Acids and Bases: Definitions

Arrhenius Definition of Acids and Bases

Acids are substances which increase the concentration of H\(^+\) ions when dissolved in water.

- An acid is a substance that produces H\(^+\) when dissolved in water.

Bases are substances which increase the concentration of OH\(^-\) ions when dissolved in water.

- A base is a substance that produces OH\(^-\) when dissolved in water.

But the *Arrhenius definition of acids and bases* is the limited to water solutions.

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Brønsted-Lowry Acids and Bases

Brønsted-Lowry Definition of Acids and Bases

The basic concept is that acid-base reactions involve the *transfer of H\(^+\) ions* from one substance to another. This involves a more general definition of acids and bases.

The H\(^+\) Ion in Water

The H\(^+\) ion interacts with H\(_2\)O by attaching itself to one of the lone pairs surrounding the O atom to yield H\(_3\)O\(^+\) (aq).

\[
\text{H}_2\text{O} (l) + \text{H}^+ (aq) \rightarrow \text{H}_3\text{O}^+ (aq)
\]

- Chemists often use H\(^+\) (aq) for simplicity and convenience when in fact, the more realistic structure is H\(_3\)O\(^+\).

Proton - Transfer Reactions

When HCl dissolves in water, the following reaction occurs:

\[
\text{HCl} (g) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{Cl}^- (aq)
\]

We see that the HCl molecule actually transfers a H\(^+\) ion to a water molecule.

Definitions

A *Brønsted-Lowry acid* is a molecule or ion that can donate a proton to another molecule or ion.

A *Brønsted-Lowry base* is a molecule or ion that can accept a proton from another molecule or ion.
### Brønsted-Lowry Acids and Bases

#### Using Acid-Base Definitions

Consider the following reaction:

\[
\text{NH}_3 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq)
\]

- NH\textsubscript{3} is an Arrhenius base because it leads to an increase in OH\textsuperscript{−} ions in water.
- NH\textsubscript{3} is a Brønsted-Lowry base because it accepts a proton from H\textsubscript{2}O.
- To be a Brønsted-Lowry base, a molecule or ion must have a nonbonding pair of electrons that can be used to bind to the H\textsuperscript{+} ion.

Substances which can act as either a Brønsted-Lowry base or acid are called amphoteric.

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### Examples of Conjugate Acid-Base Pairs

<table>
<thead>
<tr>
<th>Conjugate Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl\textsuperscript{−}</td>
</tr>
<tr>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>HSO\textsubscript{4}\textsuperscript{−}</td>
</tr>
<tr>
<td>HSO\textsubscript{4}\textsuperscript{−}</td>
<td>SO\textsubscript{4}\textsuperscript{2−}</td>
</tr>
<tr>
<td>NH\textsubscript{4}\textsuperscript{+}</td>
<td>NH\textsubscript{3}</td>
</tr>
<tr>
<td>H\textsubscript{3}O\textsuperscript{+}</td>
<td>H\textsubscript{2}O</td>
</tr>
<tr>
<td>H\textsubscript{2}O</td>
<td>OH\textsuperscript{−}</td>
</tr>
</tbody>
</table>

H\textsubscript{2}O is amphoteric and acts both as an acid and as a base.

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### Conjugate Acid-Base Pairs

Acid-Base Conjugate Pairs are two species that differ by a proton. Every acid has a conjugate base formed by removing H\textsuperscript{+} from the acid. A conjugate acid is the species that contains the proton that is transferred. Every base has a conjugate acid formed by adding H\textsuperscript{+} to the base. A conjugate base is the species formed by loss of the proton.

HNO\textsubscript{2}/NO\textsubscript{2}\textsuperscript{−} is called a conjugate acid-base pair because they differ only in the presence or absence of a proton.

NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} is called a conjugate acid-base pair because they differ only in the presence or absence of a proton.

H\textsubscript{2}O/H\textsubscript{3}O\textsuperscript{+} and H\textsubscript{2}O/OH\textsuperscript{−} are also conjugate acid-base pairs.

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### Relative Strengths of Acids and Bases

The stronger a conjugate acid \(\rightleftharpoons\) the weaker its conjugate base.

The stronger a conjugate base \(\rightleftharpoons\) the weaker its conjugate acid.

The position of the equilibrium in every acid-base reaction favors the transfer of the proton to the stronger base:

\[
\text{HC}_2\text{H}_3\text{O}_2 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{C}_2\text{H}_3\text{O}_2^− (aq)
\]

With the above comments, it is possible to group acids and bases into three broad categories based on their interaction with H\textsubscript{2}O:

1. **Strong Acids** completely transfer protons to water leaving no undissociated molecules in solution.
2. **Weak Acids** only partly dissociate in aqueous solution and exist as a mixture of undissociated molecules and ions from dissociated molecules.
3. **Substances with negligible acidity** which contain H but do not demonstrate any acidic behavior.
Chapter 16  Acid - Base Equilibria

The Autoionization of Water

One molecule of H$_2$O can donate a proton to another H$_2$O molecule:

\[ \text{H}_2\text{O} (l) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \]

and this process is called the **autoionization** of water.

Although only about 2 out of every 10$^9$ H$_2$O molecules are ionized at room temperature, the autoionization process is very important.

Neutral, Acidic, and Basic Solutions

- If \([\text{H}^+] = \text{[OH}^-] \), the solution is **neutral**.
- If \([\text{H}^+] > \text{[OH}^-] \), the solution is **acidic**.
- If \([\text{H}^+] < \text{[OH}^-] \), the solution is **basic**.

The pH Scale

Since the molar concentration of \([\text{H}^+] \) is very small, it can be expressed in terms of pH which is given as

\[ \text{pH} = -\log[\text{H}^+] \]

For a neutral solution, \([\text{H}^+] = \text{[OH}^-] \).

\[ \text{[H}^+]\text{[OH}^-] = [\text{H}^+]^2 = 1.0 \times 10^{-14} \]

\[ [\text{H}^+] = 1 \times 10^{-7}; \quad \text{pH} = 7 \]

<table>
<thead>
<tr>
<th>Solution Type</th>
<th>[\text{H}^+]</th>
<th>[\text{OH}^-]</th>
<th>pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic</td>
<td>&gt; $1.0 \times 10^{-7}$</td>
<td>&lt; $1.0 \times 10^{-7}$</td>
<td>&lt; 7.00</td>
</tr>
<tr>
<td>Neutral</td>
<td>= $1.0 \times 10^{-7}$</td>
<td>= $1.0 \times 10^{-7}$</td>
<td>= 7.00</td>
</tr>
<tr>
<td>Basic</td>
<td>&lt; $1.0 \times 10^{-7}$</td>
<td>&gt; $1.0 \times 10^{-7}$</td>
<td>&gt; 7.00</td>
</tr>
</tbody>
</table>

Chapter 16  Acid - Base Equilibria

The Ion Product of Water

Because the autoionization of H$_2$O is an equilibrium process, it can be written as an equilibrium constant expression:

\[ K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C \]

The following equilibrium for the dissociation of H$_2$O is used very frequently:

\[ \text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (aq) + \text{OH}^- (aq) \]

The following equilibrium expression can be written for the ion product of water:

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

The above equation is valid for any dilute aqueous solution.
The pOH Scale

The negative log can also be used to express the OH\(^-\) concentration:

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

Taking the negative log of both sides of the equation

\[
[H^+][OH^-] = 1.0 \times 10^{-14} = K_w
\]

yields

\[
-\log[H^+] + -\log[OH^-] = 14
\]

\[
pH + pOH = 14
\]

Relation Between pH and pOH

\[
pH + pOH = 14
\]

The pH Scale

Measuring pH with pH Meter

A pH Meter measures voltage by placing two electrodes into a solution. The voltage varies as pH.

Acid-Base Indicators

are usually dyes which are themselves weak acids and change color depending on whether they are in acidic or basic solution. This property enables them to be used to measure pH. An acid-base indicator is also a base which changes color depending on whether the acid form (HIn) or base form (In\(^-\)) is the predominant species in solution.

\[
Hln (aq) \rightleftharpoons H^+ (aq) + ln^- (aq)
\]

\[
K_a = \frac{[H^+][ln^-]}{[Hln]}
\]

\[
\frac{[ln^-]}{[Hln]} = K_a
\]

\[
\frac{[H^+]}{[Hln]} = K_a
\]
Some Common Acid-Base Indicators
The pH ranges for the color changes of some common acid-base indicators are given in the figure below:

Most indicators have a useful range of about 2 pH units.

Strong Acids
Strong acids are *strong electrolytes* and exist in solution entirely as ions.
The seven most common strong acids include the following:
- HCl, HBr, HI, HNO$_3$, HClO$_3$, HClO$_4$, and H$_2$SO$_4$.
The typical behavior of a strong acid can be illustrated by the following:

$$\text{HNO}_3 \text{(aq)} + \text{H}_2\text{O} \text{(l)} \rightarrow \text{NO}_3^- \text{(aq)} + \text{H}_3\text{O}^+ \text{(aq)}$$

Note that equilibrium arrows were not used in the above equation because it lies completely to the right.
For example, a 0.20 M HNO$_3$ produces

$$[\text{H}^+] = [\text{NO}_3^-] = 0.20\text{M}$$

Strong Bases
Strong bases are *strong electrolytes* and exist in solution entirely as ions.
The most common soluble strong bases include
- Hydroxides of the Group 1A alkali metals (e.g. NaOH, KOH).
- Hydroxides of the Group 2A alkaline earth metals (e.g. Ca(OH)$_2$).

For example, a 0.20 M NaOH produces

$$[\text{Na}^+] = [\text{OH}^-] = 0.20\text{M}.$$
Chapter 16  Acid - Base Equilibria

Conductivity of Strong and Weak Acids

Strong acids are better conductors of electricity than weak acids.

Percent Ionization vs Concentration of Weak Acids

The percent ionization of a weak acid decreases as the concentration of the acid increases as shown below:

- The $[H^+]$ is only a small fraction of the weak acid that is dissolved in solution.
- The percent ionization of weak acid at a particular temperature depends on both the identity of the acid and its concentration.

Weak Acids: Example of Percent Ionization

A 0.020 M solution of niacin (one of the B vitamins) has a pH of 3.26

(a) What percentage of the acid is ionized in this solution?

\[ C_5H_4N-COOH (aq) \rightleftharpoons H^+ (aq) + C_5H_4N-COO^- (aq) \]

\[ K_a = \frac{[H^+][C_5H_4N-COO^-]}{[C_5H_4N-COOH]} \]

\[ pH = -\log[H^+] = 3.26; \quad [H^+] = 10^{-3.26} \]

\[ [H^+] = 10^{-3.26} = 10^{0.74} \cdot 10^{-4} = 5.50 \times 10^{-4} \]

\[ \text{percent ionization} = \frac{[H^+]}{\text{initial conc. } C_5H_4N-COOH} \times 100 \% = \frac{5.50 \times 10^{-4}}{0.020} \times 100 \% = \cdot 2.8 \% \]

(b) What is the acid-dissociation-constant, $K_a$, for niacin?

\[ C_5H_4N-COOH (aq) \rightleftharpoons H^+ (aq) + C_5H_4N-COO^- (aq) \]

\[ K_a = \frac{[H^+][C_5H_4N-COO^-]}{[C_5H_4N-COOH]} \]

\[ K_a = \frac{(5.50 \times 10^{-4}) (5.50 \times 10^{-4})}{(0.020 - 5.50 \times 10^{-4})} = 1.6 \times 10^{-5} \]
Chapter 16

Weak Acids: Example of Using $K_a$ to Calculate pH

The $K_a$ for niacin is $1.6 \times 10^{-5}$. What is the pH of a solution of a 0.010 M?

$$C_3H_2N-COOH (aq) \rightleftharpoons H^+ (aq) + C_3H_2N-COO^- (aq)$$

<table>
<thead>
<tr>
<th>Initial</th>
<th>$C_3H_2N-COOH (aq)$</th>
<th>$H^+ (aq)$</th>
<th>$C_3H_2N-COO^- (aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.010 M</td>
<td>0.000 M</td>
<td>0.000 M</td>
</tr>
</tbody>
</table>
<box>(51,93),(409,193)</box>

$K_a = \frac{[H^+][C_3H_2N-COO^-]}{[C_3H_2N-COO^\text{H}]} = \frac{x^2}{0.010 - x} = 1.6 \times 10^{-5}$

Assume $x$ is negligible with respect to 0.010; this is OK, if $x < 5\%$ of initial value.

$$0.010 \times x \approx 0.010$$

$$\frac{x^2}{0.010} \approx 1.6 \times 10^{-5}$$

$$x = [H^+] = 4.0 \times 10^{-4}; \quad \text{pH} = -\log(4) + (-\log(10^{-4})) = 3.40$$

Check to make sure that $x < 5\%$ of 0.010. Yes.

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Weak Bases

Weak bases react with $H_2O$ and abstract $H^+$ to form the conjugate acid of the base and $OH^-$ ions.

$$B (aq) + H_2O (l) \rightleftharpoons BH^+ (aq) + OH^- (aq)$$

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

$K_b$ is called the base-dissociation constant and refers to the equilibrium between the base $B$ reacting with water and the conjugate acid ($BH^+$) and hydroxide ion ($OH^-$).

Ammonia ($NH_3$) is the most commonly encountered weak base:

$$NH_3 (aq) + H_2O (l) \rightleftharpoons NH_4^+ (aq) + OH^- (aq)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

Chapter 16

Polyprotic Acids

Polyprotic acids are those acids that have more than one ionizable proton. For example, sulfuric acid ($H_2SO_4$):

$$H_2SO_3 (aq) \rightleftharpoons H^+ (aq) + HSO_3^- (aq); \quad K_{a1} = \frac{[H^+][HSO_3^-]}{[H_2SO_3]} = 1.7 \times 10^{-2}$$

$$HSO_3^- (aq) \rightleftharpoons H^+ (aq) + SO_3^{2-} (aq); \quad K_{a2} = \frac{[H^+][SO_3^{2-}]}{[HSO_3^-]} = 6.4 \times 10^{-8}$$

$K_{a2} < < K_{a1}$: in a polyprotic acid, it is always easier to remove the first proton than the second.

Types of Weak Bases

1. Neutral molecules containing an atom with a nonbonding pair of electrons that can serve as a proton acceptor.

These substances include ammonia ($NH_3$) and a related class of compounds called amines.

Amines can be derived from ammonia ($H-NH_2$) by taking away a hydrogen atom and replacing it by a large organic group.

Thus, methylamine ($CH_3-NH_2$) is formed by replacing one $H$ atom with a methyl group ($CH_3$).
Types of Weak Bases

2. Anions of weak acids are also weak bases.

Consider sodium fluoride (NaF) or sodium hypochlorite (NaClO). Both of these ionic compounds are strong electrolytes and dissolve completely in H₂O to yield Na⁺, F⁻ and Na⁺, ClO⁻, respectively.

No reaction occurs for Na⁺ in H₂O.

However, both F⁻ and ClO⁻ are anions of weak acids and will act as weak bases in water:

\[ \text{ClO}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HClO} (aq) + \text{OH}^- (aq) \]

\[ \text{F}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{HF} (aq) + \text{OH}^- (aq) \]

---

Example Problem Involving Weak Base Calculation

A solution of NH₃ in H₂O has a pH of 10.50. What is the molarity of the solution?

\[ \text{NH}_3 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq) \]

\[ [\text{NH}_3] = (x - 3.16 \times 10^{-4}) M \approx 5.6 \times 10^{-3} M \]

\[ pOH = 14.00 - pH = 14.00 - 10.50 = 3.50 \]

\[ pOH = -\log[\text{OH}^-]; \quad [\text{OH}^-] = 10^{-pOH} = 10^{-3.50} = 10^{0.50} \times 10^{-4} = 3.16 \times 10^{-4} \]

The same amount of hydroxide and ammonium ions are formed:

\[ [\text{OH}^-] = [\text{NH}_4^+] = 3.16 \times 10^{-4} \]

---

Example Problem Involving Weak Base Calculation

To illustrate the relationship between \( K_a \) and \( K_b \), the following two equations can be added together:

\[ \text{NH}_4^+ (aq) \rightleftharpoons \text{NH}_3 (aq) + \text{H}^+ (aq); \quad \text{K}_a = \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \]

\[ \text{NH}_3 (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{NH}_4^+ (aq) + \text{OH}^- (aq); \quad \text{K}_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

Adding the above two equations gives:

\[ \text{H}_2\text{O} (l) \rightleftharpoons \text{H}^+ (aq) + \text{OH}^- (aq) \]

This turns out to be the ion-product of H₂O (\( K_w \)).

The product of the acid-dissociation constant for an acid and the base-dissociation constant for its conjugate base is equal to the ion product of water.

\[ \text{K}_a \times \text{K}_b = \left( \frac{[\text{NH}_3][\text{H}^+]}{[\text{NH}_4^+]} \right) \times \left( \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \right) = [\text{H}^+][\text{OH}^-] = K_w \]
Relationship Between $K_a$ and $K_b$

From the product of acid-dissociation constant for an acid and the base-dissociation-constant for the conjugate base,

$$K_w = K_a \times K_b$$

we can discern the following

- Because of the inverse relationship between $K_a$ and $K_b$,
  $$K_a = \frac{K_w}{K_b}$$
  the strength of an acid increases (larger $K_a$) as the strength of the conjugate base decreases (smaller $K_b$);
- $K_a$ for an acid can be calculated if $K_b$ is known; likewise, $K_b$ for an acid can be calculated if $K_a$ is known.

Example Problem for Relationship Between $K_a$ and $K_b$

(a) Which of the following bases has the largest base-dissociation constant: $\text{NO}_2^-$, $\text{PO}_4^{3-}$, or $\text{N}_3^-$?

From Table 16.2, p.685 and Appendix D, p. 1126:

<table>
<thead>
<tr>
<th>Anion</th>
<th>$K_a$</th>
<th>$K_b = \frac{K_w}{K_a}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NO}_2^-$</td>
<td>$4.5 \times 10^{-4}$</td>
<td>$2.2 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\text{PO}_4^{3-}$</td>
<td>$4.2 \times 10^{-13}$</td>
<td>$2.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>$\text{N}_3^-$</td>
<td>$1.9 \times 10^{-5}$</td>
<td>$5.3 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

Clearly, $\text{PO}_4^{3-}$ has the largest base-dissociation constant.

(b) The conjugate acid of the base quinoline has a $pK_a = 4.90$. What is the base-dissociation constant of quinoline?

$$pK_a = -\log K_a = 4.90$$

$$K_a = 10^{-4.90} = 10^{0.10} \cdot 10^{-5} = 1.26 \times 10^{-5}$$

The base-dissociation-constant is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.26 \times 10^{-5}} = 7.9 \times 10^{-10}$$

Acid-Base Properties of Salt Solutions

When salts dissolve in water, they are completely dissociated into ions in solution making them strong electrolytes.

The cations and ions may exhibit acid-base properties so that the resulting solution can be acidic or basic.

Hydrolysis is the reaction of ions in solution with $\text{H}_2\text{O}$ to generate $\text{H}^+$ (aq) or $\text{OH}^-$ (aq).
Chapter 16

Acid-Base Properties of Salt Solutions

Acid-Base Properties of Salt Solutions

An Anion's Ability to React with Water

The ability of an anion to react with H₂O to produce OH⁻ depends on the strength of the conjugate acid of the anion.

To determine the conjugate acid of anion X⁻ and assess its strength, first add a

add proton to X⁻ to give HX:

If the acid (HX) is one of the seven strong acids, then X⁻ will have little tendency to react with H₂O.

- The anion will not affect the pH of the solution, and the equilibrium will lie far to the left:
  \[ \text{Cl}^- (aq) + \text{H}_2\text{O} (l) \leftrightharpoons \text{HCl} (aq) + \text{OH}^- (aq) \]

- An anion that is the conjugate base of a strong acid will not affect the pH of a solution.

Anion's Ability to React with Water

If the acid (HX) is not the one of seven strong acids, then X⁻ is the conjugate base of a weak acid.

- There will be an equilibrium mixture of weak acid (HX), X⁻, OH⁻, and the solution will be basic.

- X⁻ will react with water to produce the weak acid and OH⁻ ions raising the pH of the solution:
  \[ \text{C}_2\text{H}_3\text{O}_2^- (aq) + \text{H}_2\text{O} (l) \leftrightharpoons \text{HC}_2\text{H}_3\text{O}_2^- (aq) + \text{OH}^- (aq) \]

- An anion that is the conjugate base of a weak acid will increase the pH of a solution.

Example: Dissolution of NaNO₃ in Water

One way to analyze the acid-base properties of salt solutions is to consider a two-step process of dissolving the salt in water and then analyzing the resulting cation and anion in solution.

Dissolve in water:

\[ \text{NaNO}_3 (s) \rightarrow \text{Na}^+ (aq) + \text{NO}_3^- (aq) \]

Analyze the effect of the resulting ions in solution.

- Na⁺ is a cation which does not react with H₂O.
- NO₃⁻ in the anion of strong conjugate acid (HNO₃) and doesn’t react with water.
- Thus, the NaNO₃ solution has a neutral pH.

For a solution containing a cation which is the conjugate acid of a weak base and an anion which is the conjugate base of a weak acid, the ion with the largest ionization constant will have the greatest influence on pH.

For example, ammonium carbonate, (NH₄)₂CO₃ is basic.

A Cation's Ability to React with Water

Polyatomic cations such as NH₄⁺ will donate a proton to water producing H₃O⁺ ions and lowering the pH:

\[ \text{NH}_4^+ (aq) + \text{H}_2\text{O} (l) \leftrightharpoons \text{NH}_3 (aq) + \text{H}_3\text{O}^+ (aq) \]

NH₄⁺ can be considered to the the conjugate acid of the weak base NH₃, and its strength inversely related to K_b.

2. Many metal ions react with H₂O to decrease the pH of an aqueous solution.

3. Exceptions are ions of Group 1A and heavier members of Group 2A (Ca²⁺, Sr²⁺, Ba²⁺).