The Concept of Chemical Equilibrium

A chemical reaction is at equilibrium when it is proceeding in the forward and backward directions at the same rate. The concentrations of all the species remain constant once equilibrium is established.

For the reaction:

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

at equilibrium, the equilibrium constant is defined as:

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

Where [A] represents the concentration of reactant A at equilibrium, [B] the concentration of B, etc.. $K_{eq}$ is the Equilibrium Constant for the reaction at that temperature.

Many important reactions can be considered as going to completion:

$$ \text{HCl} (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}_3\text{O}^+ (aq) + \text{Cl}^- (aq) $$

or

$$ \text{HCl} (g) + \text{H}_2\text{O} (l) \rightarrow \text{H}^+ (aq) + \text{Cl}^- (aq) $$
How do we most often measure concentrations?

**Molarity:** \( M \)

Concentration is usually expressed as the number of moles of solute per litre of solution, \( \text{mol} \ L^{-1} \).

\[
M = \frac{\text{Moles solute}}{\text{Volume of solution in liters}}
\]

Thus a 0.10 molar solution has a concentration of 0.10 \( \text{mol} \ L^{-1} \), and is written as 0.10 \( M \).

Generally square brackets mean moles per liter i.e. \([A]\)

Molarites can be used to calculate:

The number of moles of solute in a given volume of solution

or

The volume of solution containing a given # of moles of solute.

These calculations permit us to use volumetric glassware, burette, pipette, volumetric flask (Lab. Manual) to prepare and measure out chemical reagents.

**Examples**

1. What is the molarity of a solution containing 1.50 mol of solute in 750 mL of solution?

\[
M = \frac{\text{Moles}}{\text{Volume (in litres)}} = \frac{\text{Moles}}{V} = \frac{1.5}{0.75} = 2.0
\]

Therefore: Moles = MV = 8 x 0.05 = 0.4
2. How many moles of HBr are there in 50.0 mL of 8.00 M solution?

\[
\text{Molarity} = \frac{\text{Moles}}{\text{V}}
\]

\[
\text{Moles} = \text{Molarity} \times \text{Volume} = 8 \text{ moles/ liter} \times 0.050 \text{ liters} = 0.4 \text{ moles HBr}
\]

3. What volume (mL) of 0.480 M HBr solution contains 2.40 mol of HBr?

\[
\text{M} = \frac{\text{Moles}}{\text{V}}
\]

\[
0.480 \text{ moles L}^{-1} = 2.40 \text{ moles/ V}
\]

\[
\text{V} = 0.2 \text{ L} = 200 \text{ mL}
\]
**Strong Aids and Bases**

An acid is defined as a substance that increases the Hydrogen Ion concentration when dissolved in water.

The Hydrogen ion, \( H^+ \), is a 'bare' proton. It is never found as such in solution or in an ionic compound.

The ion \( H_3O^+ \) is the hydronium ion. All \( H^+ \) in water is in this form.

We write \( H_3O^+ \), \( H^+(aq) \) or (lazily) just \( H^+ \)

Some examples of acids in water

\[
\begin{align*}
HCl & + H_2O \rightarrow H^+(aq) + Cl(aq) \\
HNO_3 & + H_2O \rightarrow H^+(aq) + NO_3^-
\end{align*}
\]

**For strong acids we assume that reaction goes to completion, i.e. these acids are 100% dissociated (or ionized).**

These contain hydrogen, which dissociates as a proton (or more properly a hydronium ion in solution and hence are called protonic acids.

HCl, HBr and HNO\(_3\) are monoprotic, giving 1 \( H^+ \) per molecule;

\[\text{i.e., } 1 \text{ mol acid} \rightarrow 1 \text{ mol } H^+(aq)\]

\( H_2SO_4 \) and \( H_2CO_3 \) are diprotic, giving 2 \( H^+ \) per molecule and \( H_3PO_4 \) is triprotic.

\[\text{E.g., } H_2SO_4 + H_2O \rightarrow 2 H^+(aq) + SO_4^{2-}\]

(The discussion of weak acids, which do not dissociate completely, will be left to later in the course.)
In many cases different names are used for the pure substance and for the aqueous solution, those generally considered to be strong acids (ionize completely in water) are underlined

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Acid Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>hydrochloric acid</td>
</tr>
<tr>
<td>HBr</td>
<td>hydrobromic acid</td>
</tr>
<tr>
<td>HI</td>
<td>hydroiodic acid</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>nitric acid</td>
</tr>
<tr>
<td>HNO(_2)</td>
<td>nitrous acid</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>sulfuric acid</td>
</tr>
<tr>
<td>H(_2)SO(_3)</td>
<td>sulfurous acid</td>
</tr>
</tbody>
</table>
**Bases** are substances which either

1. Increase OH\(^-\) ion concentration in water, or
2. Decrease H\(_3\)O\(^+\) ion concentration in water

To see why these statements are equivalent, we must consider the autoionization of water again.

It is an equilibrium

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

and \( K_{eq} = [\text{H}_3\text{O}^+] \times [\text{OH}^-] / [\text{H}_2\text{O}]^2 \)

where \([\ ]\) means the concentration of the species within the braces in \(\text{mol L}^{-1}\)

But in aqueous solution, the concentration of water, \([\text{H}_2\text{O}]\), is very nearly constant and \(= 55 \text{ mol L}^{-1}\) (55 molar).

(1 L has a mass of 1000 g and contains 1000/MM \(\text{H}_2\text{O}\) mols of water

\[= 1000 \text{ g L}^{-1} / 18 \text{ g mol}^{-1} = 55 \text{ mol L}^{-1}\]

Omitting \([\text{H}_2\text{O}]\) from the \(K_{eq}\) expression and defining the new “reduced” equilibrium constant as \(K_w\) gives

\[K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}\]

or more simply as \([\text{H}^+] [\text{OH}^-]\)

this is called the Ion **Product of Water**

Its numerical value at 25\(^\circ\) is \(1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}\)

Since \([\text{H}_3\text{O}^+] = [\text{OH}^-]\) in pure water then it follows……

\[[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{(1 \times 10^{-14})} = 1 \times 10^{-7} \text{ mol L}^{-1} = 1 \times 10^{-7} \text{ M}\]

This is a very small concentration of ions. Pure water is not good conductor of electricity.
Note that $[\text{H}_3\text{O}]^+$ and $[\text{OH}^-]$ are inversely related —

as $[\text{H}_3\text{O}]^+$ increases, $[\text{OH}^-]$ decreases.

Thus in acidic solution as $[\text{H}_3\text{O}]^+$ is high,

$[\text{OH}^-]$ must be very low.

For example:

In 0.1 M HCl, the acid is 100% dissociated (remember; it is a strong acid) and hence the $[\text{H}_3\text{O}]^+$ concentration is also 0.1 M

$$K_w = [\text{H}_3\text{O}]^+ [\text{OH}^-] = 1 \times 10^{-14} \text{M}^2$$

$$[0.1] [\text{OH}^-] = 1 \times 10^{-14} \text{M}^2$$

$$\therefore [\text{OH}^-] = 1 \times 10^{-13} \text{M}$$
Examples of Bases:

1. Soluble hydroxides of the Group 1 metals

   \[ \text{NaOH} + \text{H}_2\text{O} \rightarrow \text{Na}^+(aq) + \text{OH}^-(aq) \]

2. \[ \text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(aq) + \text{OH}^-(aq) \]
   ammonia \hspace{1cm} ammonium

In 0.1 M NaOH solution, [OH\(^-\)] = 0.1 M

\[ \therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{(1.0 \times 10^{-14})}{0.1} = 1.0 \times 10^{-13} \text{ M} \]

Many metal oxides and hydroxides are insoluble in water, but act as bases by reacting with acids by decreasing [H\(^+\)]

\[ \text{Mg(OH)}_2(s) + 2 \text{H}^+ \rightarrow \text{Mg}^{2+} + 2 \text{H}_2\text{O} \]

\[ \text{ZnO(s)} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{O} \]

Mg(OH\(_2\)) is acting as a base. As does zinc oxide
The reaction of acid and base (Neutralization) occurs very rapidly.

The key reaction is:

\[ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

**Example:**

\[ \text{HBr} + \text{NaOH} \rightarrow \text{NaBr} + \text{H}_2\text{O} \]

Strong acid strong base ionic salt

\[ \text{H}^+ + \text{Br}^- \quad \text{Na}^+ + \text{OH}^- \quad \text{Na}^+ + \text{Br}^- \]

The \( \text{Na}^+ \) and \( \text{Br}^- \) are spectator ions, taking no part in the reaction except to balance charge.
Expressing Acidity — the pH Scale

The quantity pH (power of hydrogen) is defined as
\[ \text{pH} = -\log [\text{H}^+] \]

The pH scale is a convenient one for expressing the concentration of H\(^+\) (hydronium) ions.

In pure water,
\[ [\text{H}^+] = 1.0 \times 10^{-7} \]
\[ \text{pH} = -\log (1.0 \times 10^{-7}) = 7.00 \]
This is called a neutral solution.

Because of the minus sign, pH decreases as [H\(^+\)] in solution increases
\[ \text{pH} < 7.00 \quad [\text{H}^+] > 1.0 \times 10^{-7} \quad \text{solution is acidic} \]
\[ \text{pH} > 7.00 \quad [\text{H}^+] < 1.0 \times 10^{-7} \quad \text{solution is basic} \]

Now some example problems:

1. A solution has [H\(^+\)] = 1.6 x 10\(^{-3}\) M. What is the pH?
   \[ \text{Log} (1.6 \times 10^{-3}) = -2.80 \quad \text{pH} = +2.80 \text{ (acidic)} \]

2. What is [H\(^+\)] in a solution of pH 8.63?
   \[ \text{Remember that} \quad -\log[H^+] = 8.63, \text{ and therefore} \quad \text{Log} [\text{H}^+] = -8.63 \]
   \[ \therefore [\text{H}^+] = 10^{-8.63} = 2.3 \times 10^{-9} \text{ M (basic)} \]
   \[ [\text{H}^+] = 10^{-\text{pH}} \]

Calculate [OH\(^-\)] in each of the above cases
\[ \text{Remember that} \quad [\text{H}^+] [\text{OH}^-] = 1.0 \times 10^{-14} = K_w \]

1. \[ [\text{OH}^-] = K_w / [\text{H}^+] = 1.0 \times 10^{-14} / 1.6 \times 10^{-3} = 6.3 \times 10^{-12} \text{ M} \]
2. \[ [\text{OH}^-] = 1.0 \times 10^{-14} / 2.3 \times 10^{-9} = 4.3 \times 10^{-6} \text{ M} \]
Similarly, we use pOH to express [OH⁻] concentration
\[ \text{pOH} = -\log [\text{OH}^-] \]

Since \([H^+][OH^-] = K_w\) Take logs to get
\[ \log [H^+] + \log[OH^-] = \log K_w \]
or if \(pK_w = -\log K_w\)

\[ \text{pH} + \text{pOH} = pK_w = 14.00 \text{ (at } 25^\circ) \]
or \(\text{pOH} = 14 - \text{pH}\)

As pH ranges from 0 (acidic) to 14 (basic), pOH ranges from 14 to 0.

e.g., in example 1 above, pH = 2.80

\[ \therefore \text{pOH} = 14.0 - 2.80 = 11.20 \]

**Stoichiometry** of reaction for acids and bases is easy—

\(H^+\) and \(OH^-\) react in 1:1 ratio

Concentrations are always given in molarities, M units of mol L⁻¹. And. Acid + base = salt + water
Problems are of two types

1. Neutralization – equal amounts of H+ and OH–
2. Mixing problems – either H+ or OH–

EXAMPLES

What volume of 0.120 M NaOH will neutralize 25.0 ml of 0.160 M HCl?

The reaction is:

\[ \text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} \]

1 mol of HCl reacts with 1 mol NaOH

Now from the definition of molarity we know: that for neutralization:

\[ \text{Moles of Acid} = \text{Moles of Base} \]

And

\[ M_{(\text{acid})} \times V_{(\text{acid in litres})} = \text{Moles of Acid} = \text{Moles of Base} = M_{(\text{base})} \times V_{(\text{base in litres})} \]

Or

\[ M_A V_A = M_B V_B \]

\[ 0.160 \times 0.0250 = 0.120 \times V_B \]

\[ V_B = 0.033 \text{ L} = 33 \text{ mL} \]
Another EXAMPLE

5.00 g NaOH is dissolved in 750 mL of water. A 25.0 mL portion neutralizes 16.0 mL of H$_2$SO$_4$ solution. What is the H$_2$SO$_4$ concentration?

Write the balanced reaction

H$_2$SO$_4$ + 2 NaOH → Na$_2$SO$_4$ + 2 H$_2$O

Note that 2 moles of NaOH react with one mole of H$_2$SO$_4$.

If we know how many moles of NaOH reacted we can easily calculate the number of moles H$_2$SO$_4$ present and hence the concentration.

Begin with concentration of NaOH:

M$_{NaOH}$ – Moles NaOH/Volume solution = (mass NaOH/Molar mass NaOH)/Volume

M$_{NaOH}$ = (5/40)/0.75 = 0.167

Now the number of moles of NaOH = MV = 0.167 x 0.025 = 0.004175 moles

Therefore the number of moles H$_2$SO$_4$ = 4.17 x 10$^{-3}$/2 = 2.08 x 10$^{-3}$

And $M_AV_A = \text{moles acid} = 2.08 \times 10^{-3} = MA \times 0.016$

So that: $M_A = 0.13$
Yet another EXAMPLE

An organic acid is known to be diprotic. When 0.125 g is dissolved in water, it requires 17.5 mL of 0.0893 M KOH to neutralize. What is the molar mass of the acid?

Since we are told the acid is diprotic, we know that each mol of the acid will require 2 mol of KOH.

First, compute the number of mol of KOH = \( M_{KOH} V_{KOH} \) in litres

\[
= \left( \frac{17.5 \text{ mL}}{1000 \text{ ML L}^{-1}} \right) \times 0.0893 = 1.563 \times 10^{-3} \text{ mol}
\]

This will react with

\[
1.563 \times 10^{-3} \div 2 = 7.81 \times 10^{-4} \text{ mol acid}
\]

So now we now know that:

\[
0.125 \text{ g of this acid is } 7.81 \times 10^{-4} \text{ mol}
\]

\[
\therefore \text{ MM} = \frac{\# \text{ g}}{\# \text{ mol}} \]

\[
= 0.125 \text{ g} \div 7.81 \times 10^{-4} \text{ mol} = 160 \text{ g mol}^{-1}
\]
A Special Class of Problems: MIXING PROBLEMS

When acids and bases are mixed, an excess of one often remains (Either the acid or the base turns out to be the limiting reagent). For example,

What is the pH of a solution made by mixing 25.0 mL of 0.140 M NaOH with 16.0 mL of 0.150 M HCl? (As always write down the reaction: HCl + NaOH → NaCl + H₂O)

Compute # of mols:
NaOH: \(\frac{25.0}{1000} \times 0.140 = 0.00350\) mol OH⁻
HCl: \(\frac{16.0}{1000} \times 0.150 = 0.00240\) mol H⁺
There is therefore an excess of OH⁻:
\(0.00350 - 0.00240 = 0.00110\) mol

But the total volume of solution is
\(16.0 + 25.0 = 41.0\) mL = 0.041 L
\[\therefore [\text{OH}^-] = \frac{0.00110}{0.041} = 0.0268\] M

pOH = –log[0.0268] – 1.57; pH = 14.0 – 1.57 = 12.43
Another Mixing EXAMPLE
What mass of solid Ca(OH)$_2$ must be added to 10.0 L of an acidic solution to change its pH from 1.0 to 2.5?
Since of solid Ca(OH)$_2$ is used, assume no change in solution volume.

We are given 2 values of pH, so we can compute the [H$^+$] values in each case

For the pH = 1 soln: \[ [H^+] = 10^{-1} \text{ M} = 0.100 \text{ M} \]

\[ \therefore 10 \text{ L contains } 10 \text{ L} \times 0.100 \text{ M} = 1.00 \text{ mol H}^+ \]

At pH = 2.5, \[ [H^+] = 10^{-2.5} = 3.2 \times 10^{-3} \text{ M} \]

So 10 L contains 10.0 x 3.2 x 10$^{-3}$ mol = 0.032 mol H$^+$

Adding Ca(OH)$_2$ therefore decreased [H$^+$] by 1.00 – 0.32

0.97 mol H$^+$ (= mols of OH added)

(Remembering that: Ca(OH)$_2$ + 2 H$^+$ → Ca$^{2+}$ + 2 H$_2$O)

Need 0.97 mol /2 of Ca(OH)$_2$ = 0.48 mol

= 0.48 x MM g of Ca(OH)$_2$

= 0.48 x 74 g Ca(OH)$_2$

= 36 g Ca(OH)$_2$