7 Acids and bases

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The nature

acids: taste sour

bases: taste bitter, feel slippery

※ Definition

✓ Arrhenius (1859-1927) acid and base (1887)

Acid

Produces hydrogen ions (H^+) in aqueous solution

Base

Produces hydroxide ions (OH^-) in aqueous solution

✓ Brønsted acid and base (1923 by Brønsted and Lowry)

Acid: A proton (H^+) donor

Base: A proton acceptor

Hydronium ion

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

acid base conjugate acid conjugate base

↿ conjugate (共軛) acid-base pair ↾

Can be represented as

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

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

Ex. $NH_3(g) + HCl(g) \leftrightarrows NH_4Cl(s)$

Brønsted base
Proton acceptor

Brønsted acid
Proton donor

$[NH_4]^+ [Cl]^-$

✓ Lewis acid and base

Acid: An electron-pair acceptor
Base: An electron-pair donor

Ex. $BF_3 + :NH_3 \leftrightarrows F_3B–NH_3$

Lewis acid Lewis base

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※ Acid strength

Recall:

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

or

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

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

HA is a strong acid
when K_a is large
or equilibrium lies far to the right

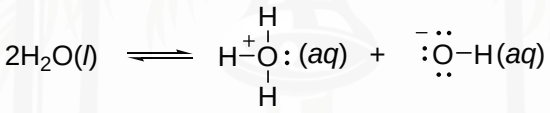
K_a is a measurement of acid strength

Strong acid gives weak conjugate base
Weak acid gives strong conjugate base

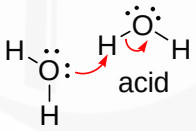
Ex. $pK_a = -\log K_a$

H_2O	15.7
NH_4^+	9.25
H_3O^+	–1.7
H_2SO_4	–3
HCl	–6 ~ –7
HI	–9.5 ~ –10

✓ Autoionization of water



Amphoteric: behaves as an acid or a base



(curved arrows represent flow of e^-s)

$K_w = [H_3O^+][OH^-]$

Ion-product constant or dissociation constant

At 25 °C $K_w = 1.0 \times 10^{-14}$

$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ M$ ⇨ neutral condition

※ The pH

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

At neutral condition $[H^+] = 1.0 \times 10^{-7}$

$pH = 7.00$

$pH < 7.00$ acidic

$pH > 7.00$ basic

◎ Note about significant figures

$\log(1/45) = -\log 45$

$= -\log(4.5 \times 10)$

$= -[(\log 4.5) + 1]$

$\log 4.5 = 0.65$ ← two significant figures

exact number (from the order)

$= -1.65$

Ex. $[H^+] = 1.0 \times 10^{-7}$

two significant figures

$pH = 7.00$

two significant figures

Overall: three significant figures

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※ Calculating pH

✓ Strong acid: complete dissociation

✓ The pH of a mixture of weak acids

Ex. 1.00 *M* HCN $K_a = 6.2 \times 10^{-10}$
5.00 *M* HNO_2 $K_a = 4.0 \times 10^{-4}$ pH?

$$H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq) \qquad K_w = 1.00 \times 10^{-14}$$

HNO_2 is the strongest acid, the other two can be neglected

	$HNO_2(aq)$	$\leftrightarrows$	$H^+(aq)$	+	$NO_2^-(aq)$	
ini	5.00		0		0	(*M*)
final	5.00 – x		x		x	

$$K_a = 4.0 \times 10^{-4} = \frac{x^2}{5.00 - x} \approx \frac{x^2}{5.00}$$

Small (assumption)

$x = 4.5 \times 10^{-2}$ *M* = $[H^+]$ ⇨ pH = 1.35

Check: $[H^+]$ is indeed small compared to 5.00 *M*

(tolerance: ±5%)

$$HCN\,(aq) \leftrightarrows H^+(aq) + CN^-(aq)$$

final $\quad 1.00 - x \quad 4.5 \times 10^{-2} \quad x \quad (M)$

↑ Controlled by HNO_2 (assumption)

$$K_a = 6.2 \times 10^{-10} = \frac{(4.5 \times 10^{-2})x}{1.00 - x} \approx \frac{(4.5 \times 10^{-2})x}{1.00}$$

$$x = 1.4 \times 10^{-8}\ M = [CN^-]$$

Check: $[CN^-]$ is small indeed
also $[H^+]$ is mainly from HNO_2

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※ Percent dissociation

$$\frac{\text{amt dissociated}}{\text{initial conc}} \times 100\%$$

For weak acid: more dilute ⇨ higher percent dissociation

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

$$K_a = \frac{x^2}{[HA]_o - x} \approx \frac{x^2}{[HA]_o}$$

$$x = \sqrt{K_a[HA]_o}$$

$$\text{percent dissociation} = \frac{x}{[HA]_o} \bullet 100\% = \left(\sqrt{\frac{K_a}{[HA]_o}}\right) \bullet 100\%$$

$[HA]_o \downarrow \rightarrow$ percent dissociation $\uparrow$

※ Bases

NaOH(*aq*), KOH(*aq*) dissociate completely in H_2O
→ Strong bases

$Ca(OH)_2$: similar but solubility is small
does not produce high $[OH^-]$

Slaked lime (熟石灰)

In acidic soln: $Ca(OH)_2(aq) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2H_2O(l)$

✓Removal of Ca^{2+} in hard water

$CaO + Na_2CO_3$ (the lime-soda process)

$$CaO(s) + H_2O(l) \leftrightarrows Ca(OH)_2(aq)$$

$$CO_3^{2-}(aq) + H_2O(l) \leftrightarrows HCO_3^-(aq) + OH^-(aq)$$

$$Ca(OH)_2(aq) + Ca^{2+}(aq) + 2HCO_3^-(aq) \rightarrow 2CaCO_3(s) + 2H_2O(l)$$

in hard water

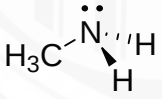
◎ Other bases

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

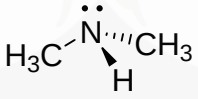
ammonia

$pK_a = 9.25$

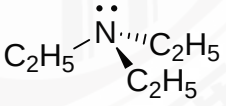
Amine bases



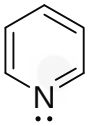
methylamine



dimethylamine



triethylamine



pyridine

In general

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

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

$K_b \uparrow \rightarrow$ base strength $\uparrow$

$$K_w = K_a \cdot K_b$$

In practice

the base strength is often measured by the pK_a of its conjugate acid

p$K_a \uparrow \rightarrow$ base strength $\uparrow$

Ex. $NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

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

	$NH_3(aq)$ + $H_2O(l)$ $\rightarrow$	$NH_4^+(aq)$ +	$OH^-(aq)$
Ini	0.15 *M*	0	0
Final	0.15 – x	x	x

$$\frac{x^2}{0.15 - x} = 1.8 \times 10^{-5} \quad \Rightarrow \quad x \sim 1.6 \times 10^{-3}\ M$$

About 1% conversion

In a buffer of pH = 7.4 $\Rightarrow$ $[OH^-] \sim 10^{-7}\ M$

$$\frac{[NH_4^+][10^{-7}]}{[NH_3]} = 1.8 \times 10^{-5} \Rightarrow \frac{[NH_4^+]}{[NH_3]} = 180 \Rightarrow [NH_4^+] \sim 0.15\ M$$

※ Polyprotic acids

H_2SO_4, H_3PO_4 ···

Dissociate stepwise

$H_3PO_4(aq) \leftrightarrows H^+(aq) + H_2PO_4^-(aq)$ $\quad K_{a1} = 7.5 \times 10^{-3}$

$H_2PO_4^-(aq) \leftrightarrows H^+(aq) + HPO_4^{2-}(aq)$ $\quad K_{a2} = 6.2 \times 10^{-8}$

$HPO_4^{2-}(aq) \leftrightarrows H^+(aq) + PO_4^{3-}(aq)$ $\quad K_{a3} = 4.8 \times 10^{-13}$

In general $\quad K_{a1} >> K_{a2} >> K_{a3}$

Ex. For a 5.0 *M* H_3PO_4 solution

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

ini	5.0	0	0	(*M*)
final	5.0 – x	x	x	

$$K_{a1} = 7.5 \times 10^{-3} = \frac{x^2}{5.0 - x} \approx \frac{x^2}{5.0}$$

$x = 1.9 \times 10^{-1}\ M$ ← Within 5% error

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = \frac{(0.19)[HPO_4^{2-}]}{(0.19)} = [HPO_4^{2-}] = 6.2 \times 10^{-8}\ \text{M}$$

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} = \frac{(0.19)[PO_4^{3-}]}{(6.2 \times 10^{-8})} \Rightarrow [PO_4^{3-}] = 1.6 \times 10^{-19}\ M$$

Ex. Fractions of H_2CO_3, HCO_3^-, and CO_3^{2-} at pH 9.00

$$CO_3^{2-}: \frac{[CO_3^{2-}]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]} = \frac{1}{\frac{[H_2CO_3]}{[CO_3^{2-}]}+\frac{[HCO_3^-]}{[CO_3^{2-}]}+1}$$

$$K_{a1} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \Rightarrow \frac{K_{a1}}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3]}$$

$$K_{a2} = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \Rightarrow \frac{K_{a2}}{[H^+]} = \frac{[CO_3^{2-}]}{[HCO_3^-]}$$

$$\frac{K_{a1}}{[H^+]} \bullet \frac{K_{a2}}{[H^+]} = \frac{[HCO_3^-]}{[H_2CO_3]} \bullet \frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{[CO_3^{2-}]}{[H_2CO_3]}$$

$$F_{CO_3^{2-}} = \frac{1}{\frac{[H_2CO_3]}{[CO_3^{2-}]}+\frac{[HCO_3^-]}{[CO_3^{2-}]}+1} = \frac{1}{\frac{[H^+]^2}{K_{a1} \bullet K_{a2}}+\frac{[H^+]}{K_{a2}}+1}$$

$$HCO_3^-: \frac{[HCO_3^-]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]} = \frac{1}{\frac{[H_2CO_3]}{[HCO_3^-]}+1+\frac{[CO_3^{2-}]}{[HCO_3^-]}}$$

$$F_{HCO_3^-} = \frac{1}{\frac{[H_2CO_3]}{[HCO_3^-]}+1+\frac{[CO_3^{2-}]}{[HCO_3^-]}} = \frac{1}{\frac{[H^+]}{K_{a1}}+1+\frac{K_{a2}}{[H^+]}}$$

$\Rightarrow$ At pH 9.0 $F_{HCO_3^-} = 0.95$

($K_{a1} = 4.3 \times 10^{-7}$; $K_{a2} = 4.8 \times 10^{-11}$)

Ex. pH of a 1.00×10^{-2} *M* H_2SO_4

Complete dissociation for the 1st step

	$HSO_4^-(aq)$	⇆	$H^+(aq)$	+	$SO_4^{2-}(aq)$	
ini	0.0100		0.0100		0	(*M*)
final	0.0100 – x		0.0100 + x		x	

$$K_{a2} = 1.2 \times 10^{-2} = \frac{(0.0100 + x)x}{(0.0100 - x)}$$

Assume 0.0100 >> *x* ⇨ $x = 0.012$

incorrect

$x^2 + (2.2 \times 10^{-2})x - (1.2 \times 10^{-4}) = 0$ ⇨ $x = 4.5 \times 10^{-3}$ *M*

$[H^+] = 0.0100 + 0.0045 = 0.0145$ ⇨ pH = 1.840

Cf. 1.0 *M* H_2SO_4

	$HSO_4^-(aq)$	⇆	$H^+(aq)$	+	$SO_4^{2-}(aq)$	
ini	1.0		1.0		0	(*M*)
final	1.0 – x		1.0 + x		x	

$$K_{a2} = 1.2 \times 10^{-2} = \frac{(1.0 + x)x}{(1.0 - x)} \approx x$$

Very small contribution
from the second ionization

※ Acid-base properties of salts

✓ Conjugate base of strong acid
Conjugate acid of strong base } no effect on pH

✓Conjugate base of a weak acid
$NaC_2H_3O_2$, KCN, KF ···

Ex. 0.30 *M* NaF(*aq*) K_a for HF: 7.2×10^{-4}

$\because K_w = K_a K_b \ \therefore K_b = 1.4 \times 10^{-11}$

$F^-(aq) + H_2O(l) \leftrightarrows HF(aq) + OH^-(aq)$

ini	0.30	0	0	(*M*)
final	0.30 – x	x	x	

$$K_b = 1.4 \times 10^{-11} = \frac{x^2}{0.30 - x} \approx \frac{x^2}{0.30} \Rightarrow x = 2.0 \times 10^{-6}\ M = [OH^-]$$

✓ Conjugate acid of a weak base

Ex. Ammonium salt NH_4Cl

$NH_4^+(aq) \leftrightarrows H^+(aq) + NH_3(aq)$ $K_a = 5.6 \times 10^{-10}$

A 0.10 *M* solution → pH = 5.13

✓ With highly charged metal ion

Ex. $Al(H_2O)_6^{3+}$

$AlCl_3(s) + 6H_2O(l) \leftrightarrows Al(H_2O)_6^{3+}(aq) + 3Cl^-(aq)$

$Al(H_2O)_6^{3+}(aq) \leftrightarrows Al(OH)(H_2O)_5^{2+}(aq) + H^+(aq)$

$K_a = 1.4 \times 10^{-5}$

A 0.010 *M* solution → pH = 3.43

✓ Both ions affect the pH

Ex. $NH_4^+C_2H_3O_2^-$ ammonium acetate

Basic; $K_b = 5.6 \times 10^{-10}$

Acidic; $K_a = 5.6 \times 10^{-10}$

$K_a > K_b$ acidic
$K_a < K_b$ basic
$K_a = K_b$ neutral

Ex. $NH_4^+CN^-$ ⇨ basic

$K_b = 1.6 \times 10^{-5}$

Ex. pH of a 0.100 *M* NH_4CN

$NH_4^+(aq) \leftrightarrows H^+(aq) + NH_3(aq)$ $K_a = 5.6 \times 10^{-10}$

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

$K_b = 1.6 \times 10^{-5}$

$H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq)$ $K_w = 1.0 \times 10^{-14}$

$NH_4^+(aq) + CN^-(aq) \leftrightarrows NH_3(aq) + HCN(aq)$

$$K = \frac{[NH_3][HCN]}{[NH_4^+][CN^-]} = \frac{[NH_3][H^+]}{[NH_4^+]} \bullet \frac{[HCN]}{[H^+][CN^-]} = \frac{K_{a(NH_4^+)}}{K_{a(HCN)}} = 0.90$$

The dominate process

$NH_4^+(aq)$ + $CN^-(aq)$ ⇆ $NH_3(aq)$ + $HCN(aq)$

Final 0.100–x 0.100–x x x

$$K = \frac{x^2}{(0.100 - x)^2} = 0.90 \quad \Rightarrow \quad x = 4.9 \times 10^{-2}\ M = [NH_3] = [HCN]$$

$$[NH_4^+] = [CN^-] = 0.100 - 0.049 = 0.051\ M$$

$$K_{a(NH_4^+)} = 5.6 \times 10^{-10} = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{[H^+](0.049)}{0.051}$$

$$\Rightarrow \quad [H^+] = 5.8 \times 10^{-10}\ M$$

$$K_{a(HCN)} = 6.2 \times 10^{-10} = \frac{[H^+][CN^-]}{[HCN]} = \frac{[H^+](0.051)}{0.049}$$

$$\Rightarrow \quad [H^+] = 6.0 \times 10^{-10}\ M \quad \Rightarrow \quad pH = 9.22$$

Another way

$$K_{a(NH_4^+)} \bullet K_{a(HCN)} = \frac{[H^+][NH_3]}{[NH_4^+]} \bullet \frac{[H^+][CN^-]}{[HCN]} = [H^+]^2$$

$$[H^+] = \sqrt{K_{a(NH_4^+)} \bullet K_{a(HCN)}} = 5.9 \times 10^{-10}$$

※ Dilute solutions

The contribution of H_2O is important

Ex. A 1.0×10^{-4} *M* solution of HA, $K_a = 1.0 \times 10^{-10}$

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

	HA	H^+	A^-
Final	$1.0\times10^{-4} - x$	x	x

$$K_a = 1.0\times10^{-10} = \frac{x^2}{1.0\times10^{-4} - x} \approx \frac{x^2}{1.0\times10^{-4}}$$

⇨ $[H^+] = 1.0 \times 10^{-7}$ *M* ← Can not be true!

Consider H_2O alone ⇨ $[H^+] = 1.0 \times 10^{-7}$ *M*

How about: $1.0 \times 10^{-7} + 1.0 \times 10^{-7} = 2.0 \times 10^{-7}$ *M*

From HA, From water, incorrect

Should effect each other

Expect: $1.0 \times 10^{-7} < [H^+] < 2.0 \times 10^{-7}$ *M*

HA and H_2O should be considered at the same time

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

$$H_2O(l) \leftrightarrows H^+(aq) + OH^-(aq)$$

Relationships must be followed:

1. $K_w = [H^+][OH^-]$

2. $K_a = \dfrac{[H^+][A^-]}{[HA]}$

3. Charge balance

$$[H^+] = [OH^-] + [A^-]$$

4. Material balance (mass balance)

$$[HA]_o = [HA] + [A^-]$$

$[HA]_o$: Initial concentration of HA

Known: K_w , K_a , $[HA]_o$

Need to know: $[H^+]$, $[OH^-]$, $[HA]$, $[A^-]$

Express in terms of $[H^+]$

From K_w

$$[OH^-] = \frac{K_w}{[H^+]}$$

From charge balance

$$[A^-] = [H^+] - [OH^-] = [H^+] - \frac{K_w}{[H^+]}$$

From mass balance

$$[HA] = [HA]_o - [A^-] = [HA]_o - [H^+] + \frac{K_w}{[H^+]}$$

From K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]\left([H^+] - \dfrac{K_w}{[H^+]}\right)}{[HA]_o - [H^+] + \dfrac{K_w}{[H^+]}} = \frac{[H^+]^2 - K_w}{[HA]_o - \dfrac{[H^+]^2 - K_w}{[H^+]}}$$

$$K_a = \frac{[H^+]^2 - K_w}{[HA]_o - \frac{[H^+]^2 - K_w}{[H^+]}}$$

Can be solved by successive approximations

✓ Validity check

If assume $[H^+]^2 >> K_w$ ← That is to omit H_2O

$$K_a = \frac{[H^+]^2}{[HA]_o - [H^+]}$$ ⇨ Goes back to consider HA alone

Assume this condition is met when $[H^+]^2 > 100K_w$

⇨ $[H^+]$ should be $> 10^{-6}$ *M*

Ex. 1.0 *M* HCN, $K_a = 6.2 \times 10^{-10}$

Soln Normal calculation ⇨ $[H^+] = 2.5 \times 10^{-5}$ *M*

↑ $> 10^{-6}$, OK

Ex. 1.0×10^{-4} *M* HCN

Soln Normal calculation ⇨ $[H^+] = 2.5 \times 10^{-7}$ *M*

↑ No good

Solve $$K_a = \frac{[H^+]^2 - K_w}{1.00 \times 10^{-4} - \frac{[H^+]^2 - K_w}{[H^+]}}$$

Expect: $2.5 \times 10^{-7} < [H^+] < 3.5 \times 10^{-7}$ *M*

Try 3.0×10^{-7} *M* first

$$K_a = \frac{[H^+]^2 - 1.0\times10^{-14}}{1.00\times10^{-4} - \dfrac{3.0\times10^{-7} - 1.0\times10^{-14}}{3.0\times10^{-7}}} = 6.2\times10^{-10}$$

⇨ $[H^+] = 2.68 \times 10^{-7}\ M$ (cf. 3.0×10^{-7})

⇨ New guess: 2.68×10^{-7}

⇨ Find: $[H^+] = 2.68 \times 10^{-7}\ M$

Final answer = $2.7 \times 10^{-7}\ M$

✓ A better approximation

$$K_a = \frac{[H^+]^2 - K_w}{[HA]_o - \underbrace{\dfrac{[H^+]^2 - K_w}{[H^+]}}_{\text{This term is small}}}$$

Assume $[HA]_o >> \dfrac{[H^+]^2 - K_w}{[H^+]}$

⇨ $K_a \approx \dfrac{[H^+]^2 - K_w}{[HA]_o}$

⇨ $[H^+] = \sqrt{K_a[HA]_o + K_w}$ ← True unless $[HA]_o$ is very small

Ex. $1.0 \times 10^{-4}\ M$ HCN

$$[H^+] = \sqrt{(6.2\times10^{-10})(1.0\times10^{-4}) + (1.0\times10^{-14})}$$
$$= \sqrt{7.2\times10^{-14}} = 2.7\times10^{-7}\ M$$

☠ The incorrect method

	HCN(*aq*)	⇆	$H^+(aq)$	+	$CN^-(aq)$
Ini	1.0×10^{-4}		1.0×10^{-7}		0 (*M*)
final	$1.0\times10^{-4} - x$		$1.0\times10^{-7} + x$		x

$$K_a = 6.2\times10^{-10} = \frac{(1.0\times10^{-7} + x)x}{(1.0\times10^{-4} - x)}$$

Assume $1.0 \times 10^{-4} - x \sim 1.0 \times 10^{-4}$ *M*

⇨ $x = 2.1 \times 10^{-7}$ *M*

⇨ $[H^+] = 3.1 \times 10^{-7}$ *M*

~15% larger than the correct answer!

Ex. Mixing equal volumes of 1.0×10^{-4} *M* NH_3 and 1.0×10^{-4} *M* HCl

Q: pH = ?

Soln: Start with 5.0×10^{-5} *M* NH_4^+

	$NH_4^+(aq)$	⇆	$NH_3(aq)$	+	$H^+(aq)$
final	$5.0\times10^{-5} - x$		x		x (*M*)

$$K_a = 5.6\times10^{-10} = \frac{x^2}{(5.0\times10^{-5} - x)}$$ ⇨ $x = 1.7 \times 10^{-7}$ *M*

Can not omit H_2O

Since $[NH_4^+]_o = 5.0 \times 10^{-5}$ *M* > 10^{-6} *M*

⇨ $[H^+] = \sqrt{K_a[NH_4^+]_o + K_w} = 1.9\times10^{-7} M$

※ Dilute strong acid solution

Ex. $1.0 \times 10^{-7}\ M$ HNO_3

From HNO_3 alone $[H^+] = 1.0 \times 10^{-7}\ M$

The contribution of H_2O can not be ignored

Charge balance

$$[H^+] = [NO_3^-] + [OH^-]$$

$K_w = [H^+][OH^-]$

Known: $[NO_3^-] = 1.0 \times 10^{-7}\ M$

Unknown: $[H^+]$ and $[OH^-]$

Soln: $[OH^-] = K_w/[H^+]$

From charge balance: $[H^+] = 1.0 \times 10^{-7} + K_w/[H^+]$

⇨ $[H^+] = 1.6 \times 10^{-7}\ M$

※ More examples

△ A solution of $NaHCO_3$

The principal equilibrium is

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

Q: $K = ?$

Soln:
$$K = \frac{[H_2CO_3][CO_3^{2-}]}{[HCO_3^-][HCO_3^-]} = \frac{[H_2CO_3][H^+][CO_3^{2-}]}{[HCO_3^-][H^+][HCO_3^-]} = \frac{K_{a2}}{K_{a1}}$$

Q: pH at equilibrium?

Soln:
$$K_{a1} \bullet K_{a2} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \bullet \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = \frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]}$$

At equilibrium: $[H_2CO_3] = [CO_3^{2-}]$

⇨ $[H^+] = \sqrt{K_{a1} \bullet K_{a2}}$

△ At 1 atm, 25 °C, HA has a vapor density of 5.11 g/L.
A 100.0 mL solution of 1.50 g HA has a pH of 1.80.

Q: K_a = ?

Soln: The molar volume of a gas is 24.6 L at 1 atm, 25 °C
Molar mass of HA should be
5.11 g/L × 24.6 L/mol = 126 g/mol
The mole number of 1.50 g of HA is
1.50 g ÷ 126 g/mol = 0.0119 mol = 11.9 mmol
The concentration is $\frac{11.9\,\text{mmol}}{100.0\,\text{mL}} = 0.119\,M$

$-\log[H^+] = 1.80 \Rightarrow \log[H^+] = -1.80 = -2 + 0.20$
Knowing log(1.6) = 0.20 ⇨ $[H^+] = 1.6 \times 10^{-2}\,M$

$$HA(aq) \leftrightarrows H^+(aq) + A^-(aq)$$

Equil. (0.119 – 0.016) 0.016 0.016 ⇨ $K_a = 2.5 \times 10^{-3}$

△ A 0.100 *M* salt (BHX) solution has a pH of 8.00
This salt is a combination of BH^+ and X^-

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

$$K_b = \frac{[BH^+][OH^-]}{[B]} = 1.0 \times 10^{-3}$$

$$HX(aq) \leftrightarrows H^+(aq) + X^-(aq)$$

Q: K_{HX} = ?

Soln: The principal equilibrium is
$BH^+(aq) + X^-(aq) \leftrightarrows B(aq) + HX(aq)$
At equilibrium: [B] = [HX] $[BH^+] = [X^-]$

$$\Rightarrow \frac{[BH^+]}{[B]} = \frac{[X^-]}{[HX]}$$

pH 8.00

⇨ $[H^+] = 1.0 \times 10^{-8}\ M$

⇨ $[OH^-] = 1.0 \times 10^{-6}\ M$

$$\frac{[BH^+][OH^-]}{[B]} = \frac{[BH^+](1.0\times10^{-6})}{[B]} = 1.0\times10^{-3}$$

$$\Rightarrow \quad \frac{[BH^+]}{[B]} = 1.0\times10^{3} = \frac{[X^-]}{[HX]}$$

$$K_{HX} = \frac{[H^+][X^-]}{[HX]} = (1.0\times10^{-8})(1.0\times10^{3}) = 1.0\times10^{-5}$$

△ 0.0500 *M* HCOOH, $K_{a(HCOOH)} = 1.77 \times 10^{-4}$
0.150 *M* AcOH, $K_{a(AcOH)} = 1.34 \times 10^{-5}$

Q: pH?

Soln:

$$K_{a(HCOOH)} = \frac{[H^+][HCOO^-]}{[HCOOH]} = 1.77\times10^{-4}$$

$$K_{a(AcOH)} = \frac{[H^+][AcO^-]}{[AcOH]} = 1.34\times10^{-5}$$

Charge balance

$[H^+] = [HCOO^-] + [AcO^-] + [OH^-]$

Assuming $[OH^-]$ is very small:

⇨ $[H^+] = [HCOO^-] + [AcO^-]$

Mass balance

$[HCOOH]_o = [HCOOH] + [HCOO^-] = 0.0500\ M$

$[AcOH]_o = [AcOH] + [AcO^-] = 0.150\ M$

$$[HCOOH] = \frac{[H^+][HCOO^-]}{1.77\times10^{-4}}$$

$$\Rightarrow \quad \frac{[H^+][HCOO^-]}{1.77\times10^{-4}} + [HCOO^-] = 0.0500\,M$$

$$\Rightarrow \quad [HCOO^-]\left(\frac{[H^+]}{1.77\times10^{-4}} + 1\right) = 0.0500\,M$$

$$[AcOH] = \frac{[H^+][AcO^-]}{1.34\times10^{-5}}$$

$$\Rightarrow \quad \frac{[H^+][AcO^-]}{1.34\times10^{-5}} + [AcO^-] = 0.150\,M$$

$$\Rightarrow \quad [AcO^-]\left(\frac{[H^+]}{1.34\times10^{-5}} + 1\right) = 0.150\,M$$

From charge balance: $[H^+] = [HCOO^-] + [AcO^-]$

$$\Rightarrow \quad [H^+] = \frac{0.0500}{\frac{[H^+]}{1.77\times10^{-4}} + 1} + \frac{0.150}{\frac{[H^+]}{1.34\times10^{-5}} + 1}$$

$$\Rightarrow \quad [H^+] = \frac{8.85\times10^{-6}}{[H^+] + 1.77\times10^{-4}} + \frac{2.01\times10^{-6}}{[H^+] + 1.34\times10^{-5}}$$

Make a guess first

$[H^+]$ from HCOOH alone: 2.9×10^{-3}

$[H^+]$ from AcOH alone: 1.4×10^{-3}

$\Rightarrow$ $4.3 \times 10^{-3} > [H^+] > 2.9 \times 10^{-3}$

Start from 3.6×10^{-3}

$$[H^+] = \frac{8.85\times10^{-6}}{3.6\times10^{-3}+1.77\times10^{-4}} + \frac{2.01\times10^{-6}}{3.6\times10^{-3}+1.34\times10^{-5}}$$

$$= 2.90\times10^{-3}\ M$$

New guess: $(\frac{3.6+2.9}{2})\times10^{-3} = 3.25\times10^{-3}$

$\rightarrow$ $[H^+] = 3.22 \times 10^{-3}\ M$

Another quick solution

$$[H^+] = [HCOO^-] + [AcO^-]$$

$\Rightarrow$ $[H^+]^2 = [H^+][HCOO^-] + [H^+][AcO^-]$

$= (1.77 \times 10^{-4})[HCOOH] + (1.34 \times 10^{-5})[AcOH]$

Assume $[HCOOH] \sim [HCOOH]_o = 0.0500\ M$

$[AcOH] \sim [AcOH]_o = 0.150\ M$

$\Rightarrow$ $[H^+] = 3.30 \times 10^{-3}\ M$

Check the assumption: 3.30×10^{-3} is 5.4% of 0.0500

△ Calculate $[OH^-]$ in a $3.0 \times 10^{-7}\ M$ solution of $Ca(OH)_2$

Soln: In solution, $Ca(OH)_2$ is completely ionized

$\Rightarrow$ $[Ca^{2+}] = 3.0 \times 10^{-7}\ M$

The concentration of $[OH^-]$ is small
and should consider the ionization of H_2O

Charge balance

$$2[Ca^{2+}] + [H^+] = [OH^-]$$

From: $K_w = [H^+][OH^-]$

$\Rightarrow$ $2[Ca^{2+}] + \frac{K_w}{[OH^-]} = [OH^-]$

$\Rightarrow$ $[OH^-] = 6.2 \times 10^{-7}\ M$