

2.1 Chemical equilibria

- 2.1.1 dynamical model of chemical equilibria
- 2.1.2 chemical equilibria expressed in terms of relative concentrations

Chemical equilibrium

- 2.1.3 chemical equilibria expressed in terms of partial pressures
- 2.1.4 the relationship between equilibrium constants for ideal gases expressed in different ways (concentration, pressure, mole fraction)
- 2.1.5 relation of equilibrium constant and standard Gibbs energy

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Professor Dr. Md. Abdul Jabbar

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2.2.14 definition of ionic strength
2.2.15 Debye-Hückel formula

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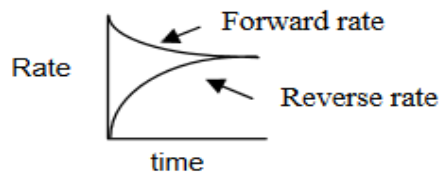
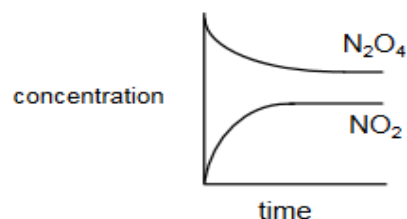
Chemical equilibrium

Many chemical reactions do not go to completion but instead attain a state of chemical equilibrium.

Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal and the concentrations of the reactants and products remain constant.

⇒ Equilibrium is a dynamic process – the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

For the reaction: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$



The Equilibrium Constant

For a reaction: $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

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

The **equilibrium constant**, K_c , is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

Example. Write the equilibrium constant, K_c , for $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Law of mass action - The value of the equilibrium constant expression, K_c , is constant for a given reaction at equilibrium and at a constant temperature.

⇒ The equilibrium concentrations of reactants and products may vary, but the value for K_c remains the same.

The relationship between chemical kinetics and chemical equilibrium

For the reaction $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Rate of forward reaction = Rate of reverse reaction

$$k_f[\text{N}_2\text{O}_4] = k_r[\text{NO}_2]^2$$

Rearrange:
$$\frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{k_f}{k_r} = K_c$$

Thus, the equilibrium constant is simply the ratio of the forward and reverse rate constants which are both constant values at a given temperature.

14.4 WHAT DOES THE EQUILIBRIUM CONSTANT TELL US?

Predicting the Direction of Reaction

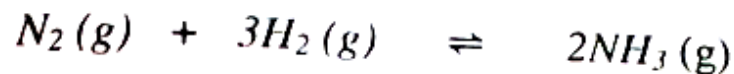
The **reaction quotient**, **Q**, is the resulting value when we substitute reactant and product concentrations into the equilibrium expression.

1. If $Q > K$, the reaction will go to the left.
 - The ratio of products over reactants is too large & the reaction will move toward equilibrium by forming more reactants.
2. If $Q < K$, the reaction will go to the right.
 - The ratio of products over reactants is too small & the reaction will move toward equilibrium by forming more products.
3. If $Q = K$, the reaction mixture is already at equilibrium, so no shift occurs.

Example. For the reaction, $\text{B} \rightleftharpoons 2\text{A}$, $K_c = 2$. Suppose 3.0 moles of A and 3.0 moles of B are introduced into a 2.00 L flask. (a) In which direction will the reaction proceed to attain equilibrium? (b) Will the concentration of B increase, decrease or remain the same as the system moves towards equilibrium?

Chemical equilibrium

Example : In the reaction between N_2 and H_2 to form NH_3 according to the equation :



K_c has a value of $6.0 \times 10^{-2} (\text{mol L}^{-1})^{-2}$ at 450°C . If, in a particular reaction vessel at this temperature, 0.250 mol L^{-1} of H_2 and 0.050 mol L^{-1} of NH_3 are present at equilibrium, what is the concentration of N_2 ?

Solution: The expression for the equilibrium constant K_c is

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = 6.02 \times 10^{-2}$$

We have at equilibrium $[H_2] = 0.250 \text{ mol L}^{-1}$

$$[NH_3] = 0.050 \text{ mol L}^{-1}$$

Substitution in the expression for K_c gives : $\frac{(0.050)^2}{[N_2](0.250)^3} = 6.02 \times 10^{-2}$

$$\begin{aligned} \text{from which we get } [N_2] &= \frac{(0.050)^2}{(0.250)^3 (6.02 \times 10^{-2})} \\ &= 2.66 \text{ mol L}^{-1} \end{aligned}$$

The equilibrium concentration of N_2 is 2.66 mol L^{-1}

Chemical equilibrium

Relation between K_p and K_c

A relation between K_p and K_c can be easily deduced for ideal gases so that if K_p is known K_c may be evaluated and *vice versa*. For n moles of a gas in a mixture of volume V L and temperature T , the partial pressure (in atmosphere) is $p = \frac{n}{V}RT$; but $\frac{n}{V}$ is equal to c mol L^{-1} , so that $p = cRT$. Substituting this value of p for each species at equilibrium in equation one obtains

$$aA + bB \rightleftharpoons lL + mM$$

$$K_p = \frac{([L]RT)^l \times ([M]RT)^m}{([A]RT)^a \times ([B]RT)^b}$$

$$K_p = \frac{[L]^l [M]^m \times (RT)^{l+m}}{[A]^a [B]^b \times (RT)^{a+b}}$$

$$= K_c (RT)^{(l+m) - (a+b)}$$

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

where Δn = difference in the number of moles of the product gases and the number of moles of the reactant gases in the equilibrium mixture. When there is no difference in the number of moles of the gas during the reaction, i.e., $\Delta n = 0$, $K_p = K_c$.

Determination of equilibrium constant

Determination of the Equilibrium constant of the reaction,

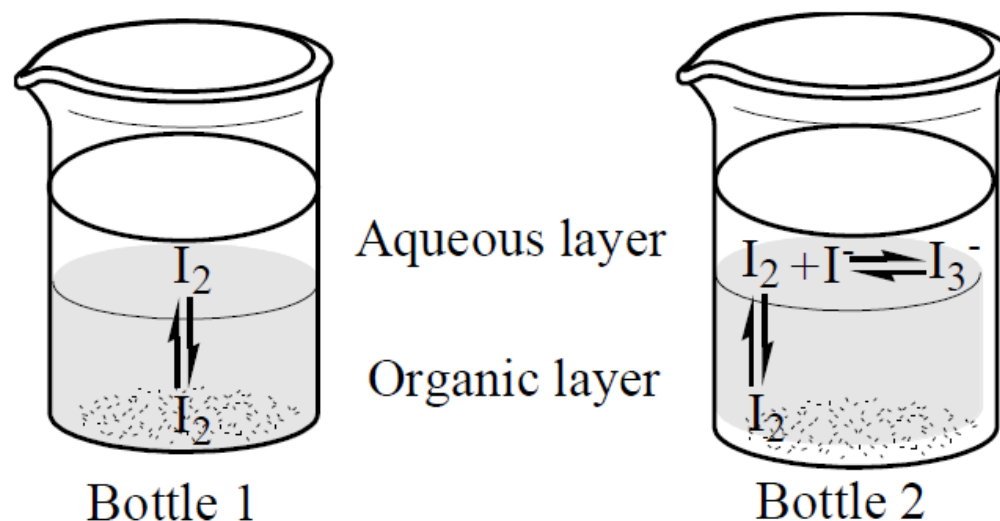
$\text{I}_2(\text{aq}) + \text{I}^-(\text{aq}) \rightleftharpoons \text{I}_3^-(\text{aq})$ by determining the partition co-efficient (K_d) for the distribution of I_2 between an aqueous layer and an organic layer

Principle

The equilibrium constant of a reaction of the above reaction is defined as

$$K = [\text{I}_3^-]/[\text{I}_2][\text{I}^-] \quad (1)$$

It can be determined by mixing reactants in an aqueous medium, which is in contact with an organic medium immiscible with water. The reaction is allowed to come to equilibrium.



Distribution equilibria of I_2 in organic and aqueous solvents

Determination of equilibrium constant

Titration of an aliquot portion from the aqueous phase gives C_1 the total concentration of I_2 .

$$C_1 = C_2 + C_3 \quad (2)$$

Where C_2 and C_3 are concentration of free I_2 and I_3^- .

Titration of an aliquot from the organic layer gives C_4 the concentration of I_2 in this layer. If K_d is the partition coefficient of I_2 between the organic layer and water, then

$$C_2 = C_4/K_d \quad (3)$$

Putting this value of C_2 in equation (2), the value of C_3 can be obtained.

If the initial concentration of the of I^- is C_0 , then the equilibrium concentration C_5 is given by

$$C_5 = C_0 - C_3$$

Equation (1) can be written as

$$K = C_3/C_2 \times C_5 \quad (4)$$

It may be noted that without the help of the organic layer it would not have been possible to determine the concentration of free iodine in the aqueous layer in presence of the I_3^- ion.

Nernst Distribution Law

STATEMENT OF NERNST'S DISTRIBUTION LAW

Nernst (1891) studied the distribution of several solutes between different appropriate pairs of solvents. He gave a generalization which governs the distribution of a solute between two non-miscible solvents. This is called **Nernst's Distribution law** (or *Nernst's Partition law*) or simply *Distribution law* or *Partition law*.

If a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

$$\frac{\text{Concentration of } X \text{ in } A}{\text{Concentration of } X \text{ in } B} = K_D$$

If C_1 denotes the concentration of the solute in solvent A and C_2 the concentration in solvent B , Nernst's Distribution law can be expressed as

$$\frac{C_1}{C_2} = K_D$$

The constant K_D (or simply K) is called the **Distribution coefficient** or **Partition coefficient** or **Distribution ratio**.

SOLVED PROBLEM 1. A solid X is added to a mixture of benzene and water. After shaking well and allowing to stand, 10 ml of the benzene layer was found to contain 0.13 g of X and 100 ml of water layer contained 0.22 g of X . Calculate the value of distribution coefficient.

SOLUTION

$$\text{Concentration of } X \text{ in benzene } (C_b) = \frac{0.13}{10} = 0.013 \text{ g ml}^{-1}$$

$$\text{Concentration of } X \text{ in water } (C_w) = \frac{0.22}{100} = 0.002 \text{ g ml}^{-1}$$

According to Distribution law :

$$\frac{C_b}{C_w} = \frac{0.013}{0.0022} = 5.9$$

Nernst Distribution Law

Condition for the validity of the law:

1. Constant temperature: The temperature is kept constant throughout the experiment.
2. Same molecular state: The molecular state of the solute is the same in the two solvents. The law does not hold if there is association or dissociation of the solute in one of the solvents.
3. Equilibrium concentrations: The concentrations of the solute are noted after the equilibrium has been established.
4. Dilute solutions: The concentration of the solute in the two solvents is low. The law does not hold when the concentrations are high.
5. Non-miscibility of solvents. The two solvents are non-miscible or only slightly soluble in each other. The extent of mutual solubility of the solvents remains unaltered by the addition of solute to them.

Applications:

- 1) Solvent extraction (Duel and multiple extraction)
- 2) Partition chromatography (Liquid-liquid and column chromatography)
- 3) Desilverization of lead
- 4) Detection of halides
- 5) Determination of solubility
- 6) Determination of association and dissociation of solutes in solvents
- 7) Deducing the formula of a complex ion
- 8) Distribution indicator in iodometric titration

Le Chatelier's Principle

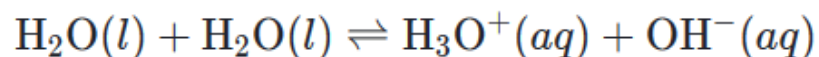
Le Chatelier's Principle is the principle when a stress is applied to a chemical system at equilibrium, the equilibrium will shift to relieve the stress. In other words, it can be used to predict the direction of a chemical reaction in response to a change in conditions of temperature, concentration, volume or pressure. While Le Chatelier's principle can be used to predict the response to a change in equilibrium, it does not explain (at a molecular level), *why* the system responds as it does.

LE CHATELIER'S PRINCIPLE		
STRESS	SHIFT	WHY?
increase concentration of a substance	away from substance	extra concentration needs to be used up
decrease concentration of a substance	towards substance	need to produce more of substance to make up for what was removed
increase pressure of system	towards <i>fewer</i> moles of gas	<u>for gas</u> : pressure increase = volume decrease
decrease pressure of system	towards <i>more</i> moles of gas	<u>for gas</u> : pressure decrease = volume increase
increase temperature of system	away from heat/ energy <i>exothermic</i> reaction is favored	extra heat/ energy must be used up
decrease temperature of system	towards heat/ energy <i>exothermic</i> reaction is favored	more heat/ energy needs to be produced to make up for the loss
add a catalyst	NO SHIFT	The rates of both the forward and reverse reactions are increased by the same amount.

Auto-ionization of water

Since acids and bases react with each other, this implies that water can react with itself! While that might sound strange, it does happen—water molecules exchange protons with one another to a very small extent. We call this process the *autoionization*, or self-ionization, of water.

The proton exchange can be written as the following balanced equation:



- In a **neutral** solution, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$
- In an **acidic** solution, $[\text{H}_3\text{O}^+] > [\text{OH}^-]$
- In a **basic** solution, $[\text{OH}^-] > [\text{H}_3\text{O}^+]$
- For aqueous solutions at 25°C , the following relationships are always true:

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14}$$

$$\text{pH} + \text{pOH} = 14$$

- The contribution of the autoionization of water to $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ becomes significant for extremely dilute acid and base solutions.

Acid-base equilibria

- For a generic monoprotic weak acid HA with conjugate base A⁻, the equilibrium constant has the form:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$



$$K = [H_3O^+][A^-]/[HA][H_2O]$$

$$K_a = K[H_2O]$$

- The **acid dissociation constant** K_a quantifies the extent of dissociation of a weak acid. The larger the value of K_a , the stronger the acid, and vice versa.

- For a generic weak base B with conjugate acid BH⁺, the equilibrium constant has the form:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$



$$K = [BH^+][OH^-]/[B][H_2O]$$

$$K_b = K[H_2O]$$

- The **base dissociation constant** (or **base ionization constant**) K_b quantifies the extent of ionization of a weak base. The larger the value of K_b , the stronger the base, and vice versa.

Strong vs. weak acids and bases

Strong acids and strong bases refer to species that completely dissociate to form ions in solution. By contrast, *weak* acids and bases ionize only partially, and the ionization reaction is reversible. Thus, weak acid and base solutions contain multiple charged and uncharged species in dynamic equilibrium.

Acid-base equilibria

Example 1: Calculating % dissociation of a weak acid

One way to quantify how much a weak acid has dissociated in solution is to calculate the percent dissociation. The percent dissociation for weak acid HA can be calculated as follows:

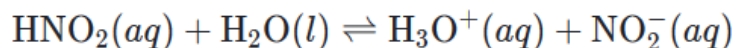
$$\% \text{ dissociation} = \frac{[A^{-}(aq)]}{[HA(aq)]} \times 100\%$$

If nitrous acid (HNO_2) has a K_a of 4.0×10^{-4} at 25°C , what is the percent dissociation of nitrous acid in a 0.400 M solution?

Let's go through this example step-by-step!

Step 1: Write the balanced acid dissociation reaction

First, let's write the balanced dissociation reaction of HNO_2 in water. Nitrous acid can donate a proton to water to form $\text{NO}_2^{-}(aq)$:



Step 2: Write the expression for K_a

From the equation in **Step 1**, we can write the K_a expression for nitrous acid:

$$K_a = \frac{[\text{H}_3\text{O}^{+}][\text{NO}_2^{-}]}{[\text{HNO}_2]} = 4.0 \times 10^{-4}$$

Acid-base equilibria

Step 3: Find $[\text{H}^+]$ and $[\text{NO}_2^-]$ at equilibrium

Next, we can use an ICE table to determine algebraic expressions for the equilibrium concentrations in our K_a expression:

	$\text{HNO}_2(aq)$	\rightleftharpoons	H_3O^+	NO_2^-
Initial	0.400 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.400 \text{ M} - x$		x	x

Plugging the equilibrium concentrations into our K_a expression, we get:

$$K_a = \frac{(x)(x)}{(0.400 \text{ M} - x)} = 4.0 \times 10^{-4}$$

Simplifying this expression, we get the following:

$$\frac{x^2}{0.400 \text{ M} - x} = 4.0 \times 10^{-4}$$

This is a quadratic equation that can be solved for x either by using the quadratic formula or an approximation method.

Either method will give $x = 0.0126 \text{ M}$. Therefore, $[\text{NO}_2^-] = [\text{H}_3\text{O}^+] = 0.0126 \text{ M}$.

Acid-base equilibria

Step 4: Calculate percent dissociation

To calculate percent dissociation, we can use the equilibrium concentrations we found in **Step 3**:

$$\begin{aligned}\% \text{ dissociation} &= \frac{[\text{NO}_2^-]}{[\text{HNO}_2]} \\ &= \frac{0.0126 \text{ M}}{0.400 \text{ M}} \times 100\% \\ &= 3.2\%\end{aligned}$$

Therefore, 3.2% of the HNO_2 in solution has dissociated into H^+ and NO_2^- ions.

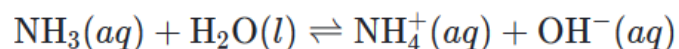
Example 2: Calculating the pH of a weak base solution

What is the pH of a 1.50 M solution of ammonia, NH_3 ? ($K_b = 1.8 \times 10^{-5}$)

This example is an equilibrium problem with one extra step: finding pH from $[\text{OH}^-]$. Let's go through the calculation step-by-step.

Step 1: Write the balanced ionization reaction

First, let's write out the base ionization reaction for ammonia. Ammonia will accept a proton from water to form ammonium, NH_4^+ :



Step 2: Write the expression for K_b

From this balanced equation, we can write an expression for K_b :

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

Step 3: Find $[\text{NH}_4^+]$ and $[\text{OH}^-]$ at equilibrium

To determine the equilibrium concentrations, we use an ICE table:

	$\text{NH}_3(aq)$	\rightleftharpoons	NH_4^+	OH^-
Initial	1.50 M		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$1.50 \text{ M} - x$		x	x

pH of weak base solution

$$K_b = \frac{(x)(x)}{1.50 \text{ M} - x} = 1.8 \times 10^{-5}$$

Simplifying, we get:

$$\frac{x^2}{1.50 \text{ M} - x} = 1.8 \times 10^{-5}$$

This is a quadratic equation that can be solved by using the quadratic formula or an approximation method. Either method will yield the solution

$$x = [\text{OH}^-] = 5.2 \times 10^{-3} \text{ M}$$

Step 4: Find pH from $[\text{OH}^-]$

Now that we know the concentration of hydroxide, we can calculate pOH:

$$\text{pOH} = -\log[\text{OH}^-]$$

$$= -\log(5.2 \times 10^{-3})$$

$$= 2.28$$

Recall that at 25 °C, $\text{pH} + \text{pOH} = 14$. Rearranging this equation, we have:

$$\text{pH} = 14 - \text{pOH}$$

Plugging in our value for pOH, we get:

$$\text{pH} = 14.00 - (2.28) = 11.72$$

pH of weak base solution

Henderson-Hasselbalch equation (Basis of preparation of buffer solution)



This equation is a mathematical re-arrangement of the acid dissociation constant equation

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad \text{Re-arrange for } [H^+], \quad [H^+] = \frac{K_a[HA]}{[A^-]}$$

Taking logarithms of both sides of the equation:

$$\log[H^+] = \log\left(\frac{K_a[HA]}{[A^-]}\right) = \log K_a + \log\left(\frac{[HA]}{[A^-]}\right)$$

Multiplying both sides by -1, and recognizing $pH = -\log[H^+]$ and $pK_a = -\log K_a$

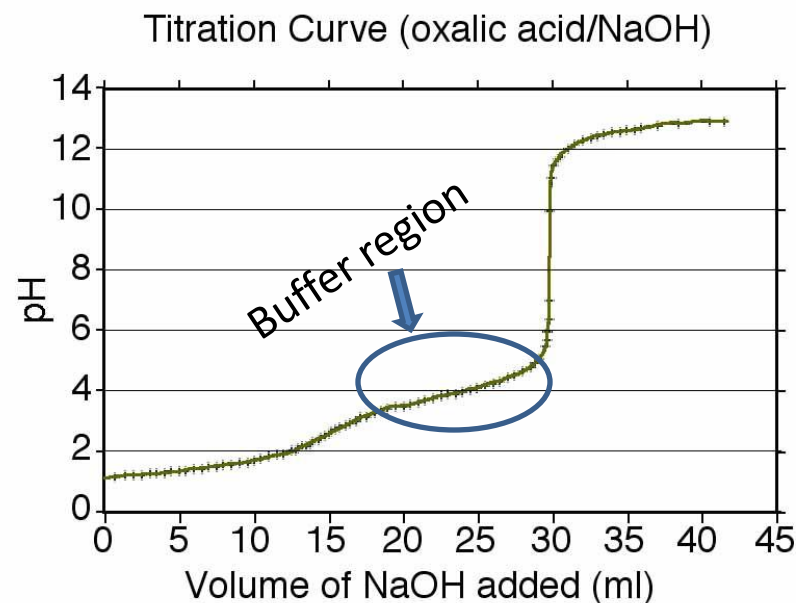
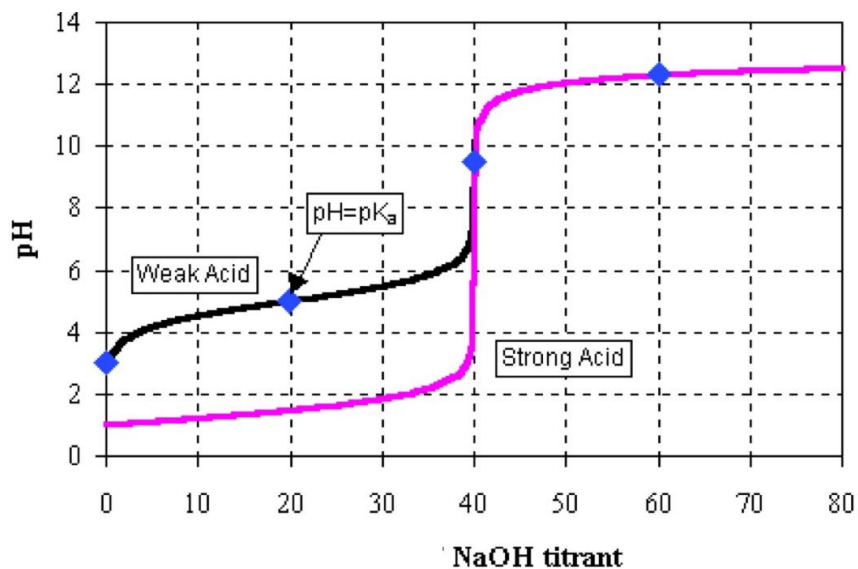
$$pH = pK_a - \log\left(\frac{[HA]}{[A^-]}\right) = pK_a - \left(-\log\left(\frac{[A^-]}{[HA]}\right)\right)$$

$$pH = pK_a + \log\frac{[A^-]}{[HA]}$$

Buffer solution and buffer region

The most important application of acid–base solutions containing a common ion is for buffering. A **buffered solution** is one that *resists a change in its pH* when either hydroxide ions or protons are added. The most important practical example of a buffered solution is our blood, which can absorb the acids and bases produced in biologic reactions without changing its pH. A constant pH for blood is vital because cells can survive only in a very narrow pH range.

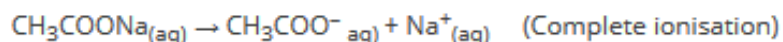
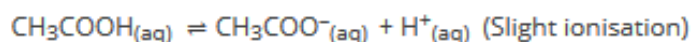
A buffered solution may contain a *weak acid* and its salt (for example, HF and NaF) or a *weak base* and its salt (for example, NH_3 and NH_4Cl). By choosing the appropriate components, a solution can be buffered at virtually any pH.



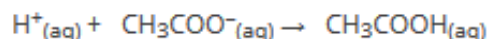
Buffer action in acidic buffer

The property of the solution to resist the changes in its pH value on the addition of small amounts of strong acid or base is known as buffer action.

Consider an acidic buffer, a mixture of acetic acid (CH_3COOH) and sodium acetate (CH_3COONa). In an aqueous medium, CH_3COOH and CH_3COONa dissociates as,

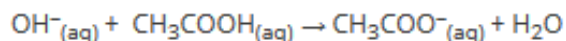
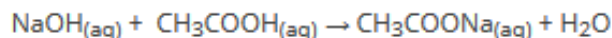


If a strong acid like HCl is added to the buffer solution, the additional H^{+} ions combine with the acetate ions in the solution to produce undissociated CH_3COOH .



Since additional H^{+} ions of acid are consumed (neutralized), the pH of the solution remains unchanged. This resistance to change in pH on the addition of a strong base is called as reserve basicity and is due to $\text{CH}_3\text{COO}^{-}$ ions.

If strong base like NaOH is added to the buffer solution, additional OH^{-} ions combine with CH_3COOH as

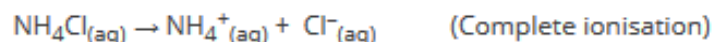
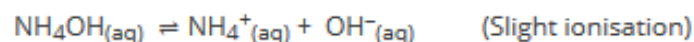


Since additional OH^{-} ions of the base are consumed or neutralized, the pH of the solution remains unchanged. This resistance to change in pH on the addition of base is called reserve acidity and is due to CH_3COOH .

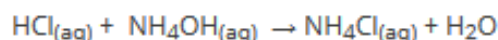
Buffer action in basic buffer

The property of the solution to resist the changes in its pH value on the addition of small amounts of strong acid or base is known as buffer action.

Consider a basic buffer, the mixture of Ammonium hydroxide (NH_4OH) and Ammonium chloride (NH_4Cl) In an aqueous medium NH_4OH and NH_4Cl dissociates as

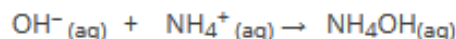


If a strong acid like HCl is added to the buffer solution, additional H^+ ions of acid combine with NH_4OH , to produce ammonium ions and water.



Since additional H^+ ions of acid are consumed (neutralized), the pH of the solution remains unchanged. This resistance to the change in pH upon the addition of strong acid is called reserve basicity and is due to NH_4OH molecules.

If a strong base like NaOH is added to the buffer solution, additional OH^- ions of the base combine with NH_4^+ ions to produce undissociated NH_4OH molecules.

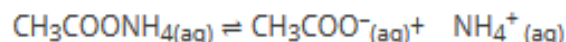


Since additional OH^- ions of the base are consumed (neutralized) pH of the solution remains unchanged. This resistance to change in pH on addition base is called as reserve acidity and is due to NH_4^+ ions in a solution.

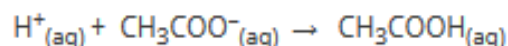
Buffer action in single salt solution

The property of the solution to resist the changes in its pH value on the addition of small amounts of strong acid or base is known as buffer action.

Consider a single salt buffer solution of ammonium acetate ($\text{CH}_3\text{COONH}_4$). In an aqueous medium $\text{CH}_3\text{COONH}_4$ dissociates as,

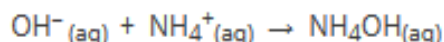


If a strong acid like HCl is added to the buffer solution, additional H^+ ions of acid combine with CH_3COO^- , to produce practically undissociated CH_3COOH



Since additional H^+ ions of acid are consumed (neutralized), the pH of the solution remains unchanged. This resistance to the change in pH upon the addition of strong acid is called reserve basicity and is due to CH_3COO^- ions.

If a strong base like NaOH is added to the buffer solution, additional OH^- ions of base combine with NH_4^+ ions to produce practically undissociated NH_4OH molecules.



Since additional OH^- ions of the base are consumed (neutralized) pH of the solution remains unchanged. This resistance to change in pH upon addition base is called as reserve acidity and is due to NH_4^+ ions in a solution.

Buffering capacity

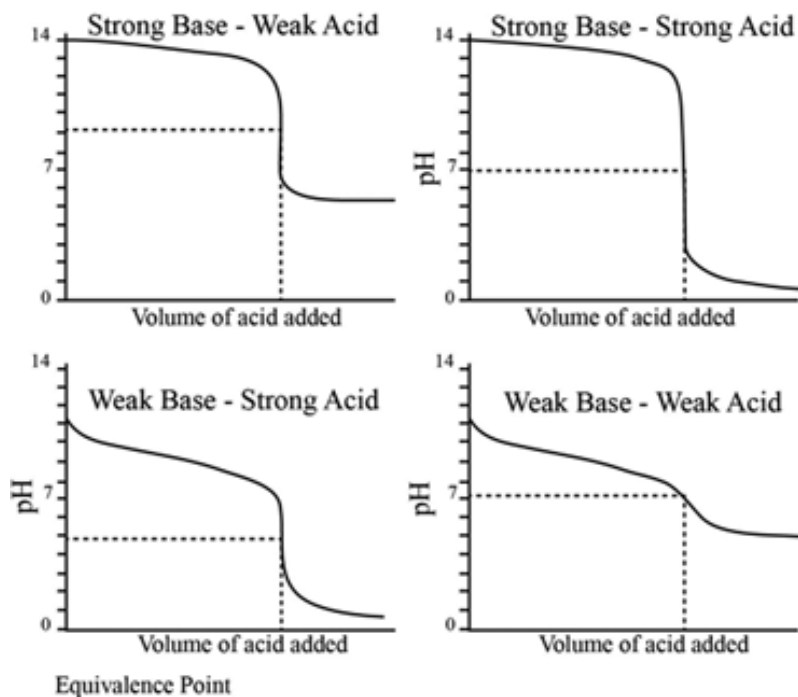
Buffering capacity refers to the amount of added acid or added base that can be neutralized by a buffer. It is determined by the concentrations of the conjugate acid and conjugate base. Buffering capacity increases as these concentrations increase.

Example of buffer solution

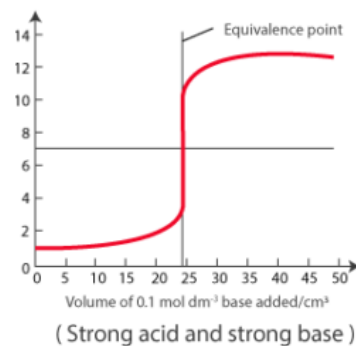
- Buffers are often prepared by mixing a **weak acid** or a **weak base**, with a **salt** of that acid or base.
- CH_3COOH and CH_3COO^- (acidic buffer)
(Weak Acid) Salt such as CH_3COONa
- NH_3 and NH_4^+ (basic buffer)
Salt such as NH_4Cl

Acid or Base	Salt
Acetic acid	Sodium acetate
Phosphoric acid	Potassium phosphate
Oxalic acid	Lithium oxalate
Carbonic acid	Sodium carbonate
Ammonium hydroxide	Ammonium nitrate

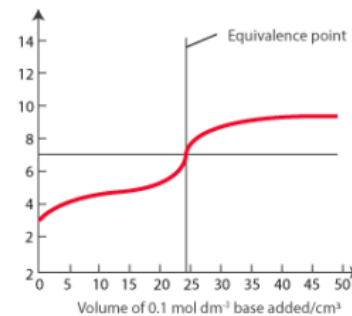
pH-titration curves



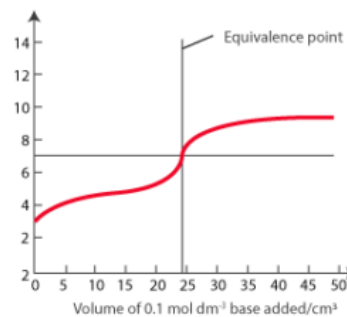
Titration of base with acid



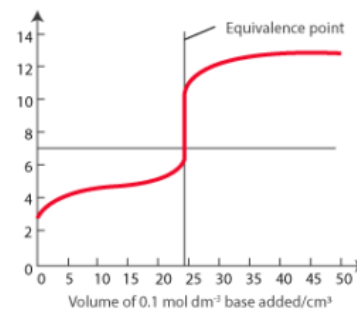
(Strong acid and strong base)



(Strong acid and weak base)



(Weak acid and weak base)



(Weak acid and strong base)

Titration of acid with base

Home work: Practice of conductance titration curves