

Chapter 15

Applications of Aqueous Equilibria

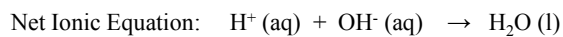
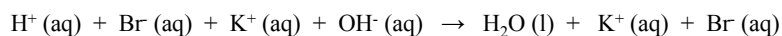
Chemistry, McMurry – Fay, 5th edition

15.1 - Neutralization Reactions

Strong Acid – Strong Base



Since HBr is a strong acid and KOH is a strong base, the total ionic equation is:

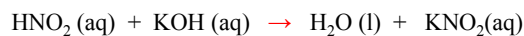


Which is also: $\text{H}_3\text{O}^+ \text{ (aq)} + \text{OH}^- \text{ (aq)} \rightleftharpoons 2 \text{H}_2\text{O (l)}$ which gives $1/K_w = 1.00 \times 10^{14}$
since this is the reverse reaction

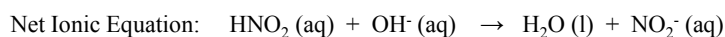
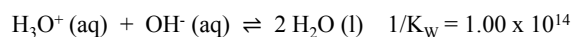
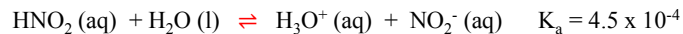
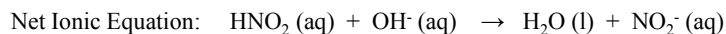
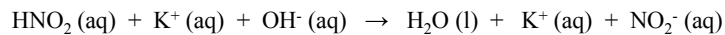
Since the equilibrium constant is very large, the reaction proceeds to completion (~100%)

What is the pH of this solution?

Take time to review section 4.5, example 4.6, and problems 3.20-22

Weak Acid – Strong Base

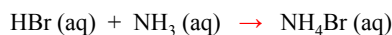
Since HNO_2 is a weak acid and KOH is a strong base, the total ionic equation is:



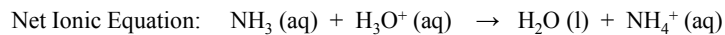
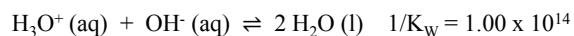
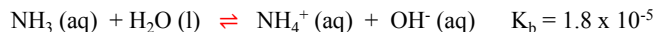
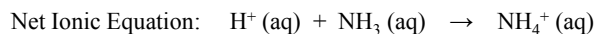
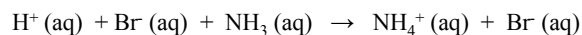
$$K_{\text{net}} = K_a \times (1/K_w) = 4.5 \times 10^{-4} \times 1.00 \times 10^{14} = 4.5 \times 10^{10}$$

Very large so ~100% completion

Is $\text{KNO}_2(\text{aq})$ an acidic or basic solution?

Strong Acid – Weak Base

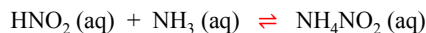
Since HBr is a strong acid and NH_3 is a weak base, the total ionic equation is:



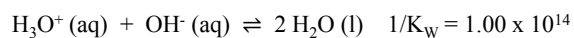
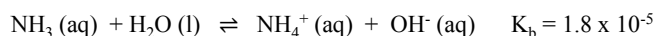
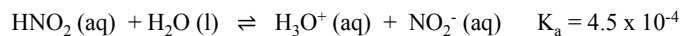
$$K_{\text{net}} = K_b \times (1/K_w) = 1.8 \times 10^{-5} \times 1.00 \times 10^{14} = 1.8 \times 10^9$$

Very large so ~100% completion

Is $\text{NH}_4\text{Br}(\text{aq})$ an acidic or basic solution?

Weak Acid – Weak Base

Neither reactant is completely ionized!



Net Ionic Equation: Same as molecular since nothing cancels out!

$$K_{\text{net}} = K_a \times K_b \times (1/K_w) = 4.5 \times 10^{-4} \times 1.8 \times 10^{-5} \times 1.00 \times 10^{14} = 8.1 \times 10^5$$

Neutralization does not proceed as far towards completion!

It does NOT go to products all the way!

Is $\text{NH}_4\text{NO}_2(\text{aq})$ an acidic or basic solution?

15.2 – The Common-Ion Effect

What happens when you added potassium acetate to an acetic acid solution?

**Acetic acid, CH_3COOH , and potassium acetate, KCH_3COO ,
have the acetate ion, CH_3COO^- , common to both of them.**

When KCH_3COO dissolves in water, it dissociates 100%:

Acetic acid in water dissociates only slightly and sets up the following equilibrium reaction:

Using Le Chatelier's principle, we know that adding CH_3COO^- ion to the acetic acid solution will shift the equilibrium to the _____ and $[\text{H}_3\text{O}^+]$ will _____.

How will this effect the pH of the resulting solution compared to acetic acid without a common ion added?

Calculations involving the addition of a common ion:

Calculate the pH of a solution containing 0.25 M HF and 0.20 M sodium fluoride.
 $K_a = 3.5 \times 10^{-4}$

Do your error check for the assumption:

What is the pH of the solution without the common ion?

If the solution has the weak acid and its conjugate base present *initially*, then the Henderson-Hasselbalch Equation can be used:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

Does it work? Apply it to our previous problem:

**The same procedure can be used for a weak base and its conjugate acid.
 Keep in mind, the H-H Equation uses $\text{p}K_a$ NOT $\text{p}K_b$!!**

What is the pH of a solution containing 0.20 M NH_3 (aq) and 0.50 M NH_4Cl ?
 $K_b = 1.8 \times 10^{-5}$

15.4 – Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

Can we predict whether the pH of a buffer solution is greater than or less than the pK_a ?

Look at the buffer solution 0.20 M HCN with 0.12 M NaCN $K_a = 4.9 \times 10^{-10}$

What is the acid? What is the base?

We can predict: since the concentration of HCN (the acid) is greater, the pH of the buffer solution is less than the pK_a .

Calculate the pH using the Henderson-Hasselbalch equation to confirm our prediction:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]}$$

15.3 – Buffer Solutions

Buffer solutions can either contain a weak acid and their conjugate base or a weak base and their conjugate acid.

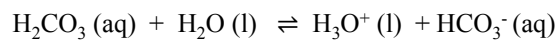
Buffer solutions resist a change in pH upon addition of an external acid or base.

How?

When an external base is added,
the buffer's weak acid reacts with it until it is consumed.

When an external acid is added,
the buffer's base (conj. base) reacts with it until it is consumed.

The following reaction is important in maintaining the pH of blood at a nearly constant Value of 7.4:



What happens to the position of this equilibrium and the pH when blood absorbs added acid?

What happens to the position of this equilibrium and the pH when blood absorbs added base?

Which of the following solutions has the greater buffer capacity:

- a) 100 mL of 0.30 M HNO_2 -0.30 M NaNO_2
- b) 100 mL of 0.10 M HNO_2 -0.10 M NaNO_2

Calculate the pH of a buffer solution containing 0.50 M CH_3COOH and 0.50 M NaCH_3COO .
 $K_a = 1.8 \times 10^{-5}$

Now, what happens when 0.020 mol of solid NaOH is added to 1.0 L of the buffer solution?



Before addition

Addition

After addition

Now, what happens when 0.020 mol of HCl is added to 1.0 L of the buffer solution?



Before addition

Addition

After addition

What is the pH of a buffer solution after 10.0 mL of 0.50 M HCl is added to the solution already containing 400.0 mL of 0.25 M NH_3 (aq) and 400.0 mL of 0.45 M NH_4Cl ?
 $K_b = 1.8 \times 10^{-5}$

The added acid reacts with the base:



Before addition

Addition

After addition

Now calculate molarity:

What was the starting pH of this buffer?

How would you select an appropriate buffer solution?

Notice pH is typically close to the $\text{p}K_a$.
 So look at a table of K_a values, calculate $\text{p}K_a$ and select a buffer pair with a $\text{p}K_a$ close to your desired pH.

How would you make a solution with a pH = 4.19?

How would you make a solution with a pH = 3.25?

15.5 – Titrations

Solution of a known concentration is added to a solution of an unknown concentration.

The **equivalence point** = the point when stoichiometric quantities of acid and base are mixed.

A titration is monitored with a pH indicator or a pH meter.

With pH meters, accurate data is recorded and plotted: **pH vs. volume of titrant added.**

Titration curves help identify the equivalence point.

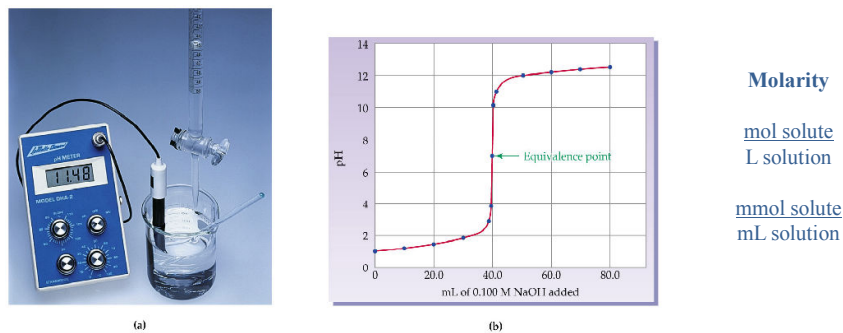


Figure 16.6 A strong acid–strong base titration curve. (a) In this pH titration, 0.100 M NaOH is added slowly from a buret to an HCl solution of unknown concentration. (b) The pH titration curve for titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

15.6 – Strong Acid-Strong Base Titrations

Consider the titration of 25.0 mL of 0.200 M HCl with 0.200 M NaOH (titrant).

Point A on the plot: *Before the addition of NaOH*
Initial [HCl]

Point C on the plot: *Before Equivalence Point*

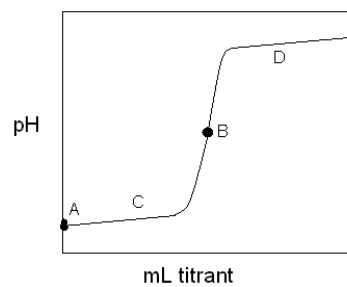
Not enough base has been added to react with all the acid present. Each drop of base added has reacted completely with the acid to produce products. There is still acid left so calculate the remaining amount to determine pH.

Point B on the plot: *Equivalence Point*

Middle of the steep part of the plot and found graphically. For strong acid-strong base, the pH = 7.0. The products are neutral ions and water.

Point D on the plot: *After Equivalence Point*

All acid is reacted and only base and product remain in the flask.



15.7 – Weak Acid-Strong Base Titrations

Consider the titration of 25.0 mL of 0.200 M HCH_3COO (flask)
with 0.200 M NaOH (titrant).

Point A on the plot: *Before the addition of NaOH - Initial $[\text{HCH}_3\text{COO}]$*

Only the weak acid is present in the flask. Set up equilibrium and use your ICE table to solve for $[\text{H}_3\text{O}^+]$ and pH.

Point B on the plot: *Equivalence Point*

We saw that the product of a weak acid and a strong base is a basic salt and water. We can expect the pH to be greater than 7.0. To find the volume of base required to reach the equivalence point use stoichiometry. Now calculate the moles of acid that was in the flask. Since all the weak acid has been converted to its conjugate base at the equivalence point, the moles of A^- are now known. Divide by total volume (acid + base added) for $[\text{A}^-]$. The conjugate base will react with water ($\text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}^-$) so set up your ICE table and solve for OH^- and pH.

Point C on the plot: *Before Equivalence Point*

This is the buffer zone. pH can be found from the H-H equation but first $[\text{A}^-]$ is calculated. Each drop of strong base added has reacted with the weak acid present in the flask. Calculate the moles of strong base added using vol and M. This is now also the # mol reacted. Now subtract the moles added from the moles of acid present in the flask. This is unreacted acid left in the flask. Calculate $[\text{A}^-]$ using the equation ($\text{HA} + \text{NaOH} \rightleftharpoons \text{H}_2\text{O} + \text{A}^-$). Divide the moles of unreacted acid by the volume (acid + base) for molarity. Do the same with A^- . Use the H-H equation for the pH.

Point D on the plot: *After Equivalence Point*

More than enough base is added to react with all the acid in the flask. No HA remains, it is all converted to A^- . To calculate $[\text{A}^-]$, find the moles of all HA reacted and divide by the total volume of the solution at this point (acid + base). To find the $[\text{OH}^-]$ use vol added and M to determine how many moles was added and subtract that from the moles of acid reacted with it. Then divide by the total volume of the resulting solution. The amount of OH^- from the reaction of A^- with water is negligible so pH is determined from $[\text{OH}^-]$ remaining.

Consider the titration of 25.0 mL of 0.200 M HCH_3COO (flask)
with 0.200 M NaOH (titrant).

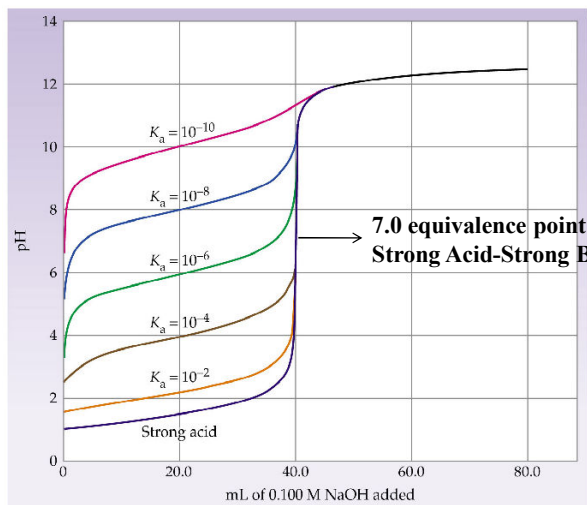
Point A on the plot: *Before the addition of NaOH - Initial $[\text{HCH}_3\text{COO}]$*

Point B on the plot: *Equivalence Point*

Point C on the plot: *Before Equivalence Point*

Point D on the plot: *After Equivalence Point*

Various Weak Acid – Strong Base Titration Curves



Typically the equivalence point is above 7.0. for a weak acid – strong base. Why?

Where would the equivalence point be for a strong acid – weak base?

Always pick a pH indicator that changes color near the equivalence point of a titration.

15.8 – Strong Acid-Weak Base Titrations

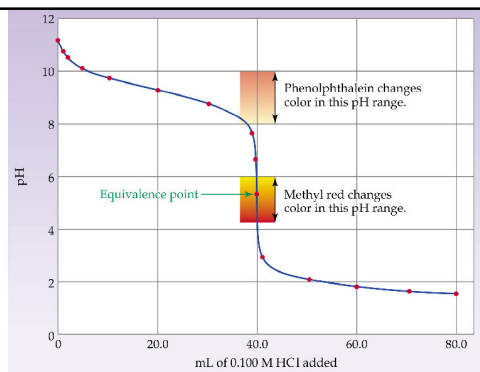
Consider the titration of 40.0 mL of 0.100 M NH_3 (flask) with 0.100 M HCl (titrant).

Before the addition of HCl

Before Equivalence Point

Equivalence Point

After Equivalence Point



Notice the curve? Why is it opposite?

See textbook example for section 16.8

15.9 – Polyprotic Acid-Strong Base Titrations

For polyprotic acids, there is an equivalence point for each H that comes off.

Point A on the plot:

Only the diprotic acid is present. It is in equilibrium with water.
 $\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HSO}_4^- + \text{H}_3\text{O}^+$

Point B on the plot:

The first H is starting to come off as base is added.
 You have pK_{a1} and 50% is H_2SO_4 and 50% is HSO_4^-

Point C on the plot:

This is the first equivalence point. You have 100% HSO_4^-

Point D on the plot:

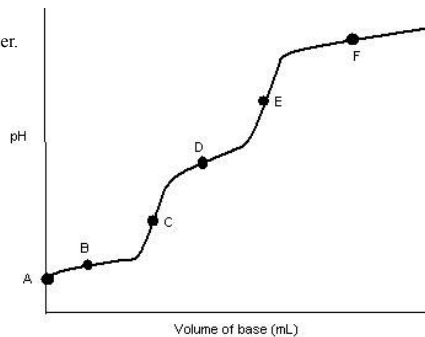
At this point you have pK_{a2} and 50% HSO_4^- and 50% SO_4^{2-}

Point E on the plot:

This is the second equivalence point. You have 100% SO_4^{2-}
 All the acid has reacted completely.

Point F on the plot:

All the acid has reacted completely. Only excess base and SO_4^{2-} present.



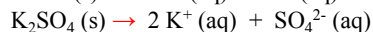
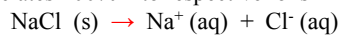
Example 16.18: Consider the titration of 40.0 mL of 0.0800 M H_2SO_3 ($K_{a1} = 1.5 \times 10^{-2}$ $K_{a2} = 6.3 \times 10^{-8}$) with 0.160 M NaOH. Calculate the pH after addition of the following volumes of 0.160 M NaOH:

- a. 20.0 mL b. 30.0 mL c. 35.0 mL

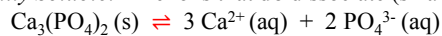
15.10 – Solubility Equilibria

A table of solubility rules is used to help determine which ionic compounds are soluble or insoluble in water.

Soluble: Dissociates 100% into respective ions in water



Insoluble/Slightly Soluble: The ions that **do** dissociate (small amount) set up equilibria

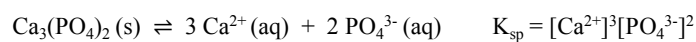
**Solution Terminology:**

Unsaturated: more solid can dissolve in the solution
([ion] is not at the max yet).

Saturated: a solution containing the maximum possible amount of dissolved solute at equilibrium - no more can dissolve!
([ion] is at the max).

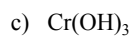
Supersaturated: a solution containing a greater-than-equilibrium amount of solute (undissolved solid sitting at the bottom).

K_{sp} is the solubility product for saturated solution equilibria.

**Writing K_{sp} :**

The K_{sp} expression is like all other equilibrium expressions, the solid is excluded.

Write the solubility product for the following:



15.11 – Measuring K_{sp} and Calculating Solubility from K_{sp}

Solubility: Maximum grams of a compound that can dissolve in 1.00 L of solvent. (g/L)

Molar solubility: Max moles of a compound that can dissolve in 1.00 L of solvent. (mol/L)

K_{sp} values can be determined experimentally and are tabulated in reference books.

They also can be calculated from solution concentrations:

A particular saturated solution of lead chloride has $[Pb^{2+}] = 4.5 \times 10^{-2} M$ and $[Cl^-] = 1.6 \times 10^{-2} M$. What is the value of K_{sp} for $PbCl_2$?

**K_{sp} is a measure of dissolution at equilibrium (saturation).
(How much solid is actually dissolving into its separate ions)**

*The presence of other ions in the solution typically won't affect K_{sp} calculations.
If the solution does become too concentrated, then there can be some electrostatic interactions.
There also are some side reactions that can occur.
For now, ignore complications and assume solubility and K_{sp} values are approximate.*

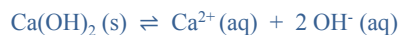
Calculate the solubility of calcium fluoride in water at 25°C. $K_{sp} = 1.5 \times 10^{-10}$

The solubility of calcium hydroxide is 0.233 g/L. Calculate K_{sp} .

15.12 – Factors That Affect Solubility**The Common Ion Effect**

From the solubility of calcium hydroxide (0.233 g/L), K_{sp} and the molar solubility of each ion can be calculated (see previous slide).

What happens when solid CaCl_2 is added to a saturated solution of Ca(OH)_2 ?



K_{sp} has to remain constant at a given temperature so:

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = 1.24 \times 10^{-7}$$

Adding a common ion *decreases* solubility!

What is the concentration of silver ion and bromide ion if 0.0244 g of AgBr and 0.0111 g of NaBr are placed in 1.00 L of water? K_{sp} for AgBr is 7.7×10^{-13}

Start by looking at a solubility table. Which compound is soluble in water? That compound is a one way reaction, single arrow, all solid is dissolved.

Now look at AgBr: $(0.0244\text{g} (1 \text{ mol}/187.77 \text{ g}))/1.00\text{L} = 1.30 \times 10^{-4} \text{ mol/L}$
Only **IF** all the solid dissolved would this be the $[\text{Ag}^+]$ and $[\text{Br}^-]$.
How can we tell if it all dissolved? Look at Q!

How does Q compare to K_{sp} ? $Q > K_{sp}$ so all the AgBr does NOT dissolve.

Set up ICE table to determine the amount of AgBr dissolved:



Initial:
Change:
Equilibrium

What is the solubility of calcium hydroxide in a 0.10 M $\text{Ca}(\text{NO}_3)_2$ solution?
 K_{sp} of $\text{Ca}(\text{OH})_2 = 6.5 \times 10^{-6}$

The pH of the Solution

As pH decreases (acidity increases) the ionic compound containing the conjugate base anion of a weak acid becomes more soluble.

$[\text{H}_3\text{O}^+]$ increases and it can react with the anion of a weak acid.

OH^- is the conjugate base of the weak acid H_2O .

H_3O^+ can donate a proton to OH^- forming two water molecules!

The $[\text{OH}^-]$ decrease so the equilibrium will shift right . . . more solid dissolves!

[Dissolution of \$\text{Mg}\(\text{OH}\)_2\$ by Acid Movie](#)

What happens when the pH increases?

This holds true for any anion that is a conjugate base of a weak acid.

Which of the following compounds are more soluble in acidic solution than pure water?

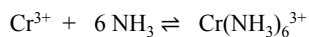
- a. $\text{Pb}(\text{CN})_2$ b. AgI c. $\text{Al}(\text{OH})_3$

Formation of Complex Ions

A complex ion has a central metal ion (typically a transition metal) covalently bonded to multiple ions or molecules (called ligands, L) and it has a charge.

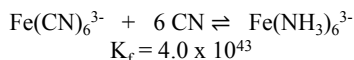


Complex ions are in equilibrium with their metal ion and the species bonded to them:



The solubility of an ionic compound increases dramatically if the solution contains a Lewis base that can form a complex ion with the metal cation.

The complex ion is measured by the K_f value (formation constant).
The larger the K_f (typically very positive numbers) the more stable the complex ion.



$$K_f = 4.0 \times 10^{43}$$

Recall: very positive number means the equilibrium lies to the right favoring products!

15.13 – Precipitation of Ionic Compounds

Will a precipitate form when two solutions are mixed?

$Q_{sp} = K_{sp}$: the solution is saturated and no change occurs.

$Q_{sp} > K_{sp}$: the solution is momentarily supersaturated and will precipitate until $Q_{sp} = K_{sp}$

$Q_{sp} < K_{sp}$: The solution is unsaturated and no precipitate will form

Does a precipitate form when 100. mL of 0.30 M $\text{Ca}(\text{NO}_3)_2$ is mixed with 200. mL of 0.060 M NaF?

Look at the two solution and determine what the possible precipitate might be.
Write a net ionic equation for the precipitate and locate the K_{sp} value from a table.



$$Q_{sp} = [\text{Ca}^{2+}][\text{F}^{-}]^2 \quad \text{find the value and compare it to } K_{sp}$$

When 5.45 mg of lead sulfate is placed in 2.00 L of water will it all dissolve?

15.14 – Separation of Ions by Selective Precipitation

SKIP

15.15 – Qualitative Analysis

Read through and review for lab

Please Keep in Mind the Following:

- 1. Make sure you can identify the six strong acids.** pH and concentration do not tell whether it is a strong or weak acid. Only if the acid ionizes 100% is it a strong acid. You can have a dilute strong acid with a pH of 6 or a concentrated weak acid with a pH of 2. That doesn't tell you the strength of the acid or its ability to donate a proton! pH just tells you the mol/L of H^+ not where the H^+ came from!!
- 2. Make sure you can identify a weak acid and its conjugate base and a weak base and its conjugate acid.** Be able to write the reaction of a weak acid in water and a weak base in water.
- 3. Make sure you can recognize neutral, basic, and acidic ions.**
Neutral ions come from strong acids and strong bases.
Acidic ions come from weak bases.
Basic ions come from weak acids.
Know if these ions make neutral, acidic, or basic solutions in water. Be able to write a reaction for it.
- 4. Know if a reaction is one way or sets up equilibrium.**