# Introduction to Chemical Equilibrium

## Dynamic Equilibrium

> Chemical equilibrium is a **dynamic state** where the rate of the forward reaction equals the rate of the reverse reaction. At the molecular level, reactions are continuously occurring in both directions.

At equilibrium, **macroscopic properties** like concentration, temperature, and pressure remain constant.

## The Equilibrium Constant (K_{eq})

For a general reversible reaction:

$$aA + bB \rightleftharpoons cC + dD$$

The equilibrium constant expression is:

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

Equilibrium makes sense when we have (g) & (aq) states of matter.

- Square brackets indicate **molar concentrations** (mol/L) for aqueous solutions and gases.
- **Pure solids and liquids** are excluded from the (K_{eq}) expression because their concentrations remain constant.

## Significance of (K_{eq})

- $K_{eq} > 1$: Products are favored at equilibrium.
- $K_{eq} < 1$: Reactants are favored at equilibrium.
- $K_{eq} \approx 1$: Neither reactants nor products are significantly favored.

# Le Chatelier's Principle

> Le Chatelier's Principle states that if a **stress** (change in condition) is applied to a system at equilibrium, the system will shift in a direction that relieves the stress.

## Types of Stresses and Their Effects

### Change in Concentration

- Adding Reactant: Equilibrium shifts right (towards products). →
- Adding Product: Equilibrium shifts left (towards reactants). ←
- Removing Reactant: Equilibrium shifts left (towards reactants). ←
- Removing Product: Equilibrium shifts right (towards products). →

### Change in Temperature

| | | |
|---|---|---|
| Endo | heat ↑ → | heat ↓ ← |
| Exo | heat ↑ ← | heat ↓ → |

- Endothermic Reactions (absorb heat):
  - Increasing temperature: shifts equilibrium to the right (towards products).
  - Decreasing temperature: shifts equilibrium to the left (towards reactants).
- Exothermic Reactions (release heat):
  - Increasing temperature: shifts equilibrium to the left (towards reactants).
  - Decreasing temperature: shifts equilibrium to the right (towards products).

For the reaction:

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + heat$$

Adding $CaCO_{3(s)}$ has no effect on the equilibrium.

because $CaCO_{3(s)}$ is solid and is not even mentioned in $K_{eq}$ formula.

### Change in Pressure (for gaseous systems only)

- Increasing Pressure: Equilibrium shifts to the side with fewer moles of gas.
- Decreasing Pressure: Equilibrium shifts to the side with more moles of gas.

### Adding a Catalyst

A catalyst speeds up both forward and reverse reaction rates equally, helping the system reach equilibrium faster without changing the equilibrium position or the (K_{eq}) value.

# Acid-Base Systems

# Definitions of Acids and Bases

## Arrhenius Definition

- Acid: Produces $H^+$ ions (or $H_3O^+$ in water).
- Base: Produces $OH^-$ ions in aqueous solution.

## Brønsted-Lowry Definition

- Acid: A proton ($H^+$) donor.
- Base: A proton ($H^+$) acceptor.

## Conjugate Acid-Base Pairs

An acid, after donating a proton, forms its **conjugate base**. A base, after accepting a proton, forms its **conjugate acid**.

In the reaction:

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

- $HCl$ is the acid, and $Cl^-$ is its conjugate base.
- $H_2O$ is the base, and $H_3O^+$ is its conjugate acid.

# Strong vs. Weak Acids and Bases

## Strong Acids/Bases

- Ionize/dissociate **completely** (100%) in water.
- Reactions are essentially **irreversible**.

**Examples:**

- Strong Acids: $HCl$, $HBr$, $HI$, $HNO_3$, $H_2SO_4$, $HClO_4$
- Strong Bases: Group 1 hydroxides (e.g., $NaOH$, $KOH$), some Group 2 hydroxides (e.g., $Ca(OH)_2$, $Ba(OH)_2$)

## Weak Acids/Bases

- Ionize/dissociate partially in water, establishing an equilibrium.

In a 1.00 mol/L $CH_3COOH_{(aq)}$ solution, the highest concentration species is $CH_3COOH_{(aq)}$ because it's a weak acid and only partially ionizes.

## Acid Dissociation Constant ((K_a))

For a weak acid: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

[redacted]

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

acid

A smaller $K_a$ indicates a weaker acid.

## Base Dissociation Constant ((K_b))

For a weak base: $B + H_2O \rightleftharpoons BH^+ + OH^-$

[redacted]

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

base

A smaller $K_b$ indicates a weaker base.

## Relationship between (K_a) and (K_b) for a conjugate pair:

$K_a \times K_b = K_w = 1.0 \times 10^{-14}$ at $25°C$.

## pH and pOH Scales

## Ion Product of Water ((K_w))

In pure water: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

[redacted]

$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C$

## pH Calculation

$pH = -\log[H_3O^+]$

## pOH Calculation

$pOH = -\log[OH^-]$

## Relationship between pH and pOH

$pH + pOH = 14.00 \text{ at } 25^\circ C$

If the pH of rainwater is 4.50, then the pOH is $14.00 - 4.50 = 9.50$.

## Acidity/Basicity Based on pH

- pH < 7: Acidic
- pH = 7: Neutral
- pH > 7: Basic

# Acid-Base Calculations (ICE Tables)

## Purpose

Used to determine equilibrium concentrations, pH, or (K_a/K_b) for weak acid/base solutions.

## Steps

1. Write the balanced equilibrium equation.
2. Set up an ICE (Initial, Change, Equilibrium) table with concentrations.
3. Define 'x' as the change in concentration.
4. Substitute equilibrium concentrations into the (K_a) or (K_b) expression.
5. Solve for 'x'.
6. Calculate the desired quantity (e.g., pH, (K_a)).

For a 0.25 mol/L solution of an unknown acid with a pH of 4.20:

- $[H_3O^+] = 10^{-pH} = 10^{-4.20} = 6.31 \times 10^{-5}\ \mathrm{mol/L}$
- For a weak monoprotic acid HA: $HA \rightleftharpoons H^+ + A^-$

| | HA | H+ | A- |
|---|---|---|---|
| Initial | 0.25 | ≈ 0 | ≈ 0 |
| Change | -x | +x | +x |
| Equilibrium | 0.25 - x | x | x |

- Since $x = [H_3O^+] = 6.31 \times 10^{-5}\ \mathrm{mol/L}$ and $x$ is very small compared to 0.25 mol/L, approximate $[HA]_{eq} \approx 0.25\ \mathrm{mol/L}$.
- $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{0.25} = \frac{(6.31\times10^{-5})^2}{0.25} = \frac{3.98\times10^{-9}}{0.25} = 1.59 \times 10^{-8}$

## pH of Salt Solutions (Hydrolysis)

- Salts of Strong Acid + Strong Base: Neutral solutions (e.g., $NaCl$).
- Salts of Strong Acid + Weak Base: Acidic solutions (e.g., $NH_4Cl$).
- Salts of Weak Acid + Strong Base: Basic solutions (e.g., $CH_3COONa$).
- Salts of Weak Acid + Weak Base: pH depends on the relative strengths of the cation and anion hydrolysis.

A 0.45 M solution of $NH_4Cl_{(aq)}$ would be acidic because $NH_4^+$ hydrolyzes:

$NH_4^+_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_3_{(aq)} + H_3O^+_{(aq)}$

# Titrations

Titration is a quantitative analytical method used to determine the unknown concentration of a solution (analyte) by reacting it with a solution of known concentration (titrant).

## Equivalence Point

The point in a titration where the moles of acid exactly equal the moles of base.

## Titration Curve

A graph of pH versus the volume of titrant added. The steepest part indicates the equivalence point.

If a graph shows an initial high pH and then a sharp drop as $HCl$ is added, the aliquot is a monoprotic base and the titrant is a monoprotic acid.

## Indicators

Weak acids or bases that change color over a specific pH range, used to signal the end point of a titration (close to the equivalence point).

## Standardization

The process of accurately determining the concentration of a solution.

Example: Standardization of $NaOH$ using $KHP$ ($KHC_8H_4O_4$, molar mass = 204.22 g/mol)

- $KHP$ is a monoprotic acid: $KHC_8H_4O_4 + NaOH \rightarrow KNaC_8H_4O_4 + H_2O$
- Moles of $KHP$ = $\frac{\text{Mass}}{\text{Molar Mass}} = \frac{1.25 \text{ g}}{204.22 \text{ g/mol}} = 0.0061208 \text{ mol}$
- Moles of $NaOH$ = Moles of $KHP = 0.0061208 \text{ mol}$
- Volume of $NaOH = 11.20 \text{ mL} = 0.01120 \text{ L}$
- Concentration of $NaOH = \frac{\text{Moles}}{\text{Volume}} = \frac{0.0061208 \text{ mol}}{0.01120 \text{ L}} = 0.5465 \text{ mol/L} = 5.46 \times 10^{-1} \text{ mol/L}$

# Buffers

> A buffer solution is a mixture of a weak acid and its conjugate base (or a weak base and its conjugate acid) that resists significant changes in pH upon the addition of small amounts of acid or base.

## Mechanism

- When an acid is added, the **conjugate base** neutralizes it.
- When a base is added, the **weak acid** neutralizes it.

If soil pH hasn't changed much even with acid rain, the soil contains a **natural chemical buffer**.

# Exam Tips

- Understand concepts, don't just memorize.
- Practice problem-solving, especially with ICE tables and titration calculations.
- Review definitions ( $K_{eq}$, $K_a$, $K_b$, pH, pOH, conjugate pairs, etc.)
- Pay attention to units and significant figures.
- Read questions carefully.
- Use the data booklet.

# Acid-Base Chemistry Practice Questions

## Question 1: Ammonium Chloride pH

The question asks for the pH of a 0.45 M solution of ammonium chloride ($NH_4Cl$). To solve this, you'd need to recognize that $NH_4Cl$ is the salt of a weak base ($NH_3$) and a strong acid ($HCl$). This means it will form an acidic solution due to the hydrolysis of the ammonium ion ($NH_4^+$).

## Question 2: Acid Rain

This question discusses acid rain caused by nitrogen dioxide ($NO_2$) forming nitric acid ($HNO_3$). It notes that even with an average rain pH of 5.0 in a polluted area, plants aren't significantly affected, and asks for the best explanation.

The correct answer is that the **soil must contain a natural chemical buffer**. Here's why:

- **Buffers** resist changes in pH. If the soil has a buffering capacity, it can neutralize the acid rain and prevent drastic pH changes that would harm plants.

## Question 3: Calculating $K_a$

You have a 0.25 mol/L solution of an unknown acid with a pH of 4.20. You need to find the $K_a$ value in the form $b \times 10^{-x}$ and determine the value of 'b'.

Here's how to approach it:

1. **Calculate $[H^+]$:** Since $pH = -log[H^+]$, then $[H^+] = 10^{-pH} = 10^{-4.20}$.
2. **Set up the equilibrium expression:** For a weak acid $HA \rightleftharpoons H^+ + A^-$, the $K_a = \frac{[H^+][A^-]}{[HA]}$.
3. **Approximate:** Assume that the change in concentration of the acid is small, so $[HA] \approx 0.25$. Also, $[H^+] = [A^-]$
4. **Solve for $K_a$:** Substitute the values and solve for $K_a$. $K_a = \frac{(10^{-4.20})^2}{0.25}$ $K_a = \frac{10^{-8.4}}{0.25}$ $K_a = 4 \times 10^{-8.4} = 4 \times 10^{-0.4} \times 10^{-8}$ $K_a \approx 2.5 \times 10^{-9}$

## Question 4: Bicarbonate Ion $K_b$

The question asks for the $K_b$ value for the bicarbonate ion ($HCO_3^-$). To find this, you would typically use the relationship between $K_a$, $K_b$, and $K_w$:

$K_w = K_a \times K_b$

where $K_w = 1.0 \times 10^{-14}$ at 25°C. You would need to know the $K_a$ value for the conjugate acid, which is carbonic acid ($H_2CO_3$), to calculate $K_b$.

$K_b = \frac{K_w}{K_a}$

## Question 5: Titration Curve Analysis

The question provides a graph (presumably a titration curve) and asks you to interpret it. Here's what to look for:

- **Equivalence Point:** The steep vertical portion of the curve indicates the equivalence point, where the acid and base have completely neutralized each other.
- **pH at Equivalence Point:**
  - If the pH at the equivalence point is 7, it's a strong acid-strong base titration.
  - If the pH is below 7, it's a strong acid-weak base titration.
  - If the pH is above 7, it's a weak acid-strong base titration.
- **Shape of the Curve:** The shape can indicate whether a strong or weak acid/base is involved.
- **Titrant vs. Analyte (Aliquot):** The titrant is the solution in the burette, and the aliquot (or sample) is the solution being titrated.

## Question 6: Species Concentration in Acetic Acid Solution

In a 1.00 mol/L $CH_3COOH$ (acetic acid) solution, the question asks which species is present in the highest concentration.

- $H_3O^+$: Hydronium ions are present, but since acetic acid is a weak acid, it only partially dissociates.
- $CH_3COOH$: Acetic acid is a weak acid, so the majority of it remains in its undissociated form.
- $OH^-$: Hydroxide ions are present due to the autoionization of water, but their concentration is very low in an acidic solution.
- $CH_3COO^-$: Acetate ions are formed when acetic acid dissociates, but the concentration will be less than the undissociated acetic acid.

Therefore, the species with the highest concentration is $CH_3COOH$.

## Question 7: Equilibrium Shift with Calcium Carbonate

The equilibrium is: $CaO(s) + CO_2(g) \rightleftharpoons CaCO_3(s) + heat$

The question asks what happens if the mass of $CaCO_3(s)$ is doubled at constant temperature and pressure.

- The key here is that $CaCO_3$ is a **solid**. Solids and liquids do not affect the equilibrium position, so **no change will occur**.

## Question 8: Standardization of Sodium Hydroxide

In the standardization of a sodium hydroxide ($NaOH$) solution, 11.20 mL of $NaOH$ are required to neutralize 1.25 g of potassium hydrogen phthalate ($KHP$), $KHC_8H_4O_4$. You need to find the concentration of the $NaOH$ solution.

1. **Calculate moles of $KHP$:** Divide the mass of $KHP$ by its molar mass (204.22 g/mol). $moles\ of\ KHP = \frac{1.25\ g}{204.22\ g/mol} = 0.00612\ mol$
2. **Determine moles of $NaOH$:** Since $KHP$ is monoprotic, the moles of $NaOH$ will be equal to the moles of $KHP$ at the equivalence point. $moles\ of\ NaOH = 0.00612\ mol$
3. **Calculate the concentration of $NaOH$:** Divide the moles of $NaOH$ by the volume of $NaOH$ solution in liters. $[NaOH] = \frac{0.00612\ mol}{0.01120\ L} = 0.546\ mol/L$

## Question 9: Equilibrium Definition

The question asks for the best description of a chemical system in equilibrium.

- **Equilibrium** is a dynamic state where the rates of the forward and reverse reactions are equal. This means that the **macroscopic properties of the chemical remain unchanged**.

## Question 10: pH and pOH Calculation

If the pH of a rainwater sample is 4.50, you need to find the pOH.

Use the relationship: $pH + pOH = 14$

$pOH = 14 - pH = 14 - 4.50 = 9.50$

**Scholars Of Calgary Northwest**

**Chemistry 30, Unit 4: Chemical Equilibrium Focusing on Acid-Base Systems, 10 Questions**

Please wait until the exam has fully loaded in your web browser before starting. **Do not** press "Submit" at the end of the exam until you are sure of your responses, as your test will be graded immediately. Good luck!

1. A 0.45 M solution of $NH_4Cl_{(aq)}$ would have a pH of $NH_4Cl \rightarrow$

   ◯A) 0.45
   ◯B) 4.80
   ◯C) 9.20
   ◯D) 2.54

2. Automobiles produce pollution in the form of $NO_{2(g)}$. Nitrogen dioxide eventually forms $HNO_{3(aq)}$ when combined with water vapour. The presence of this chemical in the atmosphere may cause the pH of rain to decrease as low as 2.00 in some extreme cases.

   In a highly poluted area, the rain has an average pH of 5.0, but the pH of the soil has not changed very much. The best explanation as to why plants have not been affected by the acid rain is that the

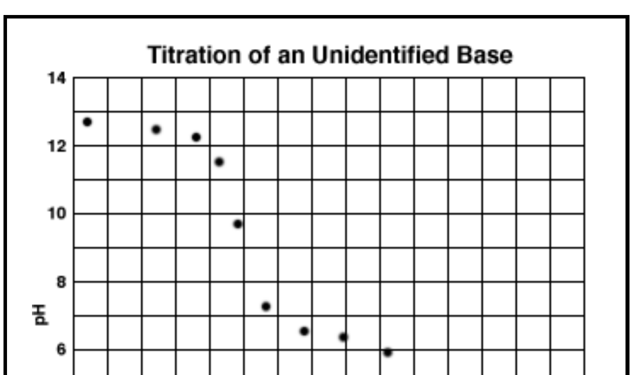
   ◯A) acid rain must be too diluted
   ◯B) acid rain must be made from a weak acid
   ◯C) plants are resistant to acid
   ◯D) soil must contain a natural chemical buffer

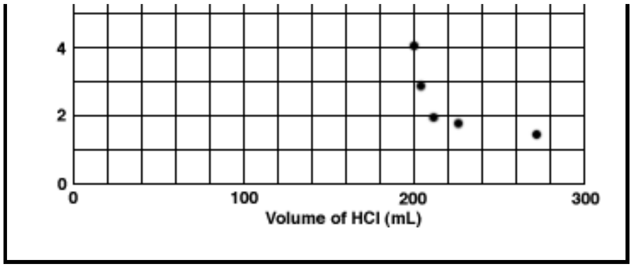
3. A 0.25 mol/L solution of an unknown acid was tested and it was found to have a pH of 4.20. When the $K_a$ is written in the form $\mathbf{b} \times 10^{\mathbf{w}}$, the value of **b** (to the nearest hundredth) is __________.

4. The $K_b$ value for bicarbonate ion is

   ◯A) $4.5 \times 10^{-7}$
   ◯B) $2.2 \times 10^{-8}$
   ◯C) $4.7 \times 10^{-11}$
   ◯D) $2.1 \times 10^{-4}$

5.






The graph shows the following information.

- A) The titrant is a monoprotic base.
- B) The titrant is a monoprotic acid.
- C) The aliquot (or sample) is a monoprotic acid
- D) The aliquot (or sample) is a monoprotic base

6. In a 1.00 mol/L $CH_3COOH_{(aq)}$ solution, which of the following species is present in the highest concentration?

- A) $H_3O^+{}_{(aq)}$
- B) $CH_3COOH_{(aq)}$
- C) $OH^-{}_{(aq)}$
- D) $CH_3COO^-{}_{(aq)}$

7.

The following equilibrium is set up in a closed container:

$CaO_{(s)} + CO_{2(g)} \longleftrightarrow CaCO_{3(s)}$ + heat

If the mass of $CaCO_{3(s)}$ is doubled at constant temperature and pressure, what change will occur in the equilibrium?

- A) no change will occur
- B) the temperature will decrease
- C) the mass of $CaO_{(s)}$ will increase
- D) the volume of the container will increase

8. In a standardization of a sodium hydroxide solution, a lab technician finds that 11.20 mL of $NaOH_{(aq)}$ are required to neutralize 1.25 g of *monoprotic* potassium hydrogen phthalate (KHP), $KHC_8H_4O_{4(s)}$. The concentration of the base must be

- A) $5.46\times 10^{-1}$ mol/L
- B) $6.12\times 10^{-3}$ mol/L
- C) 5.46 mol/L
- D) 6.12 mol/L

9. Chemical systems are best described to be in equilibrium when

- A) the reaction is finished
- B) the mass of products equals the mass of reactants
- C) the rates of forward and reverse reactions become equal
- D) the macroscopic properties of the chemical remain unchanged

10. If the pH of a sample of rainwater is 4.50, then the pOH (to the nearest hundredth) is __________.

*Request took 0.094 seconds.*



Follow us; we're friendly!

They say the holy water is watered down
And this town lost its faith
Our colors will fade eventually
So if our time is running out
day after day,
we'll make the mundane our masterpiece
oh my my
oh my my love
I take one look at you & you're taking me out
of the ordinary
I want you laying me down till we're dead
& buried,
On the edge of your knife, staying drunk on
your vine
The angles up in the clouds are jealous
knowing we found
somthing so out of the ordinary
You got me kissing the grounds of your
sanctuary
shatter me with your touch, oh Lord
return me to dust...
The angles up in the clouds are jealous
knowing we found
hopeless Hallelujah, on this side of the heaven's
gate
Oh my life how do you, breathe and take
my breath away?
at your alter, I will pray
you're the sculptor, I'm the clay

oh my my,
You're taking me out of the ordinary
I want you laying me down till we're dead and buried
on the edge of your knife, staying drunk on your vine
The angles up in the clouds are jealous
Knowing we found
Something so out of the ordinary
You got me kissing the grounds of your sanctuary
Shatter me with your touch, oh Lord
return me to dust...
The angles up in the clouds are jealous
Knowing we found

Something so heavenly, higher than ecstasy
whenever you're next to me
oh my my
wold was in B&W until I saw your light
I thought you had to die to find something
so out of the ordinary
I want you laying me down,
till we're dead and buried
on the edge of your knife,
staying drunk on your vine...