

8

Applications of Aqueous Equilibria

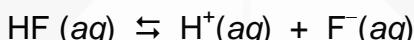


※ Effect of common ion

Ex. HF $K_a = 7.2 \times 10^{-4}$

For a 1.0 M solution of HF: about ~2.7% dissociation

With the addition of 1.0 M NaF



final	1.0 - x	x	1.0 + x	(M)
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$$K_a = \frac{x(1.0 + x)}{1.0 - x} = 7.2 \times 10^{-4} \quad \Rightarrow \quad x \sim 7.2 \times 10^{-4} \text{ M}$$

(0.00072)

\Rightarrow 0.072% dissociated

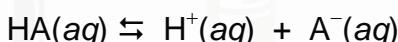
Equilibrium has been shifted to the left

※ Buffered solutions



Resists a change in pH

Ex. Blood pH 7.35~7.45



ini	[HA]	0	[A ⁻]	(M)
final	[HA] - x	x	[A ⁻] + x	

$$K_a = \frac{x([A^-] + x)}{[HA] - x} \quad x = [\text{H}^+]$$

$$\text{Assume } x \text{ is small: } K_a = [\text{H}^+] \cdot \frac{[\text{A}^-]}{[\text{HA}]} \Rightarrow [\text{H}^+] = K_a \cdot \frac{[\text{HA}]}{[\text{A}^-]}$$

Henderson-Hasselbalch equation

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right) = \text{p}K_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$

Ex. Initial $\frac{[A^-]}{[HA]} = \frac{0.50M}{0.50M} = 1.0$

With addition of 0.01 M OH⁻

$$\frac{[A^-]}{[HA]} = \frac{0.51}{0.49} = 1.04 \quad (\log 1.04 = 0.017)$$

↑ Small change

With addition of 0.10 M OH⁻ → pH change ~0.18

Ex. Initial $\frac{[A^-]}{[HA]} = \frac{0.25M}{0.75M} = 0.33 \quad (\log 0.33 = -0.48)$

With addition of 0.10 M OH⁻

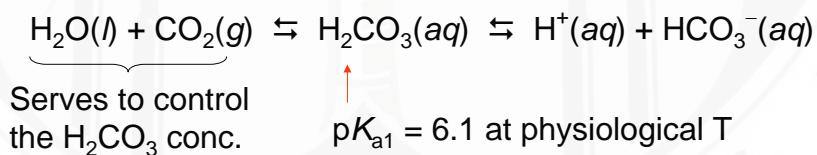
$$\frac{[A^-]}{[HA]} = \frac{0.35}{0.65} = 0.54 \quad (\log 0.54 = -0.27)$$

pH change = 0.21

Optimum buffering is to keep $[A^-]/[HA] = 1 \Rightarrow \text{pH} = \text{p}K_a$

Buffering capacity: determined by the real magnitude of $[A^-]$ and $[HA]$

✓ Buffer system in blood



For a buffer pH of 7.4

$$\text{pH} = \text{p}K_{a1} + \log\left(\frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}\right) \rightarrow \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \approx 20$$

In reality $[\text{HCO}_3^-] \sim 0.024 M$ Higher conc.
More effective to neutralize extra acid
 $[\text{H}_2\text{CO}_3] \sim 0.0012 M$
↑ Low capacity to neutralize extra base

Organs to regulate pH
lung and kidney

Receptor in brain: sensitive to $[H^+]$ and $[CO_2]$ in body

$[H^+]$ too high: increase breath rate
→ remove more CO_2
→ shift equilibrium to the left

Kidney: removes H^+ and HCO_3^-
 pH for urine $\sim 5.0\text{--}7.0$

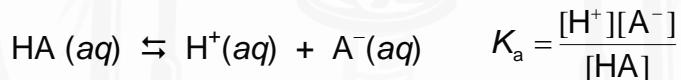
✓ Other useful buffer systems

Phosphate number 1 at $25^\circ C$, $pH 6.87$ } KH_2PO_4 ,
Phosphate number 2 at $25^\circ C$, $pH 7.41$ } Na_2HPO_4
($H_2PO_4^-$, $K_a = 6.2 \times 10^{-8}$, $pK_a = 7.21$)

※ The exact treatment



A pair of HA/A^- (from NaA)



Charge balance

$$[Na^+] + [H^+] = [A^-] + [OH^-] \quad ([Na^+] = [A^-]_o)$$

Mass balance

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

Four relationships, four unknowns: $[H^+]$, $[OH^-]$, $[HA]$, $[A^-]$

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

$$\begin{aligned} \text{From charge balance } & \Rightarrow [A^-]_o + [H^+] = [A^-] + K_w / [H^+] \\ \Rightarrow [A^-] &= [A^-]_o + [H^+] - K_w / [H^+] \end{aligned}$$

From mass balance

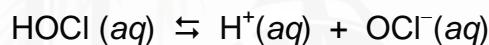
$$[\text{HA}]_o + [\text{A}^-]_o = [\text{HA}] + [\text{A}^-]_o + [\text{H}^+] - K_w / [\text{H}^+]$$

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

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

$$\text{In fact, when } \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]} \text{ is small} \Rightarrow K_a \approx \frac{[\text{H}^+][\text{A}^-]_o}{[\text{HA}]_o}$$

Ex. A buffered solution with $3.0 \times 10^{-4} M \text{ HOCl}$
 $1.0 \times 10^{-4} M \text{ NaOCl}$



$$K_a = 3.5 \times 10^{-8} = \frac{x(1.0 \times 10^{-4} + x)}{3.0 \times 10^{-4} - x}$$

$$\text{Assume } x \ll 1.0 \times 10^{-4} \Rightarrow x \sim 1.1 \times 10^{-7} M$$

Assumption OK
But this is a very small value

$$\text{Check } \frac{[\text{H}^+]^2 - K_w}{[\text{H}^+]} = \frac{(1.1 \times 10^{-7})^2 - 1.0 \times 10^{-14}}{1.1 \times 10^{-7}}$$

Small compared with 10^{-4}

In the range
of 10^{-7}

Conclusion: autoionization of H_2O has no effect unless $[\text{HA}]$ or $[\text{A}^-]$ are very small

※ Titrations and pH curves

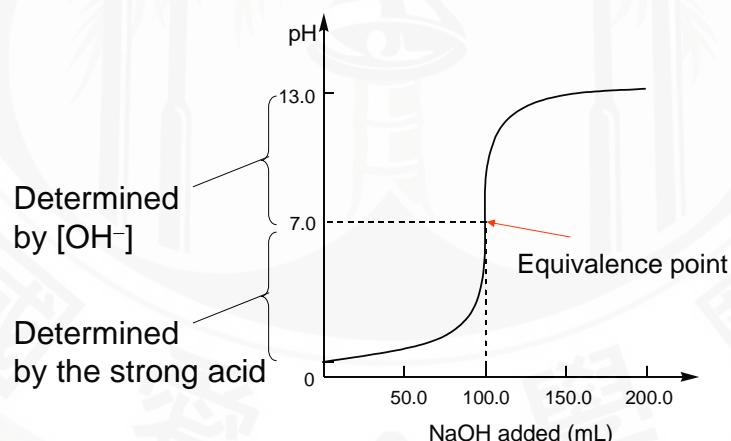
◎ Strong acid-strong base

Ex. HNO_3 (50.0 mL, 0.200 M) titrated with NaOH (0.100 M)

With the addition of 10.0 mL of the titrant

$$\frac{(50.0 \times 0.200) - (10.0 \times 0.100)}{60.0} = 0.15 \text{ M} = [\text{H}^+]$$

Equivalence point:
Addition of stoichiometric amount of the titrant



Characteristics:
with sharp pH change around equivalence point

◎ Weak acid-strong base titration

Before equivalence point
dissociation of the weak acid
After equivalence point
controlled by NaOH

Ex. Titration of acetic acid (AcOH; 50.0 mL, 0.10 M)
with NaOH (0.10 M)

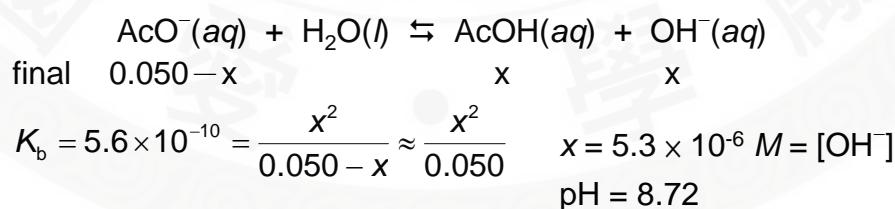
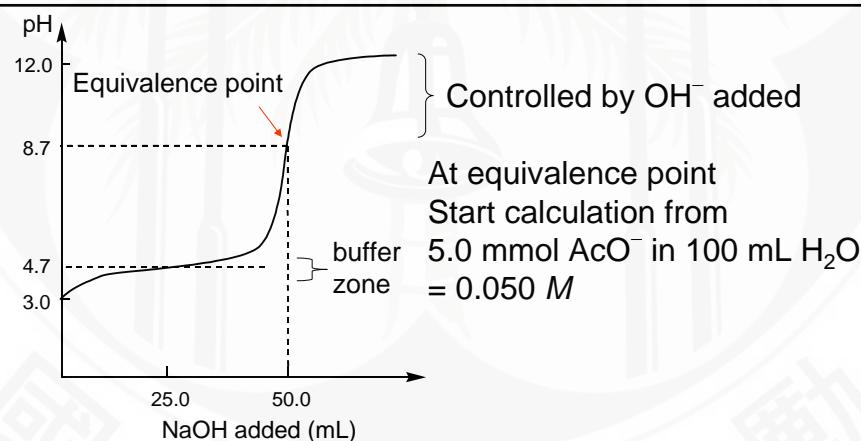
Addition of 25.0 mL of 0.10 M NaOH(aq)

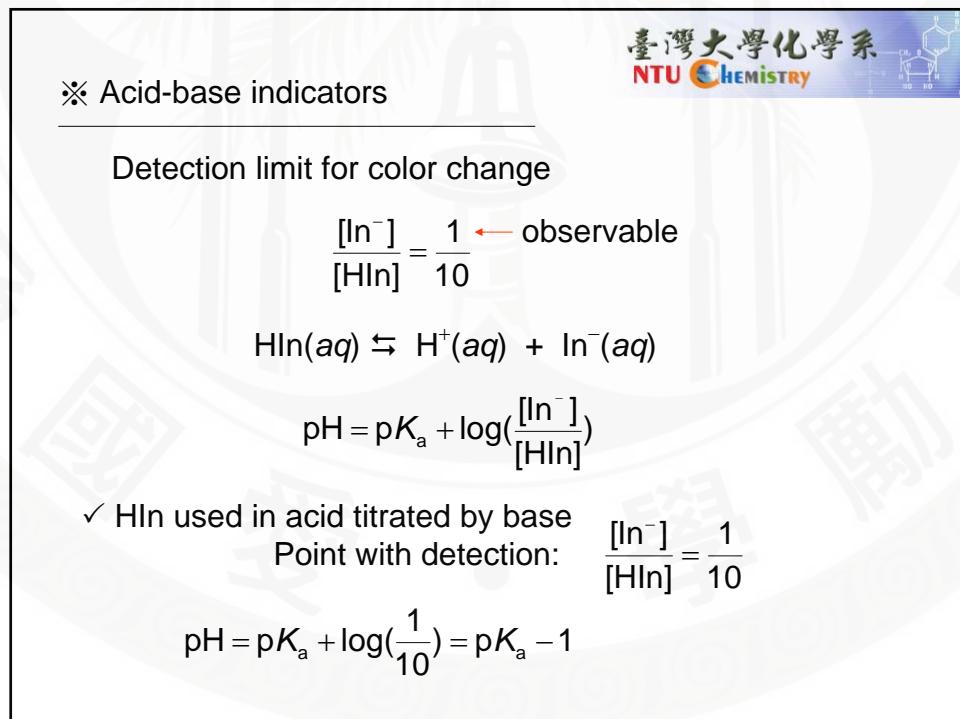
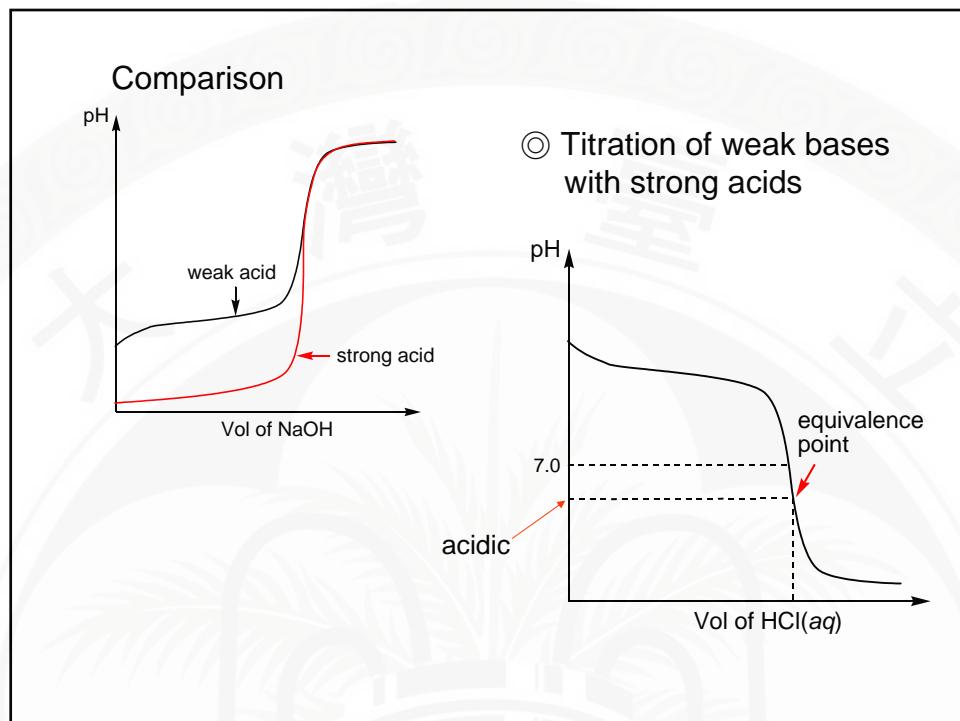


$$\text{final} \quad \frac{2.5 \text{ mmol}}{75 \text{ mL}} - x \quad \frac{2.5}{75} + x \quad x$$

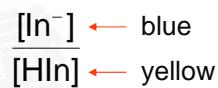
Assume x is small

$$K_a = 1.8 \times 10^{-5} = x = [\text{H}^+] \rightarrow \text{pH} = 4.74$$





Ex. Bromthymol blue, $K_a = 1 \times 10^{-7}$, $pK_a = 7$



$$\text{pH for color change: } pK_a - 1 = 6$$

✓ In base titrated by acid

$$\text{Starts with In}^-, \text{ point with detection: } \frac{[\text{In}^-]}{[\text{HIn}]} = \frac{10}{1}$$

For bromthymol blue, color change at $\text{pH} = pK_a + 1 = 8$

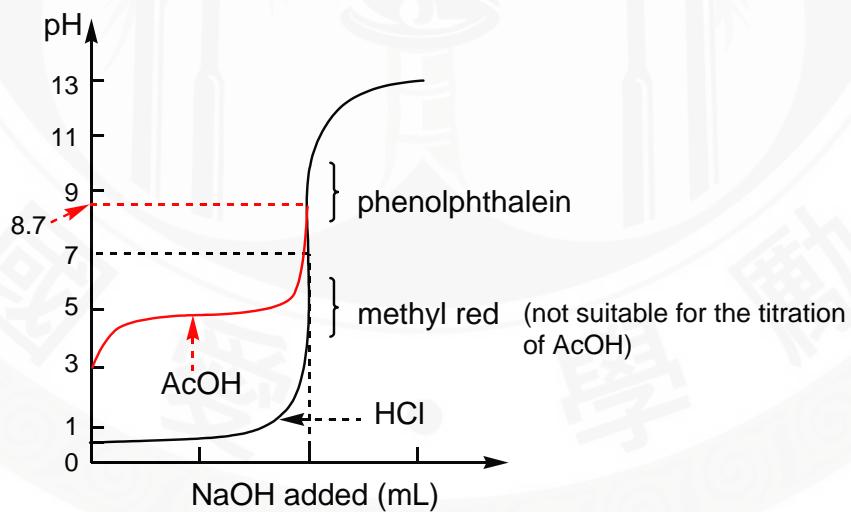
Overall, the useful range is $\text{pH} = pK_a \pm 1$

Ex. Phenolphthalein: $\text{pH} \sim 8\text{--}10$

Choice of indicator

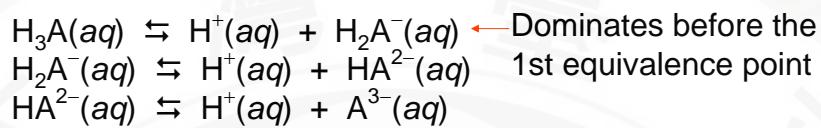
Start of color change (**end point**):

within the vertical area around the equivalence point

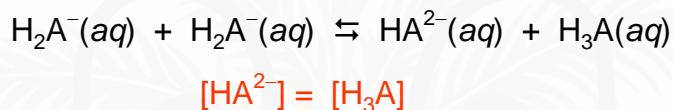
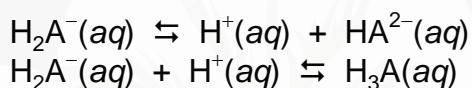


※ Polyprotic acids

General expression



- ✓ At the 1st equivalence point
 H_3A is converted to HA^{2-}



$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{A}^-]}{[\text{H}_3\text{A}]} \qquad K_{a2} = \frac{[\text{H}^+][\text{HA}^{2-}]}{[\text{H}_2\text{A}^-]}$$

$$\Rightarrow K_{a1} \cdot K_{a2} = \frac{[\text{H}^+]^2[\text{HA}^{2-}]}{[\text{H}_3\text{A}]}$$

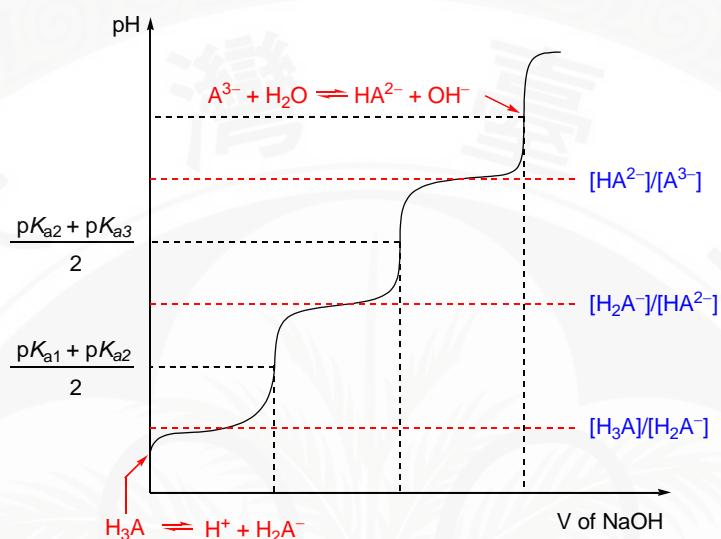
$$\Rightarrow \text{p}K_{a1} + \text{p}K_{a2} = 2 \text{pH} - \log \frac{[\text{HA}^{2-}]}{[\text{H}_3\text{A}]}$$

Since $[\text{HA}^{2-}] = [\text{H}_3\text{A}]$ at equivalence point

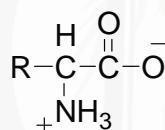
$$\Rightarrow \text{p}K_{a1} + \text{p}K_{a2} = 2 \text{pH}$$

$$\Rightarrow \text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$$

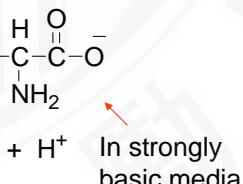
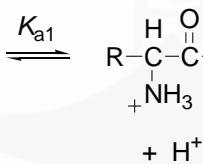
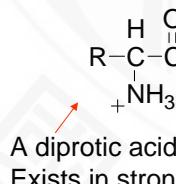
✓ Titration curve



※ The acid-base properties of amino acids



Amphoteric – both an acid and base



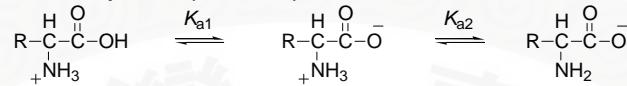
P
(positive)

Z
(neutral)

N
(negative)

$$K_{a1} = \frac{[\text{Z}][\text{H}^+]}{[\text{P}]} \quad K_{a2} = \frac{[\text{N}][\text{H}^+]}{[\text{Z}]}$$

★ Isoelectric point (等電點)



$$K_{a1} = \frac{[\text{Z}][\text{H}^+]}{[\text{P}]}$$

$$pK_{a1} = -\log[\text{H}^+] - \log \frac{[\text{Z}]}{[\text{P}]} \quad pK_{a2} = -\log[\text{H}^+] - \log \frac{[\text{N}]}{[\text{Z}]}$$

$$pK_{a1} + pK_{a2} = 2\text{pH} - \log \frac{[\text{N}]}{[\text{P}]}$$

When $[\text{N}] = [\text{P}] \rightarrow pK_{a1} + pK_{a2} = 2\text{pH}$

The net charge of amino acid is neutral

→ The isoelectric point
(the dipolar ion has the highest concentration)

→ At this point $\text{pH} = \frac{pK_{a1} + pK_{a2}}{2} = \text{pI}$

* Different amino acid has different pI

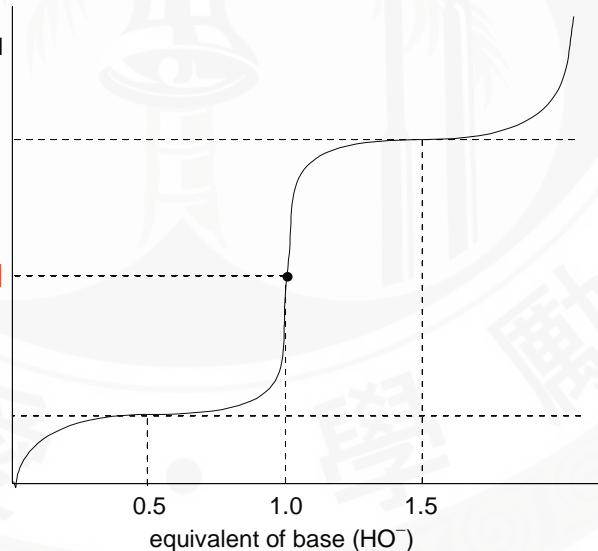
$$K_{a2} = \frac{[\text{N}][\text{H}^+]}{[\text{Z}]}$$

When $[\text{Z}] = [\text{N}]$
 $\rightarrow K_{a2} = [\text{H}^+]$
 $\rightarrow pK_{a2} = \text{pH}$

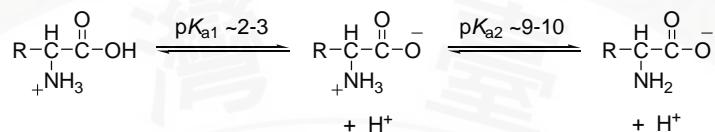
$$K_{a1} = \frac{[\text{Z}][\text{H}^+]}{[\text{P}]}$$

When $[\text{Z}] = [\text{P}]$
 $\rightarrow K_{a1} = [\text{H}^+]$
 $\rightarrow pK_{a1} = \text{pH}$

Titration curve

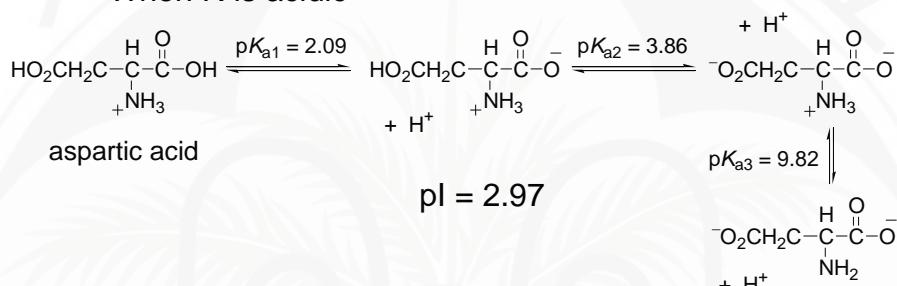


✓ In general:
When R is neutral

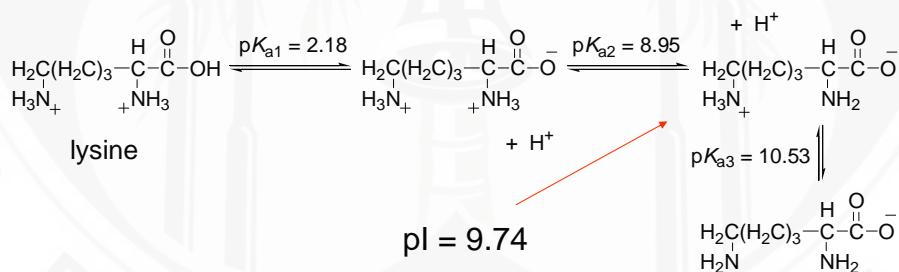


pI ~6

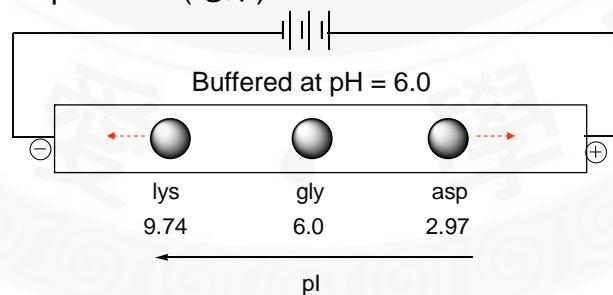
When R is acidic



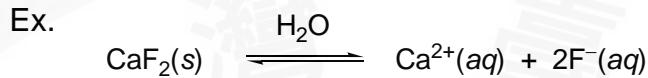
When R is basic



✓ Electrophoresis (電泳)

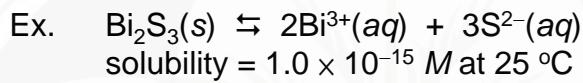


※ Solubility equilibria
and the solubility product



$$K_{sp} = [\text{Ca}^{2+}][\text{F}^-]^2$$

Solubility product constant



$$K_{sp} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3 = (2.0 \times 10^{-15})^2 (3.0 \times 10^{-15})^3 = 1.1 \times 10^{-73}$$

Solubility = x for Bi_2S_3

$$K_{sp} = (2x)^2(3x)^3 = 108x^5 \Rightarrow x = \sqrt[5]{\frac{K_{sp}}{108}}$$

✓ Relative solubility

$$\text{CuS}(s) \quad K_{sp} = 8.5 \times 10^{-45} \quad \text{solubility} = \sqrt{K_{sp}}$$

$$\text{Ag}_2\text{S}(s) \quad K_{sp} = 1.6 \times 10^{-49} \quad \text{solubility} = \sqrt[3]{K_{sp}/4}$$

$$\text{Bi}_2\text{S}_3(s) \quad K_{sp} = 1.1 \times 10^{-73}$$

Solubility $\text{Bi}_2\text{S}_3(s) > \text{Ag}_2\text{S} > \text{CuS}(s)$

✓ Common ion effect

Decrease solubility

✓ Complications

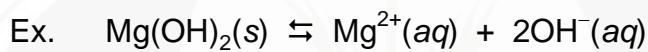
Ion pairing $(A^+)(B^-)(aq)$

The K_{sp} calculated from solubility may not be correct

Complex formation



✓ pH and solubility



Addition of H^+

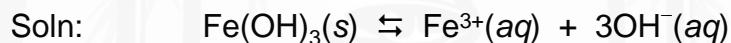
→ removes OH^-

→ drives equilibrium to the right

→ solubility increases

Ex. $Fe(OH)_3$, $K_{sp} = 4 \times 10^{-38}$

Q: Solubility in water



Assume OH^- derived from $Fe(OH)_3$ is very small

$$\Rightarrow [OH^-] = 1 \times 10^{-7} M$$

At equilibrium: $[Fe^{3+}](1 \times 10^{-7})^3 = 4 \times 10^{-38}$

$$\Rightarrow [Fe^{3+}] = 4 \times 10^{-17} M \leftarrow \text{Small indeed}$$

The exact solution:

$$[Fe^{3+}][OH^-]^3 = 4 \times 10^{-38}$$

$$[H^+][OH^-] = 1 \times 10^{-14}$$

$$3[Fe^{3+}] + [H^+] = [OH^-] \Rightarrow [H^+] = [OH^-] - 3[Fe^{3+}]$$

$$\Rightarrow ([OH^-] - 3[Fe^{3+}])([OH^-]) = [OH^-]^2 - 3[Fe^{3+}][OH^-]$$
$$= 1 \times 10^{-14}$$

$$[\text{OH}^-]^2 - 3[\text{Fe}^{3+}][\text{OH}^-] = 1 \times 10^{-14}$$

$$\Rightarrow [\text{OH}^-]^4 - 3[\text{Fe}^{3+}][\text{OH}^-]^3 = (1 \times 10^{-14})[\text{OH}^-]^2$$

$$\Rightarrow [\text{OH}^-]^4 - 3(4 \times 10^{-38}) = (1 \times 10^{-14})[\text{OH}^-]^2$$

$$\Rightarrow [\text{OH}^-]^4 - (1 \times 10^{-14})[\text{OH}^-]^2 - 12 \times 10^{-38} = 0$$

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

$$\Rightarrow [\text{OH}^-] = 1 \times 10^{-7} M$$

※ Qualitative analysis

✓ Formation of precipitate (ppt)

ion product $Q > K_{sp}$

Initial value Equilibrium value

✓ Separate through selective precipitation

Ex. A solution of $1.0 \times 10^{-4} M \text{ Cu}^+$ } + I^-
 $2.0 \times 10^{-3} M \text{ Pb}^{2+}$ }

$$\text{PbI}_2 \quad K_{sp} = 1.4 \times 10^{-8} = (2.0 \times 10^{-3})([I^-])^2$$

$$\Rightarrow [I^-] = 2.6 \times 10^{-3} M$$

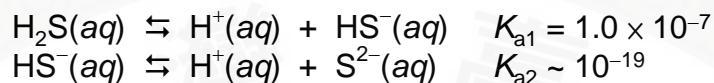
Minimum value to precipitate Pb^{2+}

$$\text{CuI} \quad K_{sp} = 5.3 \times 10^{-12} = (1.0 \times 10^{-4})([I^-])$$

$$\Rightarrow [I^-] = 5.3 \times 10^{-8} M$$

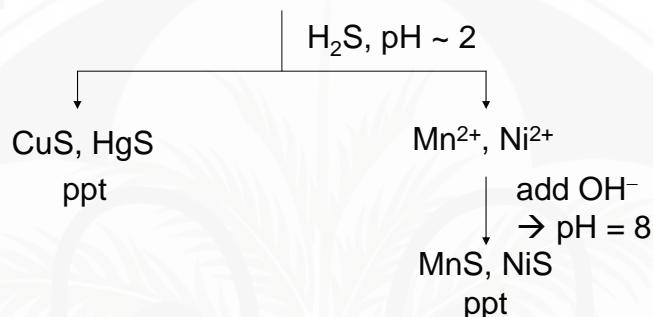
Cu^+ will precipitate first

✓ Sulfides are often used to separate metal ions

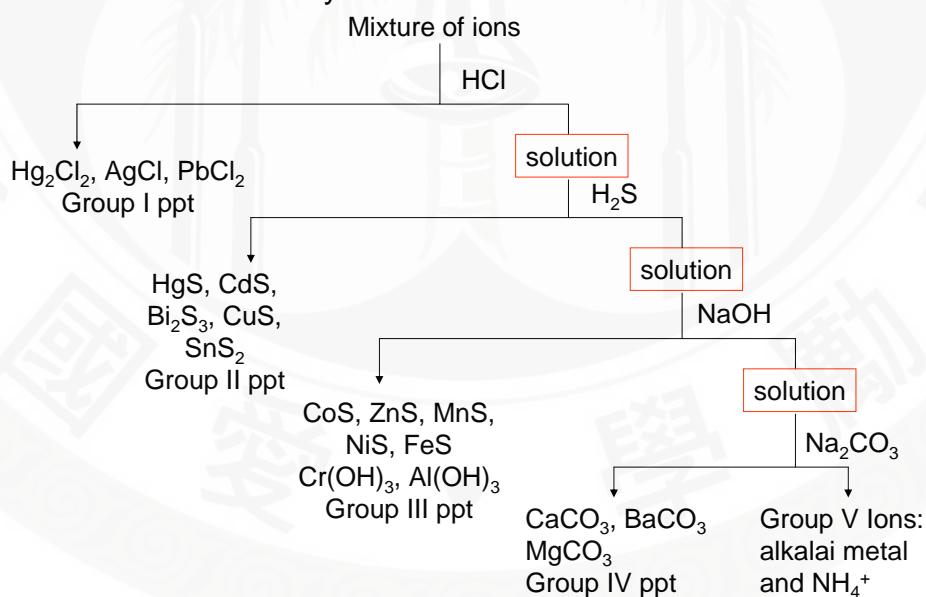


$[\text{S}^{2-}]$ can be controlled by pH

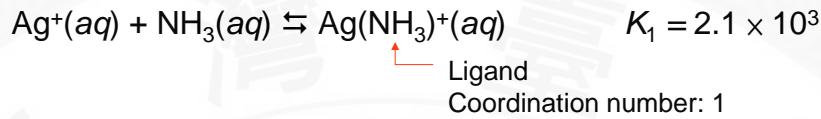
Ex. $\text{Mn}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}, \text{Hg}^{2+}$



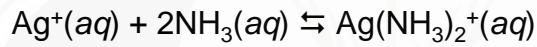
✓ Qualitative analysis



※ Complex ion equilibria



The major equilibrium:



$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{[\text{Ag}(\text{NH}_3)^+][\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3][\text{NH}_3][\text{Ag}(\text{NH}_3)^+]} = K_1 \bullet K_2 = 1.7 \times 10^7$$

With excess NH_3

all Ag^+ will be converted to $\text{Ag}(\text{NH}_3)_2^+$

Ex. Mixing 100.0 mL of 2.0 M NH_3
with 100.0 mL of 1.0×10^{-3} M AgNO_3

After mixing: $[\text{NH}_3] = 1.0 \text{ M}$ $[\text{Ag}^+] = 5.0 \times 10^{-4} \text{ M}$

$[\text{NH}_3] >> [\text{Ag}^+] = 5.0 \times 10^{-4} \text{ M}$

At equilibrium

$$[\text{NH}_3] = 1.0 \text{ M} \quad [\text{Ag}(\text{NH}_3)_2^+] = 5.0 \times 10^{-4} \text{ M}$$

$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{NH}_3][\text{Ag}(\text{NH}_3)^+]} = \frac{5.0 \times 10^{-4}}{(1.0)[\text{Ag}(\text{NH}_3)^+]} = 8.2 \times 10^3$$

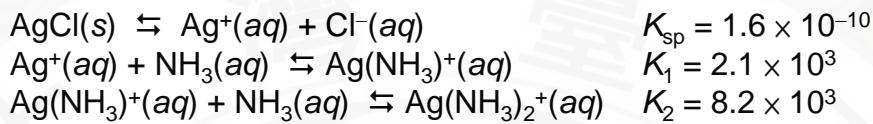
$$\Rightarrow [\text{Ag}(\text{NH}_3)^+] = 6.1 \times 10^{-8} \text{ M}$$

$$K_f = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{5.0 \times 10^{-4}}{[\text{Ag}^+](1.0)^2} = 1.7 \times 10^7$$

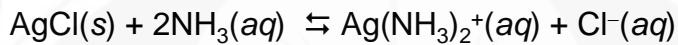
$$\Rightarrow [\text{Ag}^+] = 2.9 \times 10^{-11} \text{ M}$$

※ Complex ion and solubility

Ex.



Overall



$$K_f = K_{sp} \cdot K_1 \cdot K_2 = 2.8 \times 10^{-3}$$

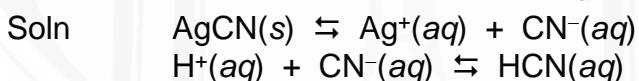
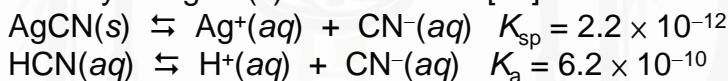
Q: Solubility of AgCl in 10.0 M NH₃

Soln: $K_f = \frac{x^2}{(10.0 - 2x)^2} = 2.8 \times 10^{-3} \Rightarrow x = 0.48 \text{ M}$

Cf. solubility of AgCl in water = $\sqrt{K_{sp}} = 1.3 \times 10^{-5} \text{ M}$

※ More examples

► Q: Solubility of AgCN(s) in a soln with [H⁺] = 1.0 M?



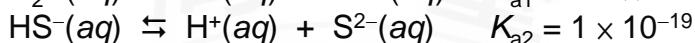
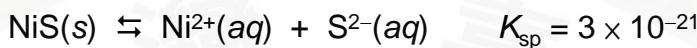
$$K = \frac{K_{sp}}{K_a} = \frac{2.2 \times 10^{-12}}{6.2 \times 10^{-10}} = 3.5 \times 10^{-3}$$



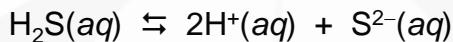
Ini	1.0	0	0
Equil	1.0 - x	x	x

$$\frac{x^2}{1.0 - x} = 3.5 \times 10^{-3} \Rightarrow x = 5.7 \times 10^{-2} \text{ M} = [\text{Ag}^+]$$

- Q: At 25 °C, water saturated with 0.10 M H₂S, pH = 3.0
Maximum possible [Ni²⁺] ?



Soln $[\text{H}^+] = 1 \times 10^{-3} \text{ M} \Rightarrow \text{controls } [\text{S}^{2-}]$



$$K = K_{a1} \cdot K_{a2} = 1 \times 10^{-26} \quad \text{very small}$$

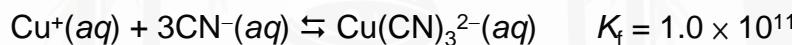
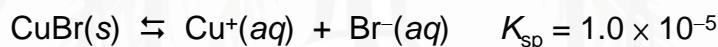
$$\frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{(1 \times 10^{-3})^2[\text{S}^{2-}]}{0.10} = 1 \times 10^{-26}$$

$$\Rightarrow [\text{S}^{2-}] = 1.0 \times 10^{-21} \text{ M}$$

$$\Rightarrow [\text{Ni}^{2+}][\text{S}^{2-}] = 3 \times 10^{-21} = [\text{Ni}^{2+}] (1.0 \times 10^{-21})$$

$$\Rightarrow [\text{Ni}^{2+}] = 3 \text{ M}$$

- Q: Solubility of CuBr(s) in 1.0 L of 1.0 M NaCN ?



Soln $\text{CuBr}(s) + 3\text{CN}^-(aq) \rightleftharpoons \text{Br}^-(aq) + \text{Cu}(\text{CN})_3^{2-}(aq)$

$$K = K_{sp} \cdot K_f = 1.0 \times 10^6 \quad \text{very large}$$

Essentially 1.0 M CN⁻ is all converted to Cu(CN)₃²⁻

$$\Rightarrow [\text{Cu}(\text{CN})_3^{2-}] = [\text{Br}^-] = 1/3(1.0 \text{ M}) = 0.33 \text{ M}$$

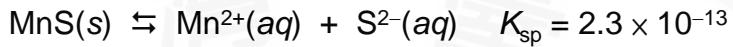
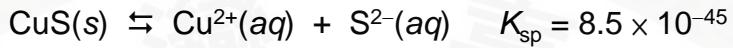
$$K_{sp} = [\text{Cu}^+][\text{Br}^-] = 1.0 \times 10^{-5} = [\text{Cu}^+][0.33]$$

$$\Rightarrow [\text{Cu}^+] = 3.0 \times 10^{-5} \text{ M}$$

$$K_f = \frac{[\text{Cu}(\text{CN})_3^{2-}]}{[\text{Cu}^+][\text{CN}^-]^3} = \frac{0.33}{(3.0 \times 10^{-5})[\text{CN}^-]^3} = 1.0 \times 10^{11}$$

$$\Rightarrow [\text{CN}^-] = 4.8 \times 10^{-3} \text{ M}$$

- Q: With 0.1 M H₂S, [Cu²⁺] = [Mn²⁺] = 1.0 × 10⁻³ M,
pH range where CuS precipitates but MnS doesn't ?

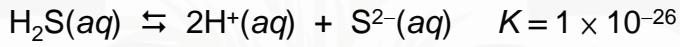


Soln [Cu²⁺][S²⁻] = 8.5 × 10⁻⁴⁵ = [1.0 × 10⁻³][S²⁻]

$$\Rightarrow [\text{S}^{2-}] = 8.5 \times 10^{-42} \text{ M for precipitation of CuS}$$

$$[\text{Mn}^{2+}][\text{S}^{2-}] = 2.3 \times 10^{-13} = [1.0 \times 10^{-3}][\text{S}^{2-}]$$

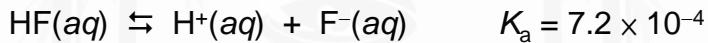
$$\Rightarrow [\text{S}^{2-}] = 2.3 \times 10^{-10} \text{ M for precipitation of MnS}$$



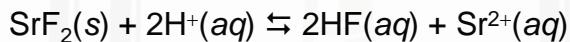
Assume [H₂S] doesn't change

$$\frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{0.10} = 1 \times 10^{-26} \Rightarrow [\text{H}^+] = \sqrt{\frac{1 \times 10^{-27}}{[\text{S}^{2-}]}}$$

- Q: In a buffer with pH = 2.00, solubility of SrF₂(s) ?



Soln [H⁺] = 1.0 × 10⁻²



Equil 1.0 × 10⁻² 2x x

$$K = \frac{[\text{HF}]^2[\text{Sr}^{2+}]}{[\text{H}^+]^2} = \frac{K_{sp}}{K_a^2} = \frac{7.9 \times 10^{-10}}{(7.2 \times 10^{-4})^2} = \frac{(2x)^2(x)}{[1.0 \times 10^{-2}]^2}$$

$$x^3 = 38 \times 10^{-9} \quad \Rightarrow \quad x = 3.4 \times 10^{-3} \text{ M}$$