2. Acids and Bases

1. The Arrhenius Definition of Acids and Bases

In this theory acids and bases are defined according to their chemical formula and their behaviour in water.

Acid according to Arrhenius: substance that releases H^+ (aq) ions when dissolved in water.

HCl, HNO_3, HCN, H_2SO_4, H_3PO_4, ...

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

Base according to Arrhenius: substance that releases OH^-(aq) ions when dissolved in water.

$NaOH$, KOH, $Ba(OH)_2$, ...

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

An acid and a base neutralize each other with formation of water. The net ionic equation is:

$H^+(aq) + OH^-(aq) \rightarrow H_2O(aq)$

with $\Delta_r H^o = -55{,}9 \ \frac{kJ}{mol}$

The standard reaction enthalpy $\Delta_r H^o$ for this reaction is independent of the original acid or base that reacted. The definition of acids and bases according to Arrhenius is limited to water as the solvent and does not provide an explanation for the base behaviour of substances such as NH_3, CO_3^{2-}, PO_4^{3-},...

2 The Brønsted-Lowry Definition of Acids and Bases

In this concept, acid-base reactions involve the transfer of H^+ between two compounds.

A Brønsted acid is a proton donor and has a proton in its chemical formula.

HCl, HNO_3, $H_2PO_4^-$, ...

A Brønsted base is a proton acceptor. In order to be able to accept the donated proton, this compound must have a lone pair of electrons to which the donated proton can covalently bond.

OH^-, NH_3, F^-, CO_3^{2-}, ...

In an acid-base reaction, a proton transfer occurs from the acid to the base; the reaction can only occur when both acid and base are present. When an acid or a base is dissolved in water, an acid-base reaction will occur because water acts as a reacting partner:

$HCl\ (g) + H_2O\ (aq) \rightarrow Cl^-\ (aq) + H_3O^+\ (aq)$

Transfer of H^+ from the acid HCl to H_2O that acts as a base (O in water has two lone electron pairs). The species H_3O^+ is called **the hydroniumion.**

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

Transfer of the acid H_2O to the base NH_3 (N in NH_3 has one lone electron pair).

From the foregoing it follows that water can react either as an acid or a base: water is an **ampholyte** (amphoteric species).

2.1 Conjugate Acid-Base Pairs

When the former reactions are considered in the reverse direction, i.e. from the right to the left, it is clear that these reverse reactions also involve transfer of a proton. In these reverse reactions H_3O^+(aq), resp. NH_4^+(aq) act as the acid and Cl^-(aq), resp. OH^-(aq) as the base. The sets of species NH_4^+/NH_3, HCl/Cl^-, H_2O/OH^- and H_3O^+/H_2O are called **conjugate acid-base pairs**. Every acid has a conjugate base and every base has a conjugate acid. A Brønsted-Lowry neutralization reaction can then be defined as the reaction of an acid with a base with formation of the corresponding conjugate base and acid. In Table 1 some examples of conjugate acid-base pairs are shown.

$Acid_1 + Base_2$	$\rightleftharpoons$	$Base_1 + Acid_2$
$HCl + H_2O$	$\rightleftharpoons$	$Cl^- + H_3O^+$
$H_2O + NH_3$	$\rightleftharpoons$	$OH^- + NH_4^+$
$HOAc + H_2O$	$\rightleftharpoons$	$OAc^- + H_3O^+$
$HOAc + NH_3$	$\rightleftharpoons$	$OAc^- + NH_4^+$
$NH_4^+ + CO_3^{2-}$	$\rightleftharpoons$	$NH_3 + HCO_3^-$
$H_2PO_4^- + OH^-$	$\rightleftharpoons$	$HPO_4^{2-} + H_2O$
$HPO_4^{2-} + SO_3^{2-}$	$\rightleftharpoons$	$PO_4^{3-} + HSO_3^-$
$H_3O^+ + OH^-$	$\rightleftharpoons$	$H_2O + H_2O$

Table 1: selected conjugate acid-base pairs.

Three important remarks can be made:

1. In every reaction or equilibrium there are 2 conjugate acid-base pairs
2. Acids and bases can be neutral, cationic or anionic
3. A particle can act as an acid or a base, dependent on the other component in the reaction.

The acid-base neutralization reaction according to Arrhenius is the last example in Table 1.

The Brønsted-Lowry theory can be used in solvents, different from water.

In $NH_3(l)$ (am = ammonia as the solvent milieu)

$$HClO_4(am) + NH_3(l) \rightleftharpoons ClO_4^-(am) + NH_4^+(am)$$

$$NH_4^+(am) + NH_2^-(am) \rightleftharpoons NH_3(am) + NH_3(am)$$

2.2 Relative Strength of Acids and Bases

The equilibrium position of the general acid-base reaction:

$HA + B \rightleftharpoons A^- + HB^+$

is determined by the relative acid strength of HA in comparison to HB^+ and the relative base strength of B in comparison with A^-. The position can be calculated by means of the equilibrium constant *K* which is determined experimentally.

$$K = \frac{\left[A^-\right]\left[HB^+\right]}{[HA][B]}$$

$HCl + H_2O \rightarrow Cl^- + H_3O^+$ $K >> 1$

The equilibrium is very strongly positioned to the right:

Relative acid strength: $HCl >> H_3O^+$

Relative base strength: $H_2O >> Cl^-$

$HF + H_2O \rightleftharpoons F^- + H_3O^+$ $K = 7.2 \times 10^{-4}$

The equilibrium is positioned to the left:

Relative acid strength: $H_3O^+ > HF$

Relative base strength: $F^- > H_2O$

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ $K = 1.8 \times 10^{-5}$

The equilibrium is positioned to the left:

Relative acid strength: $NH_4^+ > H_2O$

Relative base strength: $OH^- > NH_3$

From these examples it can be seen that strong acids have weak conjugate bases and vice versa. The equilibrium position of a general acid-base equation is positioned in the direction of the weakest Brønsted acid and the weakest Brønsted base.

In Table 2 some Brønsted acids and bases are ranked according to their relative strength.

Behaviour in water	Acid	H_2O	Base	Behaviour in water
Strong acid	$HClO_4$	$\rightarrow$	ClO_4^-	Very weak base, weaker than water
	HCl	$\rightarrow$	Cl^-	
	HNO_3	$\rightarrow$	NO_3^-	
	H_3O^+		H_2O	
Weak acid	HF	$\rightleftharpoons$	F^-	Weak base
	HNO_2	$\rightleftharpoons$	NO_2^-	
	HOAc	$\rightleftharpoons$	OAc^-	
	HOCl	$\rightleftharpoons$	OCl^-	
	NH_4^+	$\rightleftharpoons$	NH_3	
	H_2O		OH^-	
Very weak acid, weaker than water	NH_3	$\leftarrow$	NH_2^-	Strong base
	H_2	$\leftarrow$	H^-	

Table 2: relative strength of selected Brønsted acids and bases

This ranking allows to predict the equilibrium position of an acid base reaction between two acid base pairs.

$HSO_4^- + NH_3 \rightleftharpoons SO_4^{2-} + NH_4^+$

HSO_4^- is a stronger acid than NH_4^+ and NH_3 is a stronger base than SO_4^{2-} : equilibrium to the right.

$OAc^- + H_2O \rightleftharpoons HOAc + OH^-$

OAc^- is a weaker base than OH^- and HOAc is a stronger acid than H_2O: equilibrium to the left.

It can hence be concluded that, in water as the solvent, every acid that is stronger than H_3O^+ is completely converted in its conjugate base with formation of H_3O^+. H_3O^+ is the strongest acid that can exist in water, all stronger acids are converted into H_3O^+.

In a similar way every base that is stronger than OH^- will be converted into its conjugate acid and OH^-:

$S^{2-} + H_2O \rightarrow HS^- + OH^-$

OH^- is the strongest base that can exist in water, all stronger bases are converted into OH^-.

When we want to determine the difference in acid strength between for instance HCl and HNO_3 , we have to use a solvent that is a stronger acid than water, e.g. HOAc.

HOAc as a solvent is less prawn to accept a proton from HCl or HNO_3 than water. In this way, a differentiation on acid strength between HCl and HNO_3 becomes possible.

The following acid–base equilibriums occur:

$HCl(ac) + HOAc(ac) \overset{K_{HCl}}{\rightleftharpoons} Cl^-(ac) + H_2OAc^+(ac)$

$HNO_3(ac) + HOAc(ac) \overset{K_{HNO_3}}{\rightleftharpoons} NO_3^-(ac) + H_2OAc^+(ac)$

with $K_{HCl} > K_{HNO_3}$. The notation (ac) stands for acetic acid medium.

In a similar way the relative base strength of strong bases such as NH_2^-, S^{2-}, O^{2-}, ... can be determined in a solvent that is a stronger base that water, e.g. $NH_3(l)$.

3 Molecular Structure and Acid Strength

The acid strength of an acid HB in a solvent S is determined by the equilibrium position of

$HB + S \rightleftharpoons B^- + HS^+$

with $K = \frac{\left[B^-\right]\left[HS^+\right]}{\left[HB\right]}$[1]

the equilibrium constant: the acid dissociation constant of HB in the solvent S.

According to their composition, acids are classified in different groups, i.e. binary non-metal hydrides, oxoaxids, hydrated metal ions and Brønsted nitrogen bases.

3.1 Binary Non-metal Hydrides

These acids are composed of hydrogen and one non-metal element, examples are H_2O, HCl, H_3N, HF, ..

3.2 Oxoacids

Acids composed of hydrogen, oxygen and some other element are called oxoacids. A common feature to the structure of all oxoacids is the presence of O-H groups bonded to some central atom. The H-atom on this oxygen can be used in an acid-base reaction.

A general formula of oxoacids is $(HO)_mZ(O)_n$ with HO and O directly covalently bond to a central atom Z (see figure for nitric acid (HNO_3) and phosphoric acid (H_3PO_4)).

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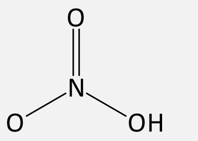
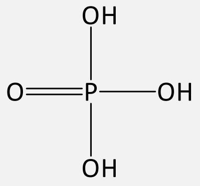
[1] Because the solvent is in excess, it's activity is one. Therefore the concentration of the solvent is omitted from this expression.



HNO_3 Z = N, m = 1, n = 2



H_3PO_4 Z = P, m = 3, n = 1

Examples of common oxoacids are HOCl, HNO_3, H_2SO_4 and H_3PO_4.

3.3 Hydrated Metal Ions

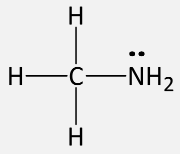
In aqueous solutions, some metal ions act as an acid. This can be explained as follows: ions are hydrated in water. When the metal ion is small and carries a charge larger than 1+, the H–O-bond in one of the water molecules of the hydration sphere of the metal ion becomes very strongly polarized. As a consequence, the hydrated metal ion acts as a Brønsted acid:

$$[M(H_2O)_x]^{n+}(aq) + H_2O \rightleftharpoons [M(H_2O)_{x-1}(OH)]^{(n-1)+} + H_3O^+$$

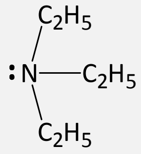
Examples: $[Ni(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$

3.4 Brønsted Nitrogen Bases

These can be considered as derivatives of NH_3 where one or more H-atoms are replaced by hydrocarbon groups (alkyl groups), examples are methylamine and triethylamine.



methylamine



triethylamine

15.4 Autoionization Constant of Water - pH-scale

Water has a very low electrical conductivity. It is therefore a very weak electrolyte that, according to the brønsted theory, reacts with itself (this process is called autoionization or autoprotolysis) according to the equation:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

with equilibrium constant:

$$\boxed{K_w = \left[H_3O^+\right]\left[OH^-\right]_{2}}$$

K_w is called the ion-product constant or dissociation constant of water. It's value is 1.00×10^{-14} at 25 °C.

$K_w = 0.12\times10^{-14}$ at 0 °C

$K_w = 9.6\times10^{-14}$ at 60 °C

In pure water the concentrations of H^+ and OH^- are equal. We have:

$$\left[H_3O^+\right] = \left[OH^-\right] = \sqrt{K_w} = 1.00\times10^{-7}\,\frac{\text{mol}}{\text{L}} \text{ at 25 °C.}$$

The autoionization of water has two important consequences:

1. Both ions are always present in aqueous solutions. When compounds are added to water, this may change $[H_3O^+]$ and hence also $[OH^-]$.

2. As K_w is a constant at a given temperature, an increase in the H_3O^+ concentration leads to a decrease in $[OH^-]$ and vice versa.

In acid solution we have $[H_3O^+] > [OH^-]$

In basic or alkaline solution we have $[H_3O^+] < [OH^-]$

In neutral solution we have $[H_3O^+] = [OH^-]$

For every solution the following relationship holds:

$$\left[H_3O^+\right] = \frac{K_w}{\left[OH^-\right]} \qquad \text{or} \qquad \left[OH^-\right] = \frac{K_w}{\left[H_3O^+\right]}$$

pH-scale

In aqueous solutions $[H_3O^+]$ can vary between 1 $\frac{\text{mol}}{\text{L}}$ and 10^{-14} $\frac{\text{mol}}{\text{L}}$. To avoid working with such inconveniently small numbers, the H_3O^+ and OH^- concentration are commonly expressed in a logarithmic p-scale. The pH is defined as the negative logarithm of the concentration of H_3O^+ in the solution, the pOH as the negative logarithm of the concentration of OH^- in the solution, or, in equation form:

$$\boxed{\begin{aligned} \text{pH} &= -\log\left[H_3O^+\right] \\ \text{pOH} &= -\log\left[OH^-\right] \end{aligned}}$$

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[2] The concentration of water is not present in this equation: water is always present in a large excess and hence it's activity is 1.

$K_w = \left[H_3O^+\right]\left[OH^-\right]$ can then be re-written as:

$$\boxed{\mathbf{pH + pOH = -\log K_w = pK_w}}$$

At 25 °C we have :

Acid solution:	**pH < 7**	**pOH > 7**
Basic solution	**pH > 7**	**pOH < 7**
Neutral solution	**pH =7**	**pOH = 7**

The pH-scale is limited to $0 \leq pH \leq 14$. When $[H_3O^+] > 1\ \frac{mol}{L}$ or $[OH^-] > 1\ \frac{mol}{L}$, the aqueous solution is no longer considered as “dilute“.

The pH of an aqueous solution is measured with a pH meter which uses a glass electrode that is sensitive to H_3O^+ ions. Less accurate values can be obtained using acid-base indicators.

5 Strong Acids and Bases in Water

5.1 Strong Acid

Common strong acids are HCl, HBr, HI, H_2SO_4(first step), HNO_3 and $HClO_4$. Strong acids are completely ionized in water: the reaction were the acid is converted into H_3O^+ and the conjugate base proceeds to completion:

$$\boxed{HCl(aq) + H_2O(aq) \rightarrow H_3O^+(aq) + Cl^-(aq) \quad \text{(completed reaction)}}$$

According to Le Chatelier’s principle this means that the autoionization of water is driven to the left:

$$2\ H_2O(l) \overset{\leftarrow}{\rightleftharpoons} H_3O^+(aq) + OH^-(aq)$$

The particles present in solution hence are:

H_3O^+, OH^- and Cl^- with $\left[H_3O^+\right] = \left[H_3O^+\right]_{HCl} + \left[H_3O^+\right]_{H_2O}$. In this equation it is justified to neglect $\left[H_3O^+\right]_{H_2O}$, the amount of hydronium ions formed during the autoionization of water in comparison with $\left[H_3O^+\right]_{HCl}$, the concentration of hydronium ions contributed by HCl. Therefore we have:

$\left[H_3O^+\right] = \left[H_3O^+\right]_{HCl} = c_{HCl}$ with C_{HCl} the formal concentration of the added HCl. It hence follows:

$$\boxed{\mathbf{pH_{strong\ acid} = -\log [H_3O^+] = -\log c_{strong\ acid}}}$$

Worked example 1

Calculate the pH of an aqueous solution of 0.02 $\frac{\text{mol}}{\text{L}}$ HNO_3 at 25°C. What is the concentration of hydroxide ions?

Answer

Reaction: $HNO_3\text{ (aq)} + H_2O\text{ (l)} \rightarrow H_3O^+\text{(aq)} + NO_3^-\text{ (aq)}$

$pH = -\log[H_3O^+] = -\log(0.02) = 1.70$

$pOH = 14 - 1.70 = 12.30 \Rightarrow [OH^-] = 5.0\text{x}10^{-13}\ \frac{\text{mol}}{\text{L}}$

5.2 Strong Base

Some common strong bases include the following: all group IA hydroxides : LiOH, NaOH, KOH, RbOH, CsOH and the group IIA hydroxides $Sr(OH)_2$ and $Ba(OH)_2$. $Mg(OH)_2$ and $Ca(OH)_2$ are slightly soluble and are therefore not considered as strong bases. Strong bases in water are completely dissociated and converted into OH^- and their conjugate acid.

$$\boxed{NaOH\text{(aq)} + H_2O\text{(l)} \rightarrow Na^+\text{(aq)} + OH^-\text{(aq)}\quad \text{(completed reaction)}}$$

According to Le Chatelier’s principle this means that the autoionization of water is driven to the left:

$$2\ H_2O\text{(vl)} \leftarrow H_3O^+\text{(aq)} + OH^-\text{(aq)}$$

As a consequence $\left[OH^-\right]_{H_2O}$ can be neglected in comparison to $\left[OH^-\right]_{NaOH}$.

In the solution we have:

$$\left[OH^-\right] = \left[OH^-\right]_{NaOH} = c_{NaOH}$$

$pOH = -\log c_{NaOH}$

$$\boxed{\mathbf{pH_{strong\ base} = pK_w + \log c_{strong\ base}}}$$

Worked example 2

Calculate the pH of a solution of 3.25 g $Ba(OH)_2$(s) in 500 mL water at 25°C. What is $[H_3O^+]$?

Answer

Reaction: $Ba(OH)_2\text{(s)} \xrightarrow{H_2O} Ba^{2+}\text{(aq)} + 2OH^-\text{(aq)}$

Molar mass = 171.3 g/mol ⇨ 3.25 g = 0.0190 mole (in 500 mL)

⇨ in 1 L: 0.0380 mole = $c_{Ba(OH)_2}$

$[OH^-] = 2 \text{ x } c_{Ba(OH)_2} = 2 \text{ x } 0.0380 \frac{mol}{L} = 0.0760 \frac{mol}{L}$

pOH = -log $[OH^-]$= 1.12 ⇨ pH = 12.88

$[H_3O^+] = 1.3\text{x}10^{-13} \frac{mol}{L}$

Notes

1. When the formal concentration of a strong acid or base is smaller than $10^{-6} \frac{mol}{L}$, the autoionization of water can no longer be neglected.
2. For practical reasons, the brønsted acid-base reaction in water is usually given in a simplified form:

   $HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$ becomes

   $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

   This simplified form corresponds to the reaction according to Arrhenius.

6 Weak Acids in Water

6.1 Monoprotic Weak Acids

Acetic acid (HOAc) will be taken as an illustration for this type of acids. HOAc reacts incompletely with water and the following equilibriums can be considered:

$$HOAc(aq) + H_2O(l) \rightleftharpoons OAc^-(aq) + H_3O^+(aq)$$

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

When the autoionization of water is neglected and we use the simplified form of the ionization of HOAc, we have:

$$HOAc(aq) \rightleftharpoons H^+(aq) + OAc^-(aq)$$

With $K_a = \frac{\left[H^+\right]\left[OAc^-\right]}{\left[HOAc\right]} = 1.8 \times 10^{-5}$ the **acid dissociation constant** at 25 °C.

In table 3, the acid dissociation constants of some selected acids are shown[3]. As strong acids are completely dissociated, their K_a value is much larger than one.

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[3] From Handbook of Chemistry and Physics – 81st edition; values at 25 °C and in dilute solution. Depending on the source, values may slightly differ from these in this table.

Acid		K_a	pK_a
$HClO_4$	perchloric acid	>> 1	
HNO_3	nitric acid		
HBr	hydrobromic acid		
HCl	hydrochloric acid		
$HClO_3$	chloric acid		
Cl_3CCOOH	trichloroacetic acid	2.2×10^{-1}	0.66
HIO_3	iodic acid	1.7×10^{-1}	0.78
$HClO_2$	chlorous acid	1.1×10^{-2}	1.94
$ClCH_2COOH$	chloroacetic acid	1.3×10^{-3}	2.87
HNO_2	nitrous acid	5.6×10^{-4}	3.25
HF	hydrofluoric acid	6.3×10^{-4}	3.20
HOCN	cyanic acid	3.5×10^{-4}	3.46
HCOOH	formic acid	1.8×10^{-4}	3.75
C_6H_5COOH	benzoic acid	6.3×10^{-5}	4.20
$CH_3CH_2CH_2COOH$	butyric acid	1.5×10^{-5}	4.83
HOAc	acetic acid	1.8×10^{-5}	4.74
CH_3CH_2COOH	propanoic acid	1.3×10^{-5}	4.87
HOCl	hypochlorous acid	4.0×10^{-8}	7.40
HOBr	hypobromous acid	2.8×10^{-9}	8.55
HCN	hydrocyanic acid	6.2×10^{-10}	9.21
C_6H_5OH	phenol	1.1×10^{-10}	9.99
H_2O	water	1.0×10^{-14}	14.00

Table 3: Acid dissociation constants of selected monoprotic acids

The extent of the ionization of HOAc is expressed by the **degree of ionization α**. The degree of ionization is, in the case of acetic acid, given by

$$\alpha = \frac{\left[\mathrm{OAc}^-\right]}{\left[\mathrm{HOAc}\right] + \left[\mathrm{OAc}^-\right]}$$

The degree of ionization is a.o. determined by measurements of the conductivity.

Worked example 3

An aqueous solution of HOAc has a concentration of 0.100 $\frac{\mathrm{mol}}{\mathrm{L}}$. Calculate pH, [HOAc], [OAc$^-$] and α. For HOAc, $K_a = 1.82 \times 10^{-5}$

Answer

Reaction: $HOAc(aq) + H_2O(l) \rightleftharpoons OAc^-(aq) + H_3O^+(aq)$

$\frac{mol}{L}$	HOAc	OAc^-	H_3O^+
Initial	0.100	1×10^{-7} (dissociation of water)	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	$1\times10^{-7} + x \approx x$	x

$$K_a = 1.82\times10^{-5} = \frac{x^2}{}$$

⇨ $x = [H_3O^+]_{eq} = [OAc^-]_{eq} = 1.34\times10^{-3}\,\frac{mol}{L}$

⇨ pH = -log $(1.34\times10^{-3}) = 2.87$

⇨$[HOAc]_{eq} = 0.100\,\frac{mol}{L} - 1.34\times10^{-3}\,\frac{mol}{L} = 0.0987\,\frac{mol}{L}$

$$\alpha = \frac{\left[OAc^-\right]}{c_{HOAc}} = \frac{1.34\times10^{-3}}{0.100} = 0.0134$$

The acid is 1.34 % ionized.

Notes

1. When K_a is very small ($< 10^{-3}$), it is justified to neglect x in comparison with $c_{\text{weak acid}}$ when $c_{\text{weak acid}} \geq 10^{-3}\,\frac{mol}{L}$, so $\left[H^+\right] = \sqrt{c_{\text{weak acid}}.K_a}$. In this case we have:

$$\boxed{\mathbf{pH = 1/2\,(p}K_a\mathbf{ - \log}\, c_{\text{weak acid}}\mathbf{)}}$$

2. The degree of ionization of a weak acid increases when it's formal concentration decreases. This can be seen when we repeat worked example 3 with gradually decreasing formal concentrations of HOAc. In Table 3 the results are given.

c_{HOAc}	α (%)	pH
$1.000\,\frac{mol}{L}$	0.42	2.37
$0.100\,\frac{mol}{L}$	1.34	2.87
$0.0100\,\frac{mol}{L}$	4.2	3.37
$0.0010\,\frac{mol}{L}$	13.5	3.89

Table 3: Degree of ionization and pH in solutions with different formal concentrations of acetic acid

This phenomenon can be understood by applying Le Chatelier's principle on the Brønsted equilibrium $HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$.

Dilution means in reality adding extra $H_2O(l)$ so the equilibrium shifts to the right: the degree of ionization increases. We see however an increase of pH because, when water is added, this leads in reality to a formal decrease of the concentration.

6.2 Polyprotic Weak Acids

Acids with more than 1 proton that can be removed are called **polyprotic acids** . Examples are

H_2SO_4, H_3PO_4, H_2S, H_2CO_3, ...

The removal of these protons occurs in subsequent steps. Each step has it's own ionization acid dissociation constant.

H_3PO_4 for example is a weak triprotic acid that dissociates in 3 steps:

step 1 $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$

$$K_{a_1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 6.9 \times 10^{-3}$$

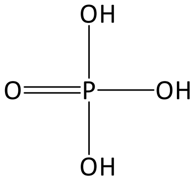
step 2 $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

$$K_{a_2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \times 10^{-8}$$

step 3 $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

$$K_{a_3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = 4.8 \times 10^{-13}$$

The structure of phosphoric acid can be represented by:



In steps 2 and 3, the acid strength gradually decreases because the conjugate base becomes increasingly negative and it becomes more difficult to release H^+.

As a result, $K_{a_1} >> K_{a_2} >> K_{a_3}$ and the behaviour of H_3PO_4 in water will almost completely be determined by the first dissociation step.

Worked example 4

Calculate the pH and the concentration of all particles in an aqueous solution of 0.100 $\frac{\text{mol}}{\text{L}}$ H_3PO_4.

Solution

The H^+-ions present in solution are formed during the dissociation of all three brønsted acids and water:

$$\left[H^+\right]=\left[H^+\right]_{H_3PO_4}+\left[H^+\right]_{H_2PO_4^-}+\left[H^+\right]_{HPO_4^{2-}}+\left[H^+\right]_{H_2O}$$

Because $K_{a_1} >> K_{a_2} >> K_{a_3}$ and $K_{a_1} >> K_w$ we can neglect the last three terms in this equation and we have:

$$\left[H^+\right]=\left[H^+\right]_{H_3PO_4}=x$$

Step 1 $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$

$\frac{\text{mol}}{\text{L}}$	H_3PO_4	H^+	$H_2PO_4^-$
Initial concentration	0.100	0	0
Change in concentration	$-x$	$+x$	$+x$
Equilibrium concentration	$0.100-x$	x	x

$$K_{a_1}=\frac{\left[H^+\right]\left[H_2PO_4^-\right]}{\left[H_3PO_4\right]}=\frac{x^2}{0,100-x}=6.9\times10^{-3}$$

Solving the quadratic equation, we find $x = 2.3\times10^{-2}$

So

$[H^+] = [H_2PO_4^-] = 2.3\times10^{-2}$ $\frac{\text{mol}}{\text{L}}$

pH = 1.64 / pOH = 12.36

Step 2 $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$

$\frac{\text{mol}}{\text{L}}$	$H_2PO_4^-$	H^+	HPO_4^{2-}
Initial concentration	2.3×10^{-2}	2.3×10^{-2}	0
Change in concentration	$-y$	$+y$	$+y$
Equilibrium concentration	$\approx2.3\times10^{-2}$	$\approx2.3\times10^{-2}$	y

$$K_{a_2} = \frac{\left[H^+\right]\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = \frac{2.3\times10^{-2}.y}{2.3\times10^{-2}} = 6.2\times10^{-8}$$

and we calculate

$y = 6.2\times10^{-8}$

$[HPO_4^{2-}] = 6.2\times10^{-8}\ \frac{mol}{L}$

Step 3 $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$

$\frac{mol}{L}$	HPO_4^{2-}	H^+	PO_4^{3-}
Initial concentration	6.2×10^{-8}	2.3×10^{-2}	0
Change in concentration	$-z$	$+z$	$+z$
Equilibrium concentration	$\approx6.2\times10^{-8}$	$\approx2.3\times10^{-2}$	z

$$K_{a_3} = \frac{\left[H^+\right]\left[PO_4^{3-}\right]}{\left[HPO_4^{2-}\right]} = \frac{2.3\times10^{-2}.z}{6.2\times10^{-8}} = 4.8\times10^{-13}$$

and it follows

$z = 1.3\times10^{-18}$

$[PO_4^{3-}] = 1.3\times10^{-18}\ \frac{mol}{L}$

Summarized we have

$[H_3PO_4]$	$7.7\times10^{-2}\ \frac{mol}{L}$
$[H_2PO_4^-]$	$2.3\times10^{-2}\ \frac{mol}{L}$
$[HPO_4^{2-}]$	$6.2\times10^{-8}\ \frac{mol}{L}$
$[PO_4^{3-}]$	$1.3\times10^{-18}\ \frac{mol}{L}$
$[H^+]$	$2.3\times10^{-2}\ \frac{mol}{L}$
$[OH^-]$	$4.3\times10^{-13}\ \frac{mol}{L}$
pH	1.64

Worked example 5

Calculate the pH and the concentration of all particles in an aqueous solution of $0.100 \frac{\text{mol}}{\text{L}}$ H_2SO_4.

For sulphuric acid, the acid ionization constant of the first step, K_{a1}, is very large; $K_{a2} = 1.2\times10^{-2}$; for water $K_w = 1\times10^{-14}$.

Answer

Step 1 $H_2SO_4(aq) \rightleftharpoons H^+(aq) + HSO_4^-(aq)$

K_{a1} very large ⇨ $[HSO_4^-] = 0.100 \frac{\text{mol}}{\text{L}}$

Step 2 $HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq)$

$\frac{\text{mol}}{\text{L}}$	HSO_4^-	H^+	SO_4^{2-}
Initial	0.100	0.100	0
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	$0.100 + x$	x

$$K_{a_2} = 1.2\times10^{-2} = \frac{(0.100+x).x}{(0.100-x)}$$

⇨ $x = [SO_4^{2-}] = 9.85\times10^{-3} \frac{\text{mol}}{\text{L}}$

Summarized we have

$[H_2SO_4]$	$0 \frac{\text{mol}}{\text{L}}$
$[HSO_4^-]$	$(0.100 - 9.85\times10^{-3}) = 0.0902 \frac{\text{mol}}{\text{L}}$
$[SO_4^{2-}]$	$9.85\times10^{-3} \frac{\text{mol}}{\text{L}}$
$[H^+]$	$(0.100 + 9.85\times10^{-3}) = 0.1098 \frac{\text{mol}}{\text{L}}$
pH	1.64
pOH	13.04

Table 5 gives the acid dissociation constants of the different steps for common polyprotic acids at 25°C.

Acid	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}
H_2SO_4 sulphuric acid	>> 1	< 0	1.1×10^{-2}	2.00		
H_2CrO_4 chromic acid	1.8×10^{-1}	0.74	3.2×10^{-7}	6.49		
HOOC-COOH oxalic acid	5.6×10^{-2}	1.25	1.5×10^{-4}	3.81		
H_3PO_3 phosphorous acid	3.0×10^{-2}	1.30	2.0×10^{-7}	6.70		
H_3SO_3 sulphurous acid	1.4×10^{-2}	1.85	6.3×10^{-8}	7.20		
$HOOC(CH_2)COOH$ malonic acid	1.4×10^{-3}	2.85	2.0×10^{-6}	5.70		
H_2S hydrogen sulfide	8.9×10^{-8}	7.05	1.0×10^{-14}	14.00		
H_2CO_3 carbonic acid	4.5×10^{-7}	6.35	4.7×10^{-11}	10.33		
H_3PO_4 phosphoric acid	6.9×10^{-3}	2.16	6.2×10^{-8}	7.21	4.8×10^{-13}	12.32
H_3AsO_4 arsenic acid	5.5×10^{-3}	2.26	1.7×10^{-7}	6.76	5.1×10^{-12}	11.29
$C_6H_8O_7$ citric acid	7.4×10^{-4}	3.13	1.7×10^{-5}	4.76	4.0×10^{-7}	6.40

Table 5: Acid dissociation constants for polyprotic acids[4]

7 Weak Bases in Water

Weak bases such as NH_3 will, in water, react according to a brønsted acid-base reaction that – for NH_3 – can be written as (see § 2):

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

The equilibrium constant is called the **base dissociation constant** and is given by:

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = 1.8\times10^{-5} \text{ (at 25°C)}$$

---

[4] Values from "Handbook of Chemistry and Physics"; 81st edition. Depending on the source, values may slightly differ from these in this table.

The base dissociation constant for some weak bases are shown in table 6.

Base	K_b	pK_b
$(CH_3)_2NH$ dimethylamine	5.4×10^{-4}	3.27
CH_3NH_2 methylamine	4.6×10^{-4}	3.34
$CH_3CH_2NH_2$ ethylamine	4.5×10^{-4}	3.35
$(CH_3)_3N$ trimethylamine	6.3×10^{-5}	4.20
NH_3 ammonia	1.8×10^{-5}	4.75
N_2H_4 hydrazine	1.3×10^{-6}	5.90
NH_2OH hydroxylamine	8.7×10^{-9}	8.06
C_5H_5N pyridine	1.7×10^{-9}	8.77
$C_6H_5NH_2$ aniline	7.4×10^{-4}	9.13

Table 6: Base constants for some weak bases[5]

Relationship between K_a and K_b for a conjugate acid base pair

For a conjugate acid-base pair HA/A^- the following brønsted acid-base reactions can be written:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$$

The sum of both reactions gives the autoionization of water.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

According to the principles, elaborated in the chapter "Chemical Equilibrium" the following relationship holds:

$$\frac{\left[H_3O^+\right]\left[H^-\right]}{[HA]} . \frac{[HA]\left[OH^-\right]}{\left[A^-\right]} = \left[H_3O^+\right]\left[OH^-\right] = K_w$$

or

$$\boxed{K_a . K_b = K_w}$$

---

[5] From 'Handbook of Chemistry and Physics", 81st edition. Dependent on the source values may slightly differ from these in this table.

with K_a the acid dissociation constant of the acid HA and K_b the base dissociation constant of the conjugate base A^-. For every conjugate acid-base pair we have:

$$\boxed{\mathbf{p}K_\mathbf{a} + \mathbf{p}K_\mathbf{b} = \mathbf{p}K_\mathbf{w}}$$

NH_3/NH_4^+

$K_b(NH_3) = 1.8\times10^{-5}$ (25 °C) $\Rightarrow$ $pK_b(NH_3) = 4.74$ $\Rightarrow$ $pK_a(NH_4^+) = 9.26$

HF/F^-

$K_a(HF) = 6.3\times10^{-4}$ (25 °C) $\Rightarrow$ $pK_a = 3.20$ $\Rightarrow$ $pK_b(F^-) = 10.80$

Worked example 6

Calculate the pH and the concentration of all particles in an aqueous solution of 0.100 $\frac{\text{mol}}{\text{L}}$ NH_3

$K_b(NH_3) = 1.82\times10^{-5}$ (25 °C)

Answer

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

$\frac{\text{mol}}{\text{L}}$	NH_3	NH_4^+	OH^-
Initial	0.100	0	1.0×10^{-7}
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	x	$1.0\times10^{-7} + x \approx x$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.100 - x} = 1.82\times10^{-5}$$

⇨ $[NH_4^+] = [OH^-] = x = 1.33\times10^{-3}\ \frac{\text{mol}}{\text{L}}$

⇨ $$[H^+] = \frac{K_w}{[OH^-]} = \frac{1\times10^{-14}}{1.33\times10^{-3}} = 7.5\times10^{-12}\ \frac{\text{mol}}{\text{L}}$$

⇨ pH = 11.12

⇨ $[NH_3] = (0.100 - 1.33\times10^{-3}) = 0.0987\ \frac{\text{mol}}{\text{L}}$

8 Mixtures of Acids or Bases

For solutions where more acids or bases are present in comparable concentrations, the following approximations are valid:

8.1 Solution of Two Strong Acids (Bases)

Solution with 0.01 $\frac{\text{mol}}{\text{L}}$ HCl and 0.02 $\frac{\text{mol}}{\text{L}}$ HNO_3.

Both acids are completely ionized. In the solution we have:

$$\left[H^+\right]=\left[H^+\right]_{HCl}+\left[H^+\right]_{HNO_3}=0.01\frac{\text{mol}}{\text{L}}+0.02\frac{\text{mol}}{\text{L}}=0.03\frac{\text{mol}}{\text{L}}$$

pH = – log (0.03) = 1.52

For solutions of two strong bases, an analogous reasoning can be made.

8.2 Solution of a Strong Acid (Base) and a Weak Acid (Base)

Strong acid $\quad HX(aq) \rightarrow H^+(aq) + X^-(aq)$

Weak acid $\quad HA(aq) \rightleftharpoons H^+(aq) + A^-(aq) \quad$ with $K_a=\frac{\left[H^+\right]\left[A^-\right]}{[HAc]}$

The global amount of $[H^+]$ is equal to:

$$\left[H^+\right]=\left[H^+\right]_{HX}+\left[H^+\right]_{HA}+\left[H^+\right]_{H_2O}$$

When we neglect $\left[H^+\right]_{H_2O}$ and with $\left[H^+\right]_{HX}=c_{HX}$, the only unknown in this equation is $\left[H^+\right]_{HA}$. This leads to the following relationship:

$$\left[H^+\right]=c_{HX}+\left[H^+\right]_{HA}=c_{HX}+x$$

When we apply the condition for equilibrium for HA and when we denote the formal concentration of HA as c_{HA}, this gives, with $\left[H^+\right]=c_{HX}+x$ and with $[A^-] = x$:

$$K_a=\frac{\left(c_{HX}+x\right)x}{\left(c_{HA}-x\right)}$$

From this equation it is possible to calculate x and it becomes possible to determine $[H^+]$.

However, when K_a is small and when $c_{HX} >> c_{HA}$, it is justified to neglect also $\left[H^+\right]_{HA}$. In this case we have: $\left[H^+\right]=c_{HX}$.

For solutions of a strong base and a weak base, an analogue reasoning holds.

8.3 Solutions of Two Weak Acids (Bases)

Calculation of the pH of this type of solutions is not straightforward and will not be discussed in this text.

9 The Lewis definition of Acids and Bases

The Lewis definition of acid and bases gives a more general definition of acids and bases than Brønsted and Lowry. In this definition emphasis is on the role of the electron pair.

A lewis base is any compound that can donate a lone electron pair

A lewis acid is any compound that can accept a lone electron pair from a lewis base.

Compounds that are the product of a the reaction between a lewis acid and a lewis base are called **lewis adducts** or simply **adducts.**

General reaction:

$A + {:}B \rightleftharpoons A\text{–}B$

with

A	lewis acid
:B	lewis base
A–B	lewis adduct

The lewis definition of an acid is, in comparison to the definitions of Arrhenius and Brønsted far more general. The lewis acid can only form a new bond with the lone electron pair of the base when it has an empty orbital available or when it can create an empty orbital by reorganization.

$BF_3 + {:}NH_3 \rightleftharpoons F_3B\text{–}NH_3$

acid base adduct

B in BF_3 is deficient in electrons, because it does not have 8 valence-electrons. A covalent B–N-bond is formed by overlap of the empty valence orbital on B and the valence orbital of N that holds the lone electron pair.

$SiF_4 + F^- \rightarrow SiF_5^-$

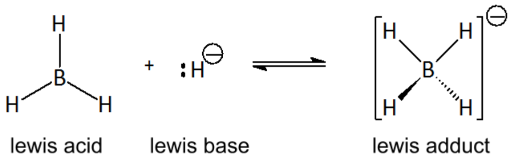
acid base adduct

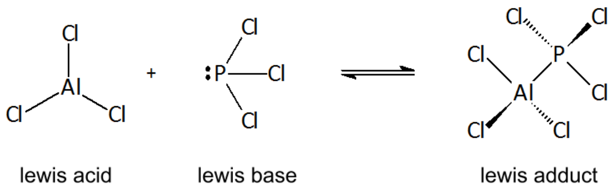
In SiF_4 the Si is sp^3-hybridised. When a 3d-orbital is involved and hybridisation towards sp^3d occurs, an empty hybride orbital becomes available on Si. This empty orbital can overlap with a p orbital of F^- that contains a lone electron pair.

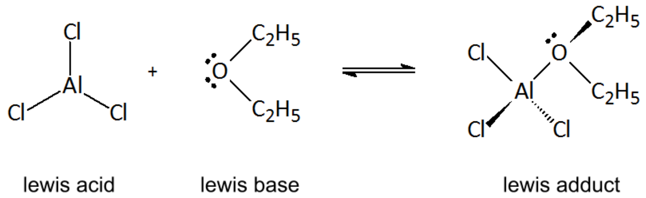
Categories of Lewis Acids

1. Molecules with vacant valence orbitals

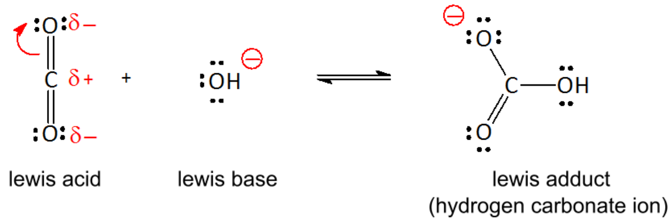
Compounds with a central atom that is deficient in electrons, examples are B, Al.

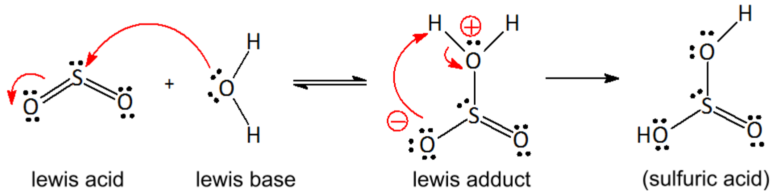






2. Molecules with delocalized π bonds involving oxygen. Examples are CO_2, SO_2, SO_3, ...





3. Cations of transition metals

Removing electrons from a transition metal atom always generates vacant valence orbitals, so these cations can act as lewis acids.

The 3d-metal ions have empty 4s- and empty 4p-orbitals. Also 3d- and 4d-orbitals can be involved. In this situation they react as lewis acids when they are dissolved in water (see section 3.3) and they form lewis adducts with the solvent.

$[Zn(H_2O)_4]^{2+}(aq)$, $[Ni(H_2O)_6]^{2+}(aq)$, $[Fe(H_2O)_6]^{3+}(aq)$

These adducts in water are also hydrated. For simplicity of the notation, the formula is usually written as Zn^{2+}(aq), Ni^{2+}(aq), Fe^{3+}(aq).

When a stronger base is added to a solution of the adduct, the weaker base will in the adduct be **substituted** by the stronger one.

$$[Ni(H_2O)_6]^{2+}(aq) + 6\ NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) + 6\ H_2O(l)$$

This kind of equilibriums will be treated in the chapter “Ionic Equilibriums”.

10 Acid-base Properties of Salts

Salts are ionic compounds that can be regarded as the neutralisation products of an acid and a base.

NaCl (NaOH + HCl)

When salts dissolve in water, they will dissociate in cations and anions, and they will not interact with each other (in dilute solutions). In water, these ions can act as an acid or a base and they will hence have an influence on the pH of the solution. This acid-base reaction between ions and water is called **hydrolysis**. The behaviour of the salt will depend on the nature of the original acid and the base from which they were formed.

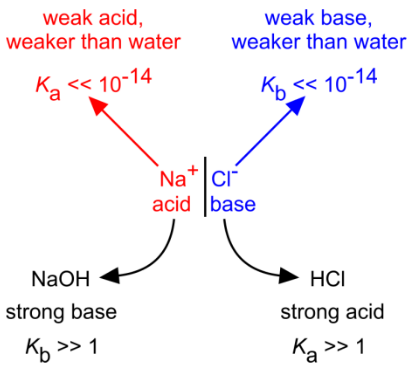
10.1 Salts of a Strong Acid and a Strong Base: none of the Ions is Hydrolysed

Example: NaCl

Dissociation: $NaCl(s) \xrightarrow{H_2O} Na^+(aq) + Cl^-(aq)$

Hydrolysis: $Na^+(aq) + H_2O(l) \leftarrow NaOH(aq) + H^+(aq)$

$Cl^-(aq) + H_2O(l) \leftarrow HCl(aq) + OH^-(aq)$



The Na^+-ion has an electric charge of only +1 and is relatively large. In solution it will remain hydrated by means of ion-dipole interactions. There will not be an additional polarization of the H-O-bonds in the hydration shell: no hydrolysis.

The Cl^--ion is the conjugate base of the strong acid HCl and is therefore a weaker base than water: it is only hydrated and does not show hydrolysis.

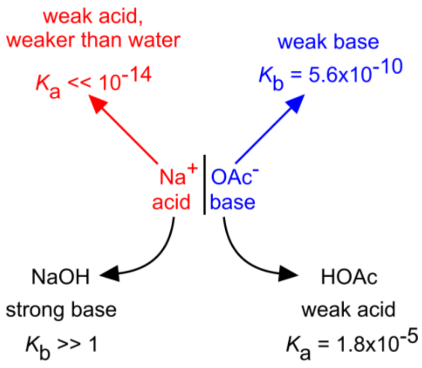
A solution of NaCl hence reacts neutral. The Cl^--, Br^--, I^--, NO_3^--, ClO_4^-- and SO_4^{2-}-salts of the metals from groups 1 and 2 react in an analogous way (exception: Be^{2+}).

Salts from a strong acid and a strong base react neutral.

10.2 Salts of a Weak Acid and a Strong Base: Hydrolysis of the Anion

Example: NaOAc

Dissociation: $NaOAc(s) \xrightarrow{H_2O} Na^+(aq) + OAc^-(aq)$



Hydrolysis: $OAc^{-}(aq) + H_2O(l) \rightleftharpoons HOAc(aq) + OH^{-}(aq)$

The Na^{+}-ion does not hydrolyse. OAc^{-} is a stronger base than water and partially hydrolyses. As a consequence $[OH^{-}]$ increases in comparison with pure water. A solution of NaOAc reacts as a weak base.

Worked example 7

Calculate the pH of an aqueous 0.100 $\frac{mol}{L}$ NaOAc solution when you know that for HOAc

$K_a = 1.8\times10^{-5}$ at 25 °C.

Answer

Dissociation: $NaOAc\,(s) \xrightarrow{H_2O} Na^{+}(aq) + OAc^{-}(aq)$

Hydrolysis: $OAc^{-}(aq) + H_2O\,(l) \rightleftharpoons HOAc\,(aq) + OH^{-}(aq)$

$\frac{mol}{L}$	OAc^{-}	HOAc	OH^{-}
Initial	0.100	0	1.10^{-7}
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	x	$1.10^{-7} + x \approx x$

$$K_h = \frac{[HOAc]\left[OH^{-}\right]}{\left[OAc^{-}\right]} = \frac{x^2}{0.100 - x} = ?$$

(h) $OAc^{-}(aq) + H_2O\,(l) \rightleftharpoons HOAc\,(aq) + OH^{-}(aq)$ K_h

(1) $2\,H_2O\,(l) \rightleftharpoons H_3O^{+}(aq) + OH^{-}(aq)$ K_w

(2) $HOAc\,(aq) + OH^{-}(aq) \rightleftharpoons OAc^{-}(aq) + H_2O\,(l)$ K_a

(h) = (1) – (2)

$$\Rightarrow K_h = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

$$\Rightarrow K_h = \frac{[HOAc]\left[OH^{-}\right]}{\left[OAc^{-}\right]} = \frac{x^2}{0.100 - x} = 5.6\times10^{-10}$$

$\Rightarrow x = 7.5\times10^{-6}\,\frac{mol}{L} = [OH^{-}]$

$\Rightarrow$ pOH = 5.12

⇨pH = 14 – 5.12 = 8.88

All salts that have a cation that does not show hydrolysis and an anion that is the conjugate base of a weak acid react in the same way. Examples are: NaF, $NaNO_2$, KCN, ...

Salts from a weak acid and a strong base react weakly basic.

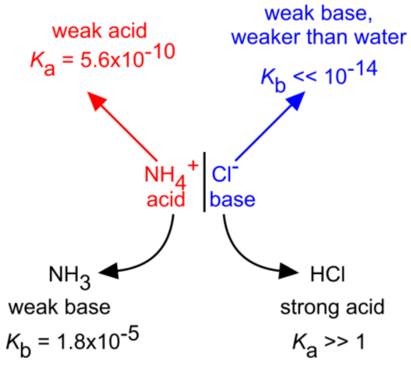
10.3 Salts from a Strong Acid and a Weak Base

Example: NH_4Cl

Dissociation: $NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$

Hydrolysis: $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

The Cl^--ion does not show hydrolysis. The NH_4^+-ion is a stronger acid than H_2O and is partially hydrolysed so $[H_3O^+]$ increases in comparison with pure water. A solution of NH_4Cl reacts slightly acid.



Worked example 8

Calculate the pH of an aqueous 0.100 $\frac{mol}{L}$ solution of NH_4Cl when you know that K_b is 1.8×10^{-5} for NH_3 (at 25 °C).

Answer

Dissociation: $NH_4Cl(s) \xrightarrow{H_2O} NH_4^+(aq) + Cl^-(aq)$

Hydrolysis: $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$\frac{mol}{L}$	NH_4^+	NH_3	H_3O^+
Initial	0.100	0	1.10^{-7}
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100-x$	x	$1.10^{-7} + x \approx x$

$$K_h = \frac{[NH_3]\left[H_3O^+\right]}{\left[NH_4^+\right]} = \frac{x^2}{0.100 - x} = ?$$

(h) $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$ K_h

(1) $2\,H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$ K_w

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

(h) = (1) – (2)

$$\Rightarrow K_h = \frac{K_w}{K_b} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10} = K_{a,NH_4^+}$$

$$\Rightarrow K_h = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.100 - x} = 5.6\times10^{-10}$$

$$x = 7.5\times10^{-6}\ \frac{mol}{L} = [H_3O^+]$$

⇨ pH = 5.12

Salts from an amine and a strong acid react analogously as do the salts from metal ions that react as an acid (see section 3.3) (because of their high charge density (ex. Al^{3+}, Be^{2+})) or because they act as lewis acids (ex. Fe^{3+}, Cu^{2+}, Zn^{2+} , ...) and anions that do not hydrolyse. Examples are $Al(NO_3)_3$, $FeCl_3$, $ZnCl_2$, $Cu(NO_3)_2$, ...

Salts from a strong acid and a weak base react as a weak acid.

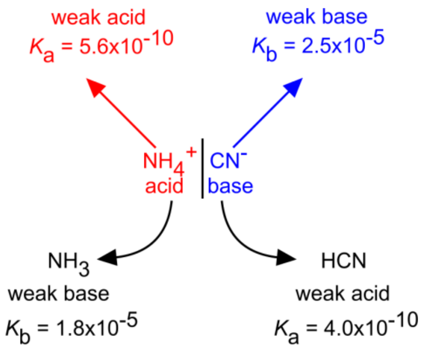
10.4 Salts from a Weak Base and a Weak Acid

Example: NH_4CN

Dissociation: $NH_4CN(s) \xrightarrow{H_2O} NH_4^+(aq) + CN^-(aq)$

Hydrolysis $NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$

$CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq)$



The hydrolysis of the cation increases $[H_3O^+]$, hydrolysis of the anion increases $[OH^-]$.

The equilibrium constant for cation hydrolysis is given by:

$$K_{a_{NH_4^+}} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = 5.6\times10^{-10}$$

The equilibrium constant for anion hydrolysis is given by:

$$K_{b_{CN^-}} = \frac{[HCN]\,[OH^-]}{[CN^-]} = \frac{K_w}{K_{a_{HCN}}} = \frac{10^{-14}}{6.2\times10^{-10}} = 1.6\times10^{-5}$$

Because $K_{b_{CN^-}} > K_{a_{NH_4^+}}$, the solution will react weakly basic.

Worked example 9

Calculate the concentration of all particles and the pH of a solution with a formal concentration of $0.100\ \frac{mol}{L}$ of NH_4CN.

K_b of NH_3 is 1.8×10^{-5}, K_a of HCN is 6.2×10^{-10} at 25°C and $K_w = 1.0\times10^{-14}$

Answer

Dissociation

$NH_4CN(aq) \longrightarrow NH_4^+(aq) + CN^-(aq)$

The pH of the NH_4CN-solution can be calculated by means of the hydrolysis of the cation $NH_4^+(aq)$ as well as by means of the hydrolysis of the anion $CN^-(aq)$. However, as the $NH_4^+(aq)$-can also react directly as an acid with the $CN^-(aq)$-ion as the base, the initial concentration of both ions will be smaller than the formal concentration of $0.100\ \frac{mol}{L}$. These concentrations have to be calculated in advance. To do so, we first have to calculate the equilibrium constant of the direct acid base reaction $NH_4^+(aq) + CN^-(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$. This can be done by combining the following equilibriums with known equilibrium constants:

Hydrolysis equilibriums

a $\quad NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \qquad K_{a_{NH_4^+}} = 5.6\times10^{-10}$

b $\quad CN^-(aq) + H_2O(l) \rightleftharpoons HCN(aq) + OH^-(aq) \qquad K_{b_{CN^-}} = 1.6\times10^{-5}$

c $\quad 2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_w = 1.0\times10^{-14}$

---

a+b-c $\quad NH_4^+(aq) + CN^-(aq) \rightleftharpoons NH_3(aq) + HCN(aq)$

$$K = \frac{K_{a_{NH_4^+}} . K_{b_{CN^-}}}{K_w} = \frac{5.6\times10^{-10} . 1.6\times10^{-5}}{1.0\times10^{-14}} = 0.90$$

$\frac{mol}{L}$	$NH_4^+(aq)$	$CN^-(aq)$	$NH_3(aq)$	HCN(aq)
initial	0.100	0.100	-	-
Δ	$-x$	$-x$	$+x$	$+x$
Equilibrium	$0.100-x$	$0.100-x$	x	x

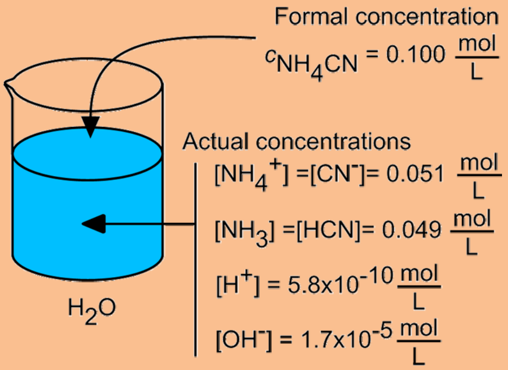
$$K=\frac{[NH_3].[HCN]}{[NH_4^+].[CN^-]}=\frac{x^2}{(0.100-x)^2}=0.90\Rightarrow\frac{x}{0.100-x}=0.95\Rightarrow x=0.049$$

$\frac{mol}{L}$	NH_4^+(aq)	CN^-(aq)	NH_3(aq)	HCN(aq)
Equilibrium	**0.051**	**0.051**	**0.049**	**0.049**

The concentration of protons, $[H^+]$, can be calculated from both hydrolysis constants:

$$[H^+]=K_{a_{NH_4^+}}\cdot\frac{[NH_4^+]}{[NH_3]}=5.6\times10^{-10}\frac{0.051\frac{mol}{L}}{0.049\frac{mol}{L}}=5.8\times10^{-10}\frac{mol}{L}\Rightarrow pH=\mathbf{9.24}$$

$$[OH^-]=K_{b_{CN^-}}\cdot\frac{[CN^-]}{[HCN]}=1.6\times10^{-5}\frac{0.051\frac{mol}{L}}{0.049\frac{mol}{L}}=1.7\times10^{-5}\frac{mol}{L}\Rightarrow pOH=4.77\Rightarrow pH=\mathbf{9.23}$$



10.5 Salts with anions of a polyprotic weak acid

Na_2S

Dissociation $Na_2S(s) \xrightarrow{H_2O} 2\ Na^+(aq) + S^{2-}(aq)$

Hydrolysis (1) $S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$

(2) $HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$

The S^{2-}-ion will undergo, stepwise, 2 hydrolysis steps because S^{2-} as well as HS^- are stronger bases than water. For each step the hydrolysis constant can be calculated when the acid dissociation constants of H_2S are known.

$$K_1=K_{b_{S^{2-}}}=\frac{[HS^-].[OH^-]}{[S^{2-}]}=\frac{K_w}{K_{a_{2_{H_2S}}}}=\frac{1.0\times10^{-14}}{1.0\times10^{-14}}=1$$

$$K_2 = K_{b_{HS^-}} = \frac{[H_2S].\left[OH^-\right]}{\left[HS^-\right]} = \frac{K_w}{K_{a_{1_{H_2S}}}} = \frac{1.0\times10^{-14}}{8.9\times10^{-8}} = 1.1\times10^{-7}$$

Because $K_1 >> K_2$, in further calculations we only have to take the first hydrolysis step into account.

Worked example 10

Calculate the pH of a solution with a formal concentration of 0.100 $\frac{\text{mol}}{\text{L}}$ of Na_2S.

H_2S : $K_{a,1} = 1.1\times10^{-7}$; $K_{a,2} = 1.0\times10^{-14}$ at 25 °C

$K_w = 1.0\times10^{-14}$

Answer

Dissociation $\quad Na_2S\,(s) \xrightarrow{H_2O} 2\,Na^+(aq) + S^{2-}(aq)$

Hydrolysis (1) $\quad S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$

(2) $\quad HS^-(aq) + H_2O(l) \rightleftharpoons H_2S(aq) + OH^-(aq)$

As for these hydrolysis steps $K_{a,1} >> K_{a,2}$, the concentration of OH^- will be determined by the first step only, i.e.:

$$S^{2-}(aq) + H_2O(l) \rightleftharpoons HS^-(aq) + OH^-(aq)$$

$\frac{\text{mol}}{\text{L}}$	S^{2-}	HS^-	OH^-
Initial	0.100	-	-
Change	$-x$	$+x$	$+x$
Equilibrium	$0.100 - x$	x	x

$$⇨ K_{h,1} = \frac{\left[HS^-\right]\left[OH^-\right]}{\left[S^{2-}\right]} = \frac{x^2}{0.100 - x} = \frac{K_w}{K_{a,2}} = 1$$

$x = [OH^-] = 9.2\times10^{-2}\ \frac{\text{mol}}{\text{L}}$

⇨pOH = 1.04; pH = 12.96

Salts such as Na_2CO_3, Na_3PO_4 and Na_2SO_3 react analogously.

10.6 Ampholytes

Ampholytes can react as an acid and as a base. Two types of ampholytes will be discussed here:

1. acid salts of polyprotic acids such as $NaHCO_3$, NaHS, NaH_2PO_4, Na_2HPO_4, ...
2. amino acids such as glycine, alanine, ...

Type 1 – Acid salts

$0.100\ \frac{mol}{L}\ NaH_2PO_4$

Dissociation $NaH_2PO_4(s) \xrightarrow{H_2O} Na^+(aq) + H_2PO_4^-(aq)$

Hydrolysis

1: acid $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons HPO_4^{2-}(aq) + H_3O^+(aq)$

or

$H_2PO_4^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H^+(aq)$

$$K_1 = K_{a_{2H_3PO_4}} = \frac{\left[H^+\right].\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = \mathbf{6.2 \times 10^{-8}}$$

2: base $H_2PO_4^-(aq) + H_2O(l) \rightleftharpoons H_3PO_4(aq) + OH^-(aq)$

or

$H_2PO_4^-(aq) + H^+(aq) \rightleftharpoons H_3PO_4(aq)$

$$K_2 = K_{b_{H_2PO_4^-}} = \frac{\left[H_3PO_4\right].\left[OH^-\right]}{\left[H_2PO_4^-\right]} = \frac{K_w}{K_{a_1}} = \frac{1.0 \times 10^{-14}}{6.9 \times 10^{-3}} = \mathbf{1.4 \times 10^{-12}} \text{ with}$$

$$K_{a_1} = \frac{\left[H^+\right].\left[H_2PO_4^-\right]}{\left[H_3PO_4\right]}$$

This means

- That both hydrolysis steps will proceed for a minor extent (6.2×10^{-8} and 1.4×10^{-12})
- That the solution will react slighty acidic because $K_1 > K_2$
- That we have to take the autoprotolysis of water into account when we calculate the pH of the solution (there is only a small difference between 1.0×10^{-14} and 1.4×10^{-12})

So:

3: water $H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$

$$K_w = 1.0\text{x}10^{-14}$$

Solution

$$\left[H^+\right] = \left[H^+\right]_{\text{formed in reaction 1}} + \left[H^+\right]_{\text{formed in reaction 3}} - \left[H^+\right]_{\text{disappeared in reaction 2}}$$

$$\left[H^+\right] = \left[H^+\right]_1 + \left[H^+\right]_3 - \left[H^+\right]_2$$

$$\left[H^+\right] = \left[HPO_4^{2-}\right] + \left[OH^-\right] - \left[H_3PO_4\right]$$

$$\left[H^+\right] = \frac{K_{a_2}.\left[H_2PO_4^-\right]}{\left[H^+\right]} + \frac{K_w}{\left[H^+\right]} - \frac{\left[H^+\right].\left[H_2PO_4^-\right]}{K_{a_1}}$$

Because the global hydrolysis (1 as well as 2) is very small, we can assume that $[H_2PO_4^-]$ is equal to the formal concentration of NaH_2PO_4, i.e. *c*. When we rearrange this equation we have:

$$\left[H^+\right]\left(1 + \frac{c}{K_{a_1}}\right) = \frac{1}{\left[H^+\right]}\left(K_{a_2}.c + K_w\right)$$

$$\left[H^+\right]^2 = \frac{K_{a_2}.c + K_w}{1 + \frac{c}{K_{a_1}}} = \frac{K_{a_2}.c + K_w}{\frac{K_{a_1} + c}{K_{a_1}}} = \frac{K_{a_1}\left(K_{a_2}.c + K_w\right)}{K_{a_1} + c}$$

$$\boxed{\left[H^+\right]^2 = \frac{K_{a_1}.K_{a_2}.c + K_{a_1}.K_w}{K_{a_1} + c}}$$

$$\left[H^+\right]^2 = \frac{K_{a_1}\left(K_{a_2}.c + K_w\right)}{K_{a_1} + c} = K_{a_1}.K_{a_2}\frac{\left(c + \frac{K_w}{K_{a_2}}\right)}{K_{a_1} + c}$$

$$\text{pH} = \frac{1}{2}\left(\text{p}K_{a_1} + \text{p}K_{a_2}\right) + \frac{1}{2}\log\frac{K_{a_1} + c}{\left(c + \frac{K_w}{K_{a_2}}\right)}$$

Filling in the appropriate numbers we have:

$$\text{pH} = \frac{1}{2}(2.16 + 7.21) + \frac{1}{2}\log\frac{6.9\times10^{-3} + 0.100}{\left(0.100 + \frac{1.0\times10^{-14}}{6.2\times10^{-8}}\right)} = 4.685 + 0.0014 = 4.69$$

When $c >> K_{a_1}$ and $c >> \frac{K_w}{K_{a_2}}$, the equation will be reduced to

$$\mathrm{pH} = \frac{1}{2}\left(\mathrm{p}K_{a_1} + \mathrm{p}K_{a_2}\right)$$

This is the case for solutions of the following ampholytic compounds when $c > 10^{-2}\ \frac{\mathrm{mol}}{\mathrm{L}}$: NaH_2PO_4, Na_2HPO_4 and $NaHCO_3$

$$\boxed{\mathbf{pH} = \frac{1}{2}\left(\mathbf{p}K_a + \mathbf{p}K_a'\right)}$$

with K_a and K_a' the acid dissociation constants you should use in the hydrolysis equilibriums when the ampholyte is dissolved in water.

Solution of 0.1 $\frac{\mathrm{mol}}{\mathrm{L}}$ $NaHCO_3$ with

$$K_a = 4.5\times10^{-7} \text{ and } K_a' = 4.7\times10^{-11}$$

$$\mathrm{pH} = \frac{1}{2}(6.35 + 10.33) = 8.34$$

Type 2 – Amino acids

Glycine $H_2N\text{-}CH_2\text{-}COOH$

This molecule contains both a basic site (the amino group $-NH_2$ with $K_b' = 5.9\mathrm{x}10^{-5}$) and an acidic site (the carbon acid group (-COOH) with $K_a = 4.5\mathrm{x}10^{-3}$). We would usually write this molecule as $H_2N\text{-}CH_2\text{-}COOH$. However, it actually exists in the solid state as a **zwitterion**, a structure which contains both a positive and a negative site but which is overall neutral. In glycine this is the case because the H^+-ion of the carbon acid group is taken up by the amino group $^+H_3N-CH_2-COO^-$. When extra acid is added, the carboxylate group is neutralized with formation of $^+H_3N-CH_2-COOH$. When extra base is added, the ammonia group is neutralised with formation of $H_2N-CH_2-COO^-$. Glycine can hence exist as a salt in three possible forms:

$^+H_3N-CH_2-COOH.Cl^-$	glycine.hydrochloride
$^+H_3N-CH_2-COO^-$	glycine as a zwitterion
$H_2N-CH_2-COO^-.Na^+$	sodium glycinate

Glycine.hydrochloride is a diprotic salt with the following ionization equilibria:

$$^+H_3N-CH_2-COOH(aq) \rightleftharpoons {}^+H_3N-CH_2-COO^-(aq) + H^+(aq) \qquad K_{a_1} = 4.5\times10^{-5}$$

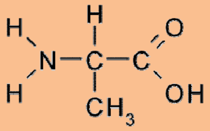
$$^+H_3N-CH_2-COO^-(aq) \rightleftharpoons H_2N-CH_2-COO^-(aq) + H^+(aq) \qquad K_{a_2} = \frac{K_w}{K_b'} = 1.7\times10^{-10}$$

As a zwitterion, glycine behaves as an ampholyte. For a solution of this salt we have:

$$\mathrm{pH}=\frac{1}{2}\left(\mathrm{p}K_\mathrm{a}+\mathrm{p}K_\mathrm{a}^{'}\right)=\frac{1}{2}(4.35+9.77)=7.06$$

Worked example 11

The amino-acid alanine (Ala) can be represented by:



For this compound, $K_b' = 6.2\times10^{-3}$ and $K_a = 7.3\times10^{-5}$. Calculate the pH of a $5.0\times10^{-2}\,\frac{\mathrm{mol}}{\mathrm{L}}$ solution which contains:

a) only the acid form	$^+H_3N\text{-}CH(CH_3)\text{-}COOH$	H_2Ala^+
b) only the zwitterion form	$^+H_3N\text{-}CH(CH_3)\text{-}COO^-$	$HAla^0$
c) only the base form	$H_2N\text{-}CH(CH_3)\text{-}COO^-$	Ala^-

Answer

$K_b' = 6.2\times10^{-3}$ ⇨ $K_{a2}=\frac{K_w}{K_b'}=1.6\times10^{-12}$

$K_{a1} = 7.3\times10^{-5}$ ⇨ $K_b=\frac{K_w}{K_{a1}}=1.4\times10^{-10}$

a) Acid form ; $c = 5.0\times10^{-2}\,\frac{\mathrm{mol}}{\mathrm{L}}$

For H_2Ala^+ we see that $K_{a1} = 7.3\times10^{-5} >> K_{a2} = 1.6\times10^{-12}$

The concentration of H^+(aq) will be determined by the first step!

$$H_2Ala^+\,(aq) + H_2O(l) \rightleftharpoons HAla^0\,(aq) + H_3O^+(aq)$$

$\frac{\mathrm{mol}}{\mathrm{L}}$	H_2Ala^+	$HAla^0$	H_3O^+
Initial	5.0×10^{-2}	-	-
Change	$-x$	$+x$	$+x$
Equilibrium	$5.0\times10^{-2}-x$	x	x

$$K_{a1}=7.3\times10^{-5}=\frac{x^2}{5.10^{-2}-x}$$

⇨ $x = [H_3O^+] = 1.86\times10^{-3}\,\frac{\mathrm{mol}}{\mathrm{L}}$

⇨ pH = 2.73

b) zwitterion; $c = 5.0\times10^{-2}\,\frac{\text{mol}}{\text{L}}$

In solution the ampholyte HAla^0 is present

$$⇨\ \text{pH} = \frac{1}{2}\left(\text{pK}_{a1} + \text{pK}_{a2}\right)$$

$$= ½\ (4.14 + 11.80)$$

$$= 7.97$$

c) base form; $c = 5.0\times10^{-2}\,\frac{\text{mol}}{\text{L}}$

In solution we have Ala^-, this hydrolyses in two steps

Hydrolysis 1: $\text{Ala}^-(aq) + H_2O(l) \rightleftharpoons \text{HAla}^0(aq) + \text{OH}^-(aq)$

The corresponding hydrolysis constant is:

$$K_{h1} = \frac{\left[\text{HAla}^0\right]\left[\text{OH}^-\right]}{\left[\text{Ala}^-\right]} = \frac{\left[\text{HAla}^0\right]\left[\text{OH}^-\right]}{\left[\text{Ala}^-\right]}\frac{\left[H_3O^+\right]}{\left[H_3O^+\right]} = \frac{K_w}{K_{a2}} = \frac{1\times10^{-14}}{1.6\times10^{-12}} = 6.25\times10^{-3}$$

Hydrolysis 2: $\text{HAla}^0(aq) + H_2O(l) \rightleftharpoons H_2\text{Ala}^+(aq) + \text{OH}^-(aq)$

The corresponding hydrolysis constant is:

$$K_{h2} = \frac{\left[H_2\text{Ala}^+\right]\left[\text{OH}^-\right]}{\left[\text{HAla}^0\right]} = \frac{\left[H_2\text{Ala}^+\right]\left[\text{OH}^-\right]}{\left[\text{HAla}^0\right]}\frac{\left[H_3O^+\right]}{\left[H_3O^+\right]} = \frac{K_w}{K_{a1}} = \frac{1\times10^{-14}}{7.3\times10^{-5}} = 1.4\times10^{-10}$$

$K_{h1} >> K_{h2}$ ⇨ step (1) determines the pH!

$$\text{Ala}^-(aq) + H_2O(l) \rightleftharpoons \text{HAla}^0(aq) + \text{OH}^-(aq)$$

$\frac{\text{mol}}{\text{L}}$	Ala^-	HAla^0	OH^-
initial	$5.0\text{x}10^{-2}$	-	-
Δ	$-x$	$+x$	$+x$
Equilibrium	$5.0\text{x}10^{-2} - x$	x	x

$$K_{a1} = 6.25\times10^{-3} = \frac{x^2}{5.0\times10^{-2} - x}$$

⇨ $x = [\text{OH}^-] = 1.48\times10^{-2}\,\frac{\text{mol}}{\text{L}}$

⇨ pOH = 1.83 (≈ 30 % of the original concentration: strong hydrolysis!)

⇨ pH = 12.17

11 Exercices[6]

1

The pH of human blood is between 7.35 and 7.45. When blood is considered as an aqueous solution and pK_w of water is 13.63 at 37 °C, calculate the concentration range $[H_3O^+]$ and $[OH^-]$. Is blood acid, neutral or basic?

2

A 0.15 $\frac{mol}{L}$ solution of 1-propane carbonic acid, $CH_3CH_2CH_2COOH$, contains 1.51×10^{-3} $\frac{mol}{L}$ of H_3O^+ ions. Calculate K_a of this acid.

3

Calculate $[H_3O^+]$, $[NO_2^-]$ and $[OH^-]$ in 0.50 $\frac{mol}{L}$ HNO_2.

4

A 0.25 $\frac{mol}{L}$ solution of a weak acid is 3.0 % ionised. Calculate the pH of the solution. Calculate K_a of this acid.

5

Calculate $[H_2S]$, $[HS^-]$, $[S^{2-}]$ and the pH of a 0.10 $\frac{mol}{L}$ H_2S solution.

6

Give the chemical equation and the expression for the equilibrium condition K_b for the brønsted-base behavior in water of:

a) NO_2^-

b) pyridine, C_5H_5N

c) CO_3^{2-}.

7

Calculate the pH of

---

[6] For values of acid/base constants that are not given, see tables in this chapter.

a) $0.050\ \frac{\text{mol}}{\text{L}}$ KCN

b) $0.30\ \frac{\text{mol}}{\text{L}}$ triethyl ammonium chloride

K_a of HCN = 6.2×10^{-10} ; K_b of triethyl amine = 5.2×10^{-4}.

8

Calculate the pH of a solution that contains 33 g Na_3PO_4 per litre.

9

Rank the following salts from the lowest pH of their aqueous solution to the highest pH.

a) KNO_3, K_2SO_3, K_2S, $Fe(NO_3)_3$

b) NH_4NO_3, $NaHSO_4$, $NaHCO_3$, Na_2CO_3

10

In a solution of $NaHCO_3$ the main equilibrium is given by:

$$2\ HCO_3^{-}(aq) \rightleftharpoons H_2CO_3(aq) + CO_3^{2-}(aq)$$

Calculate the equilibrium constant for this equilibrium. Calculate the pH of a $0.1\ \frac{\text{mol}}{\text{L}}$ $NaHCO_3$ solution.

11

Acrylic acid has a K_a value of 5.6×10^{-5}.

a) Calculate the pH of a $0.10\ \frac{\text{mol}}{\text{L}}$ solution of acrylic acid.

b) Calculate the degree of dissociation (percentage) of acrylic acid in this solution.

c) Wat is the amount of $[H_3O^+]$ needed to reduce the dissociation of acrylic acid in a $0.10\ \frac{\text{mol}}{\text{L}}$ solution to 0.010 %?

d) Calculate the pH of a $0.05\ \frac{\text{mol}}{\text{L}}$ solution of sodium acrylate.

12

A vapor of a given acid HA has at 25 °C a density of 5.11 g/L at a pressure of 1 bar. When 1.50 g of this acid is dissolved in water to a final volume of 100.0 mL, the pH of the solution is 1.80. Calculate the K_a-value of this acid.

13

50.0 mL of a solution of 0.200 $\frac{\text{mol}}{\text{L}}$ HOAc is mixed with 50.0 mL 1.00×10^{-3} $\frac{\text{mol}}{\text{L}}$ HCl. Calculate the pH of the solution, calculate the concentration of OAc^- ions.

14

To what type of acid base reactions (Arrhenius, Brønsted-Lowry of Lewis) can you assign the following reactions (one reaction can be several types or none!)

a) $Ag^+ + 2\ NH_3 \rightleftharpoons Ag(NH_3)_2^+$

b) $H_2SO_4 + NH_3 \rightarrow HSO_4^- + NH_4^+$

c) $2\ HCl \rightleftharpoons H_2 + Cl_2$

d) $AlCl_3 + Cl^- \rightleftharpoons AlCl_4^-$

e) $Cu^{2+} + 4\ Cl^- \rightleftharpoons CuCl_4^{2-}$

f) $Al(OH)_3(v) + 3\ HNO_3 \rightleftharpoons Al^{3+} + 3\ H_2O + 3\ NO_3^-$

g) $N_2 + 3\ H_2 \rightleftharpoons 2\ NH_3$

h) $CN^- + H_2O \rightleftharpoons HCN + OH^-$

15

Quinine, $C_{20}H_{24}N_2O_2$, is used as a drug against malaria and contains 2 basic groups ($pK_{b_1} = 5.1$ and $pK_{b_2} = 9.7$). Calculate the pH of a 1.5 % (mass percent) solution of quinine-monohydrochloride (the conjugate acid of quinine) ($\rho_{\text{solution}} = 1.0 \frac{\text{g}}{\text{mL}}$).

12 Answers

1

$[H_3O^+]$: 3.5×10^{-8} à 4.5×10^{-8} $\frac{\text{mol}}{\text{L}}$; $[OH^-]$: 5.1×10^{-7} à 6.6×10^{-7} $\frac{\text{mol}}{\text{L}}$; slightly basic

2

1.5×10^{-5}

3

$[H_3O^+] = [NO_2^-] = 1.66 \times 10^{-2}$ $\frac{\text{mol}}{\text{L}}$; $[OH^-] = 6.02 \times 10^{-13}$ $\frac{\text{mol}}{\text{L}}$

4

pH = 2.12 ; $K_a = 2.3 \times 10^{-4}$

5

$[H_3O^+] = [HS^-] = 9.43 \times 10^{-5}\ \frac{mol}{L}$; $[S^{2-}] = 1.0 \times 10^{-14}\ \frac{mol}{L}$; $[H_2S] = 9.99 \times 10^{-2}\ \frac{mol}{L}$; pH = 4.03

6

a) $NO_2^-(aq) + H_2O(vl) \rightleftharpoons HNO_2(aq) + OH^-(aq)$

$$K_b = \frac{[HNO_2].[OH^-]}{[NO_2^-]}$$

b) $C_5H_5N(aq) + H_2O(vl) \rightleftharpoons C_5H_5NH^+(aq) + OH^-(aq)$

$$K_b = \frac{[C_5H_5NH^+].[OH^-]}{[C_5H_5N]}$$

c) $CO_3^{2-}(aq) + H_2O(vl) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$

$$K_b = \frac{[HCO_3^-].[OH^-]}{[CO_3^{2-}]}$$

7

a) 10.95

b) 5.62

8

12.74

9

a) $Fe(NO_3)_3 < KNO_3 < K_2SO_3 < K_2S$

b) $NaHSO_4 < NH_4NO_3 < NaHCO_3 < Na_2CO_3$

10

$K = 1.04 \times 10^{-4}$; pH = 8.34

11

a) 2.62

b) 2.4 %

c) 0.56 $\frac{mol}{L}$

d) 8.48

12

2.4×10^{-3}

13

$\mathrm{pH} = 2.79$ and $[\mathrm{OAc}^-] = 1.1 \times 10^{-3}\ \frac{\mathrm{mol}}{\mathrm{L}}$

14

a) Lewis
b) Brønsted-Lowry
c) none
d) Lewis
e) Lewis
f) Arrhenius
g) none
h) Brønsted-Lowry

20

5.13