.
- Polyprotic bases can accept **more than one H^+** in an acid-base reaction.
- E.g. $H_3PO_{4(aq)}$, $SO_3^{2-}{}_{(aq)}$
- Be careful with $CH_3COOH_{(aq)}$! It has 4 H atoms, but only one can be donated to form $CH_3COO^-{}_{(aq)}$.

pH and pOH

What is pH?
- pH is a measure of the acidity or basicity in an aqueous solution. The range of pH is 0-14.
- It is a measure of the **concentration of hydronium (H_3O^+) ions in a solution**.
- A solution with pH of 7 is **neutral.** <7 is **acidic** and >7 is **basic**.

What is pOH?
- pOH is an opposite measurement of pH.
- It is a measure of the **concentration of hydroxide (OH^-) ions in a solution.**
- A solution of pOH of 7 is **neutral**. <7 is **basic** and >7 is **acidic**.

*pH + pOH = 14.

How do we calculate pH and pOH?
- **pH = -log[H_3O^+]**
  - ○ [H_3O^+] is the concentration of hydronium ions in the solution (in mol/L).
  - ○ "Log" is the logarithmic function.
- **pOH = -log[OH^-]**
  - ○ [OH^-] is the concentration of hydroxide ions in the solution (in mol/L).
  - ○ "Log" is the logarithmic function.

K_W, K_A, and K_B

Acid Ionization Constant, K_A:

- A measure of the **strength of an acid** in an aqueous solution.
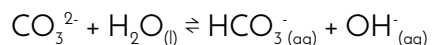- It is the **equilibrium constant** in an acid-base reaction. (Specifically, an acid reacting in water).

$CH_3COOH_{(aq)} + H_2O_{(l)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H_3O^+{}_{(aq)}$
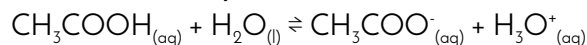
$$\frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

$K_c = K_a =$

Base Ionization Constant, K_B:

- A measure of the **strength of a base** in an aqueous solution.
- It is the **equilibrium constant** in an acid-base reaction. (Specifically, a base reacting in water).

$$CO_3^{2-} + H_2O_{(l)} \rightleftharpoons HCO_{3\ (aq)}^- + OH_{(aq)}^-$$

$$K_c = K_b = \frac{[HCO_3^-][OH^-]}{[CO_3^{2-}]}$$

Water Equilibrium Constant, K_W:

- Equilibrium constant for water-including solutions.
- $K_W = [H_3O^+][OH_{(aq)}^-] = 1.00 \times 10^{-14}$
- $K_a K_b = K_w$ (for conjugate acid-base pairs)

Approximation rule: if $1000 \cdot K_{eq} <$ initial concentration , the change in reactant concentration is small enough that it is negligible when rounded to significant digits.
- When following the approximation rule for a weak acid, the following equation can be derived:

$$K_a = \frac{[H_3O^+]^2}{[acid]}$$

- The same equation can be used for weak bases (replace the concentration of $H_3O^+_{(aq)}$ with $OH^-_{(aq)}$).

Buffers

What is a buffer?

- A buffer is a compound that maintains a **relatively constant pH** when small amounts of acid or base are added.
- Buffers are made up of two constituent substances:a **weak acid** and its **conjugate base**.
- E.g. $CH_3COOH_{(aq)}/CH_3COONa_{(aq)}$. ($CH_3COOH_{(aq)}$ acts as the weak acid and $CH_3COONa_{(aq)}$ acts as the its conjugate base.)
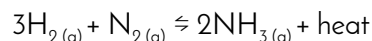
Making a buffer:

Method 1: Start with a weak acid and add some of the conjugate base.

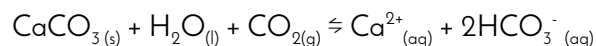Method 2: Partially neutralise a weak acid/base with a strong acid/base.

Practice Questions

1. Please write the equilibrium law expression for the following equilibrium equations:
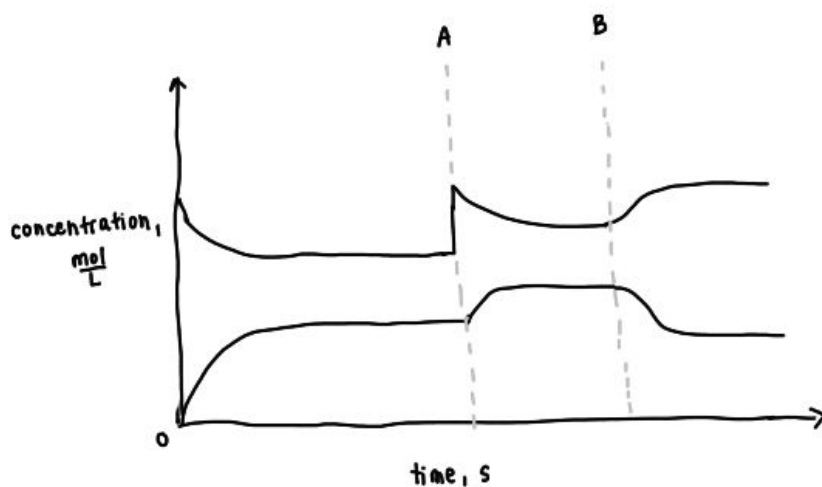   a. The Haber-Bosch process for producing ammonia:
      $3H_{2(g)} + N_{2(g)} \rightleftharpoons 2NH_{3(g)} + heat$
   b. Reaction for the formation of stalactites and stalagmites:
      $CaCO_{3(s)} + H_2O_{(l)} + CO_{2(g)} \rightleftharpoons Ca^{2+}_{(aq)} + 2HCO_3^-{}_{(aq)}$

   Use the following graph for questions 2-5.

2. In the above graph, when is equilibrium first established?

3. What kind of stress was applied to the equilibrium system at A?
4. The equilibrium system graphed above was cooled at B. Knowing this, determine whether the reaction was exothermic or endothermic.
5. The products of the reaction are $H_{2(g)}$ and a white precipitate, $AgBr_{(s)}$. Give 2 qualitative observations you could collect if you performed this reaction that would indicate an equilibrium shift at B.
6. A blood sample was taken from a patient. It was found to have a pH of 7.40. What is the concentration of hydronium ions in the patient's blood?
7. You find an unknown acid and its conjugate base in a box. The K_B of the base is labeled, so you know that $K_B = 2.80 \times 10^{-9}$. Find the K_A of the acid.

8. On the axes below, draw a titration curve for the titration of $HCl_{(aq)}$ into a solution of $PO_4^{3-}{}_{(aq)}$. Identify the buffering regions in your graph by labelling them "BR".

volume of titrant (mL)
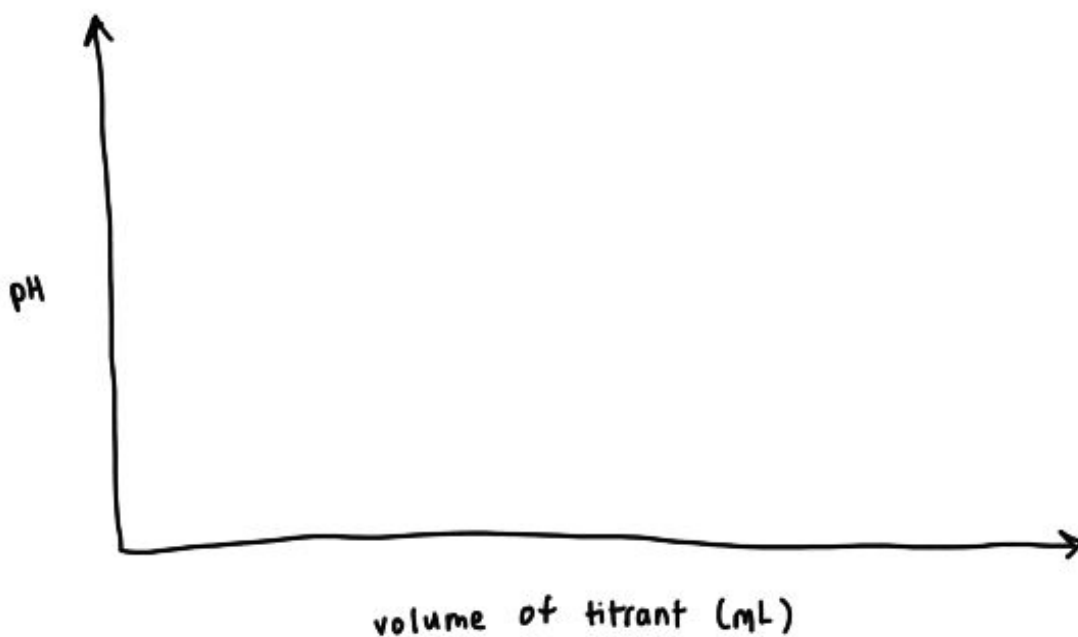
9. 4.00 moles of HI are placed in an empty 5.00 L flask to decompose. At a certain temperature, $K_{eq} = 1.6 \times 10^{-4}$. The system is allowed to reach equilibrium. What will be the equilibrium concentration of each species?

10. At a certain time, 2.00 moles of ammonia are present in an open 2.00L container. Which of the following predictions are correct?
    a. The system will reach equilibrium, producing nitrogen gas and hydrogen gas.
    b. The system will not reach equilibrium because energy has not been added.
    c. Equilibrium will not be reached because the system lacks the setting for an equilibrium reaction to occur.

11. In one container, there are 50.0mL of 2.00mol/L hydrochloric acid. In another container, there are 50.0mL of 2.00mol/L sulfuric acid. A pH probe is placed into both containers. Which of the following conclusions are correct?
    a. The pH of hydrochloric acid will be higher than the sulfuric acid.
    b. Both solutions will have the same pH.
    c. The pH of sulfuric acid will be higher than the hydrochloric acid.

12. Provide a definition for a Brønsted-Lowry acid. What makes a strong Brønsted-Lowry acid?

13. Write the equation for the reactions that will occur when the following substances are combined, and identify the strongest Brønsted-Lowry acids and bases in each:
   a. $NH4Cl_{(aq)}$ $NaOH_{(aq)}$
   b. $HCl_{(aq)}$ $NH_4^+{}_{(aq)}$
   c. $NaC_6H_5COO_{(aq)}$ $HSO_4^-{}_{(aq)}$
   d. $NaHCO_{3\ (aq)}$ $HCl_{(aq)}$
14. What is the pOH of a 1.50 mol/L $C_3H_5O(COOH)_{3\ (aq)}$ solution?
15. Calculate the pH of a 0.30 mol/L solution of $(NH_4)_2CO_{3\ (aq)}$.
16. Predict whether a reaction will occur when $HOCl_{(aq)}$ is mixed with $KNO_{2\ (aq)}^-$.
17. What is the approximate pH of a solution that is yellow in orange IV, yellow in methyl orange, and red in methyl red?
18. On Earth, the oceans serve an important purpose in the carbon cycle as carbon sinks that absorb and store carbon dioxide.
   a. Predict the reaction that occurs when 0.0040 mol of $CO_{2(g)}$ are added to 8.0L of water.
   b. Calculate the concentration of hydronium ions in the water as well as the pH of the solution.
   c. If bromothymol blue indicator was added to the water before the reaction took place, what colour would the solution turn after the $CO_{2(g)}$ was added?
19. What is the concentration of a calcium hydroxide solution, $Ca(OH)_2$, if 30.00mL of the base is completely neutralized by 10.0mL of 0.0200 mol/L HCl?

Answer Key

1. $K_c = \dfrac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3}$; $K_c = \dfrac{[Ca^{2+}_{(aq)}][HCO^{-}_{3\,(aq)}]^2}{[CO_{2(g)}]}$

2. The part where it first becomes flat (before point A) (this indicates that product and reactant concentrations have stabilized in an equilibrium state)

3. Increased concentration of products

4. Exothermic

5. Increased gas production (more bubbling), increased precipitation (solution becomes more cloudy)

6. 3.98×10^{-8} mol/L

7. 3.57×10^{-6}

8. Hint: $PO_4^{3-}{}_{(aq)}$ and $SO_4^{2-}{}_{(aq)}$ are examples of polyprotic bases.

9. $[HI_{(g)}] = 0.777$ mol/L, $[H_{2(g)}] = [I_{2(g)}] = 0.0113$ mol/L

10. C. Remember that for equilibrium reactions to take place, the reaction must proceed in a closed system. An open container is not a closed system and therefore reactants/products will escape.

11. A. Sulfuric acid is a polyprotic acid whereas hydrochloric acid is a monoprotic acid. Polyprotic acids generally have lower pH than monoprotic acids because they react with water twice (compared to only once for monoprotic) to form hydronium ions.

12. A Brønsted-Lowry acid is a substance (can be in gaseous or aqueous form) that donates or gives away protons (H^+) in a chemical reaction. Strong Brønsted-Lowry acids are substances which deprotonate **very easily** (i.e. they really don't want to hold onto their proton).

13. a) NH4+(aq) + OH-(aq) ⇌ NH3(aq) + H2O(l)
    b) H3O+(aq) + H2O(l) ⇌ H2O(l) + H3O+(aq)
    c) HSO4-(aq) + C6H5COO-(aq) ⇌ SO42-(aq) + C6H5COOH(s)
    d) H3O+(aq) + HCO3-(aq) ⇌ H2O(l) + H2CO3(aq)

14. Slightly more than 12.523 (note: sig dig is after decimal point)

15. Slightly more than 11.90

16. No reaction (SB, $NO_2^-{}_{(aq)}$, is above the SA, $HOCl_{(aq)}$ in the data table). Reactants are favoured.

17. pH between 4.4 and 4.8

18. a) H2CO3(aq) + H2O(l) ⇌ H3O+(aq) + HCO3-(aq)
    b) [H3O+(aq)] = 3.0×10^{-5} mol/L, pH = 4.52. Watch for sig digs!
    c) yellow

19. 3.33×10^{-3} mol/L