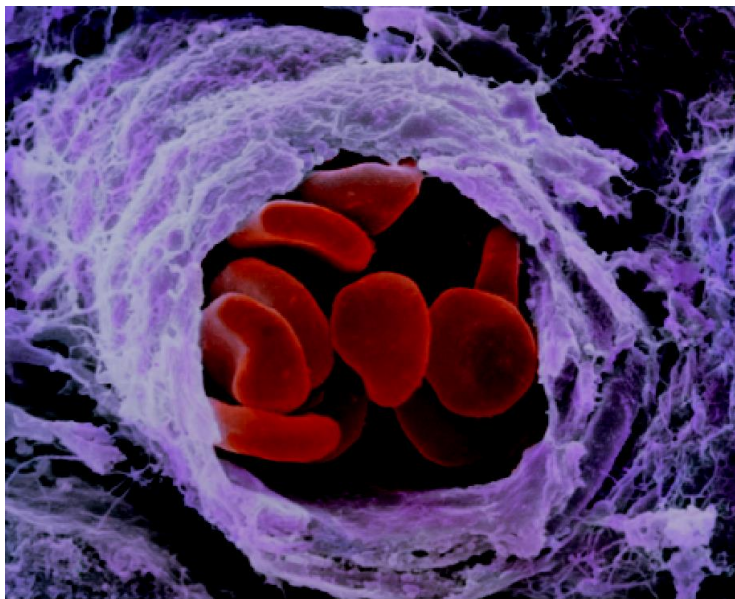


Acid-Base Equilibria and Solubility Equilibria

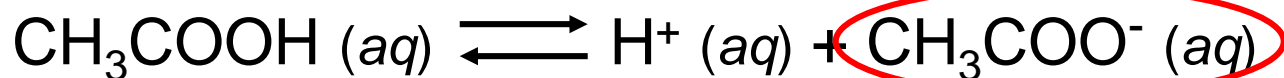
Chapter 16



The **common ion effect** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion **suppresses** the ionization of a weak acid or a weak base.

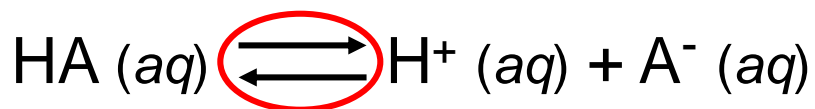
Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).



common
ion



Consider mixture of salt NaA and weak acid HA.



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

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

Henderson-Hasselbalch
equation

$$-\log [\text{H}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

$$-\log [\text{H}^+] = -\log K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

$$\text{p}K_a = -\log K_a$$

What is the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK?

Mixture of weak acid and conjugate base!



Initial (M)	0.30	0.00	0.52
Change (M)	-x	+x	+x
Equilibrium (M)	0.30 - x	x	0.52 + x

Common ion effect

$$0.30 - x \approx 0.30$$

$$0.52 + x \approx 0.52$$

$$\text{HCOOH } pK_a = 3.77$$

$$\text{pH} = pK_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

$$\text{pH} = 3.77 + \log \frac{[0.52]}{[0.30]} = 4.01$$

A **buffer solution** is a solution of:

1. A weak acid or a weak base **and**
2. The salt of the weak acid or weak base

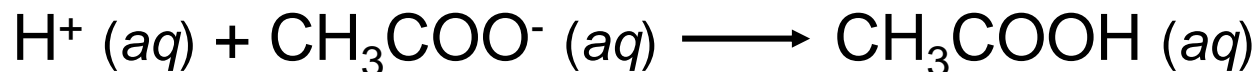
Both must be present!



A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

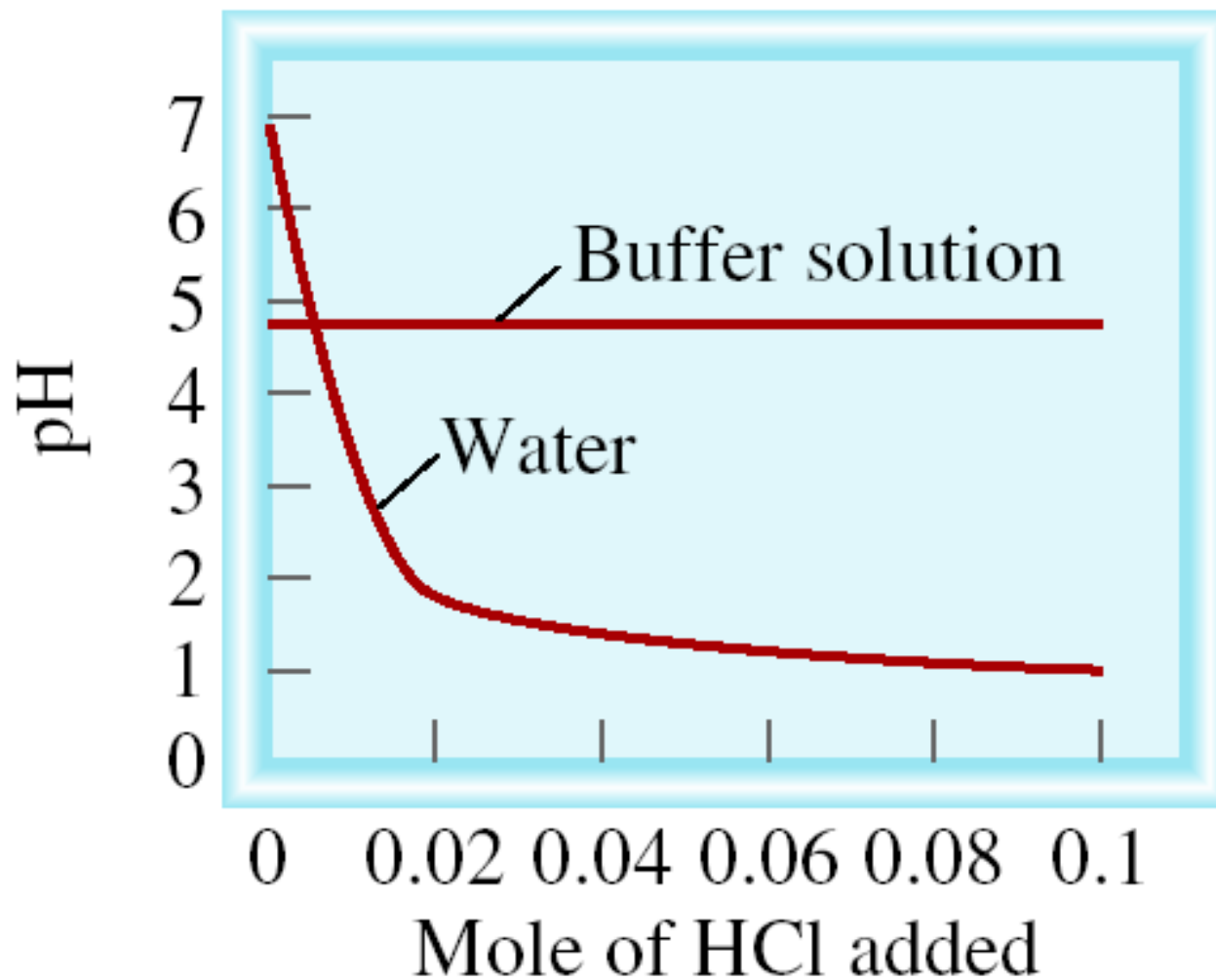
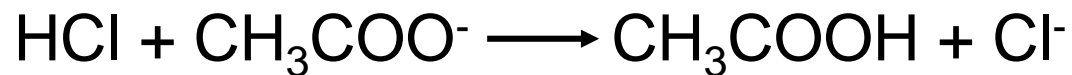
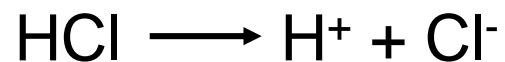
Consider an equal molar mixture of CH_3COOH and CH_3COONa

Add strong acid



Add strong base





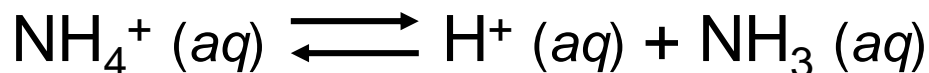
Which of the following are buffer systems? (a) KF/HF
(b) KBr/HBr, (c) $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$

(a) KF is a weak acid and F^- is its conjugate base
buffer solution

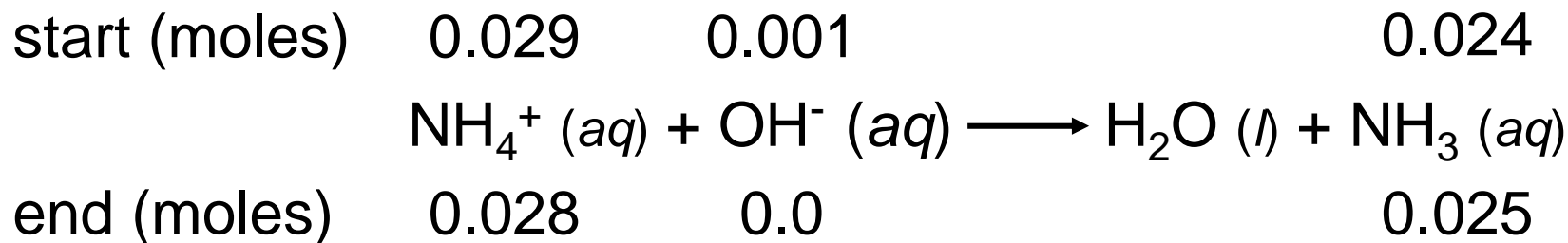
(b) HBr is a strong acid
not a buffer solution

(c) CO_3^{2-} is a weak base and HCO_3^- is its conjugate acid
buffer solution

Calculate the pH of the 0.30 M NH₃/0.36 M NH₄Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 M NaOH to 80.0 mL of the buffer solution?



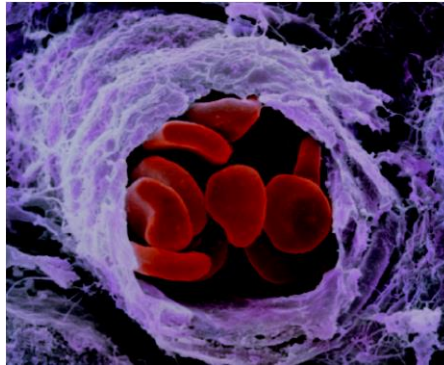
$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \quad \text{p}K_a = 9.25 \quad \text{pH} = 9.25 + \log \frac{[0.30]}{[0.36]} = 9.17$$



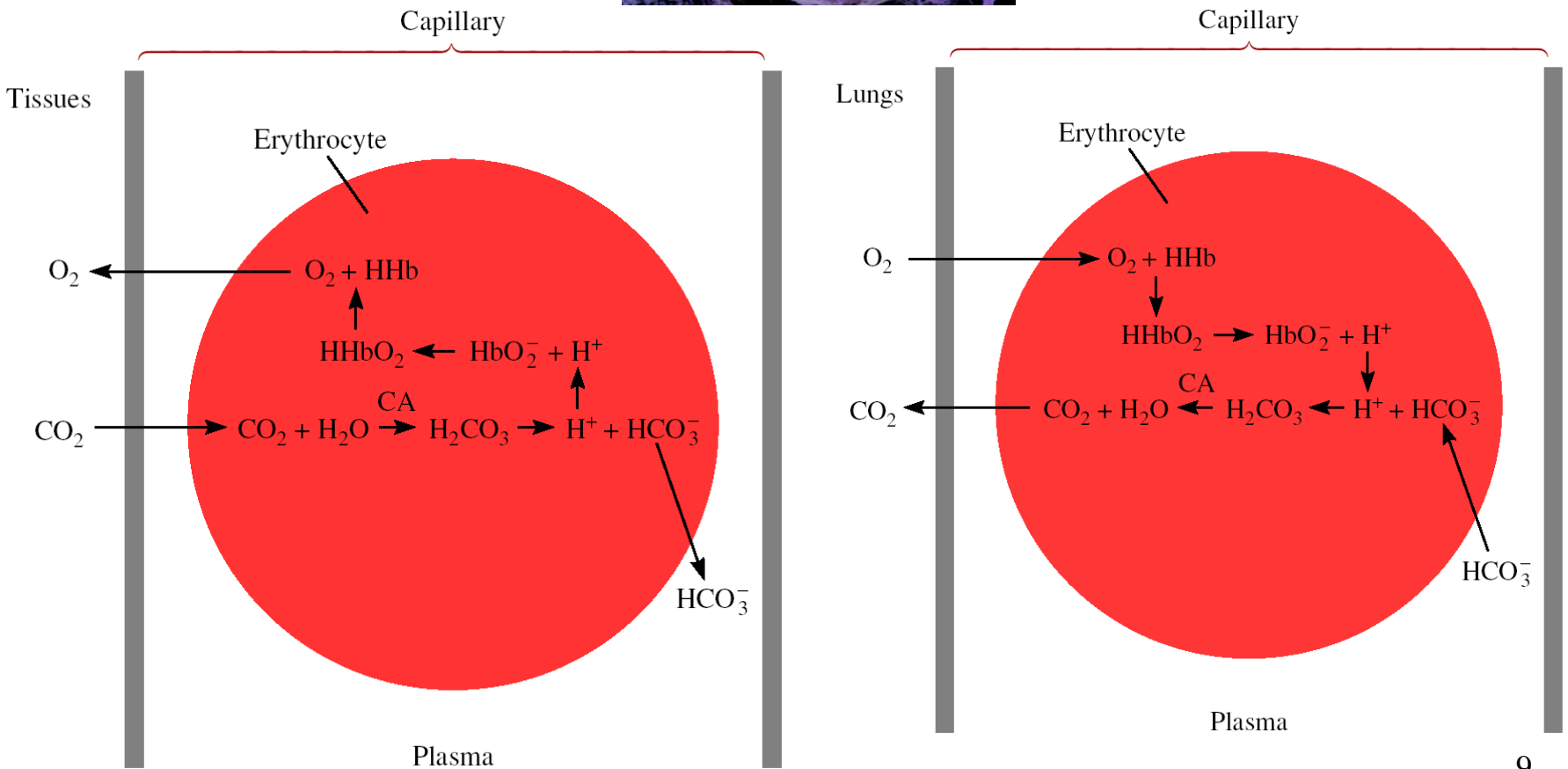
$$\text{final volume} = 80.0 \text{ mL} + 20.0 \text{ mL} = 100 \text{ mL}$$

$$[\text{NH}_4^+] = \frac{0.028}{0.10} \quad [\text{NH}_3] = \frac{0.025}{0.10} \quad \text{pH} = 9.25 + \log \frac{[0.25]}{[0.28]} = 9.20$$

Chemistry In Action: Maintaining the pH of Blood



Red blood cells in a capillary

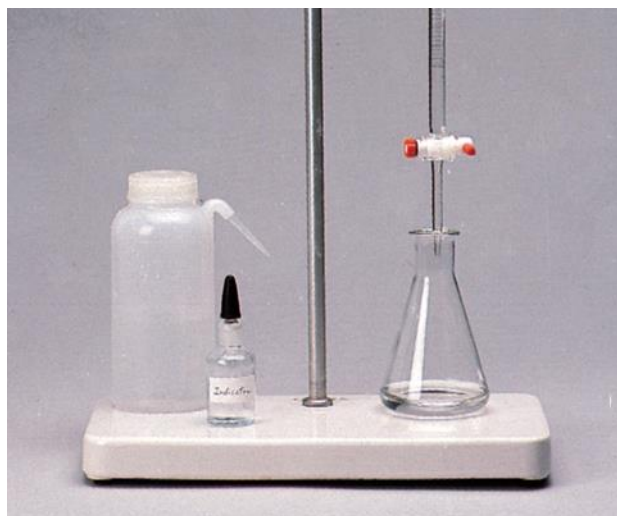


Titration (Review)

In a ***titration*** a solution of accurately known concentration is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

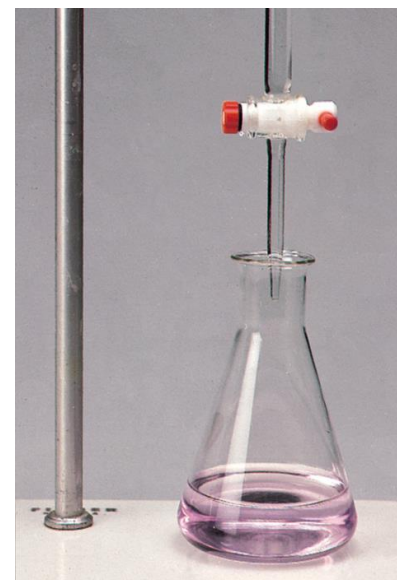
Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point

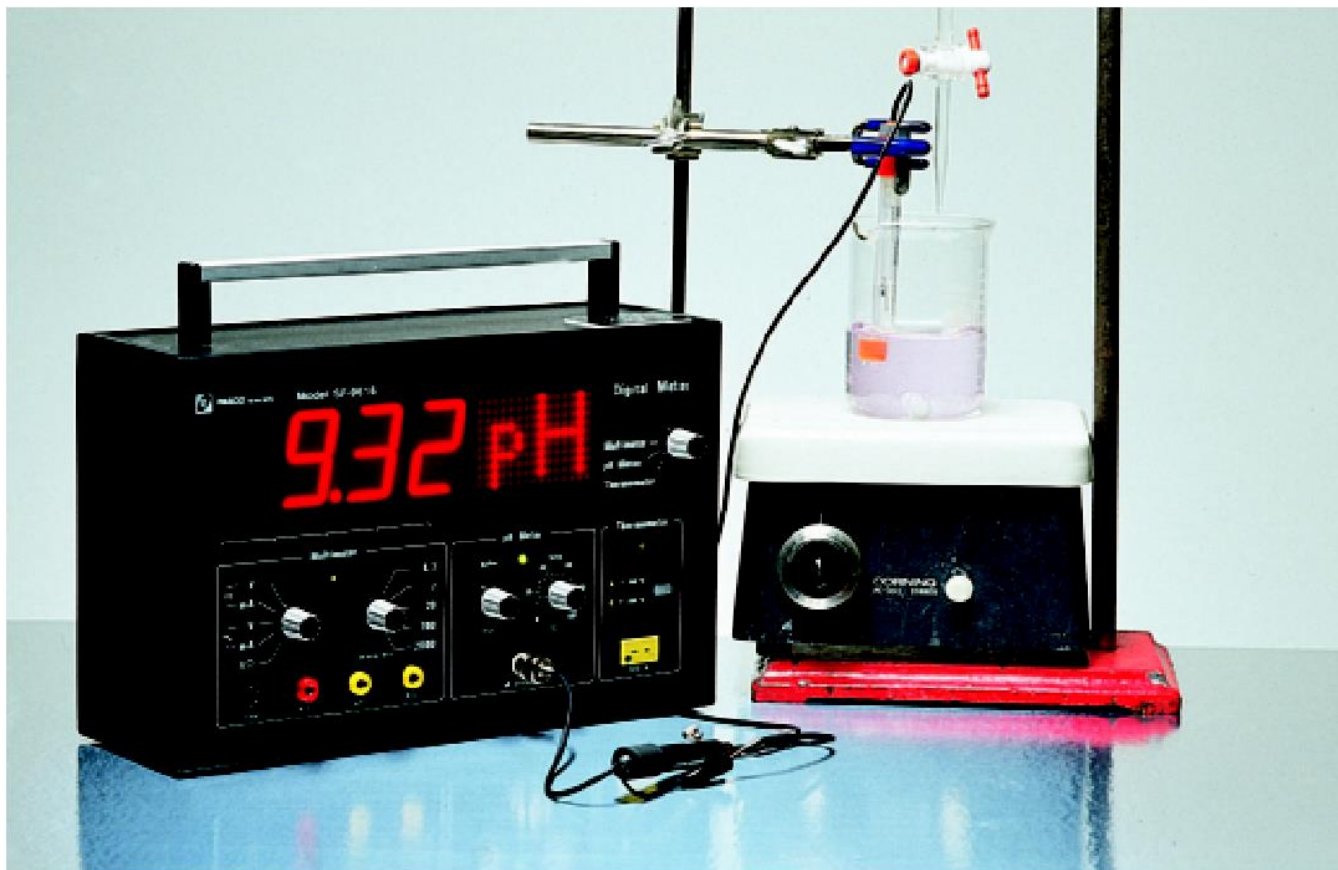


Slowly add base
to unknown acid
UNTIL

The indicator
changes color
(pink)

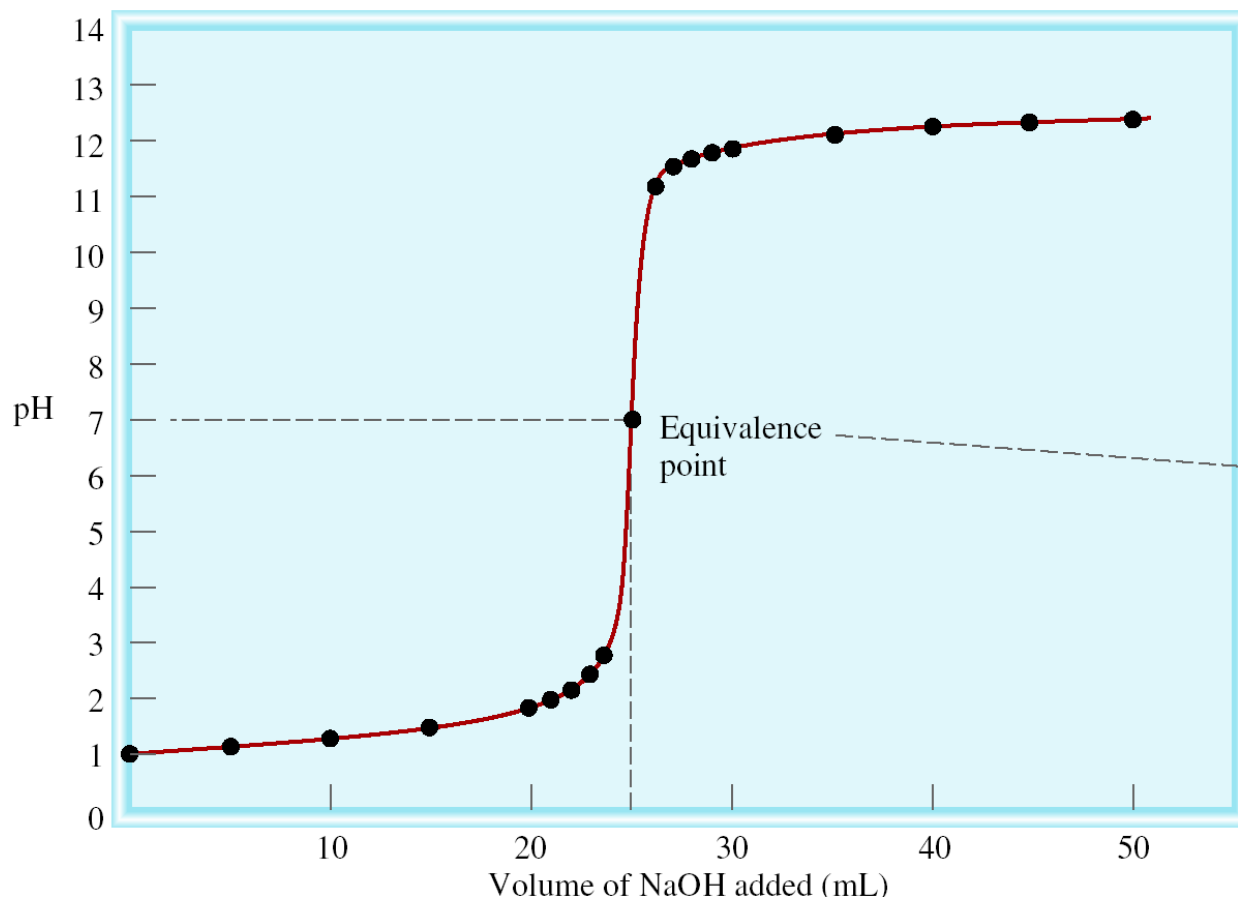
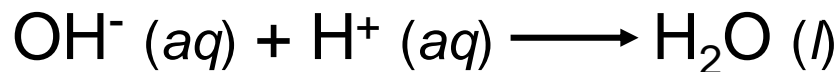


Alternative Method of Equivalence Point Detection



monitor pH

Strong Acid-Strong Base Titrations

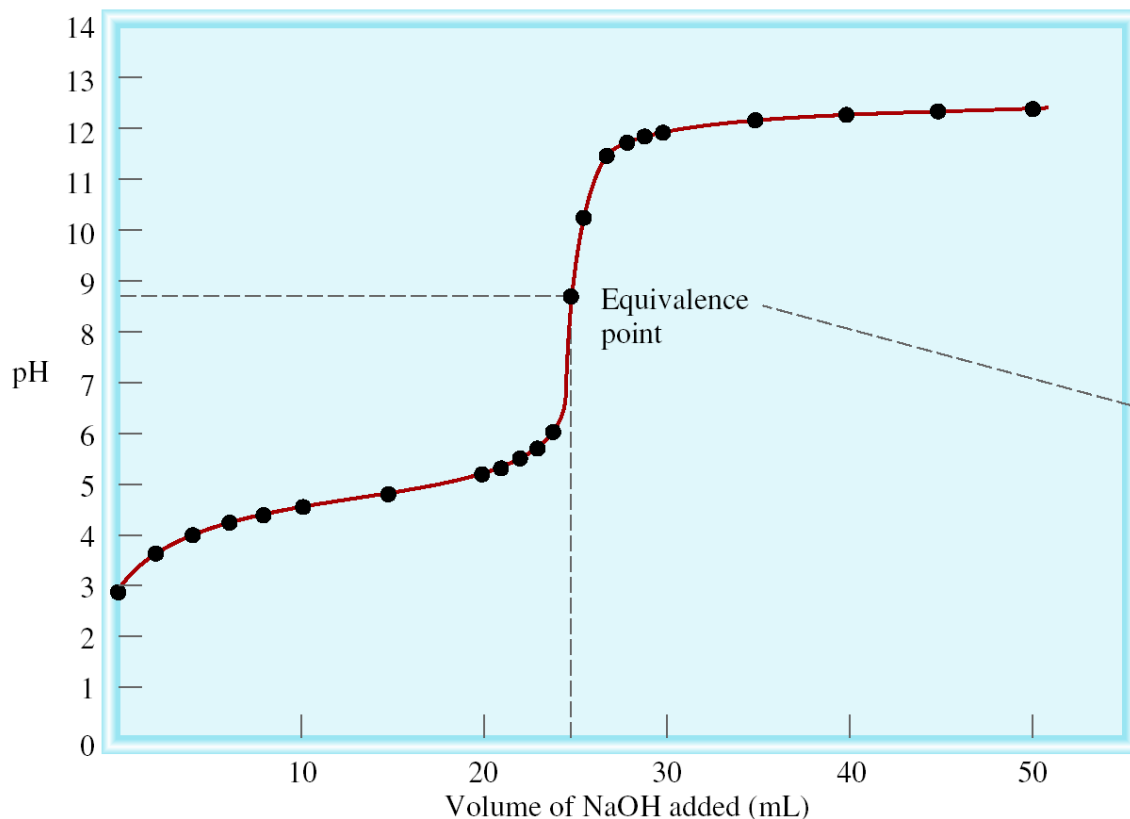
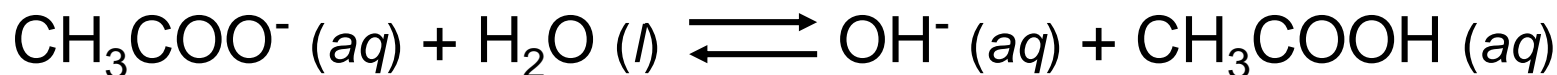


Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Weak Acid-Strong Base Titrations

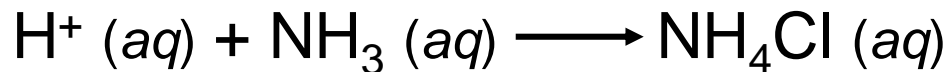
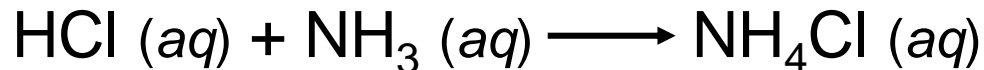


At equivalence point ($\text{pH} > 7$):

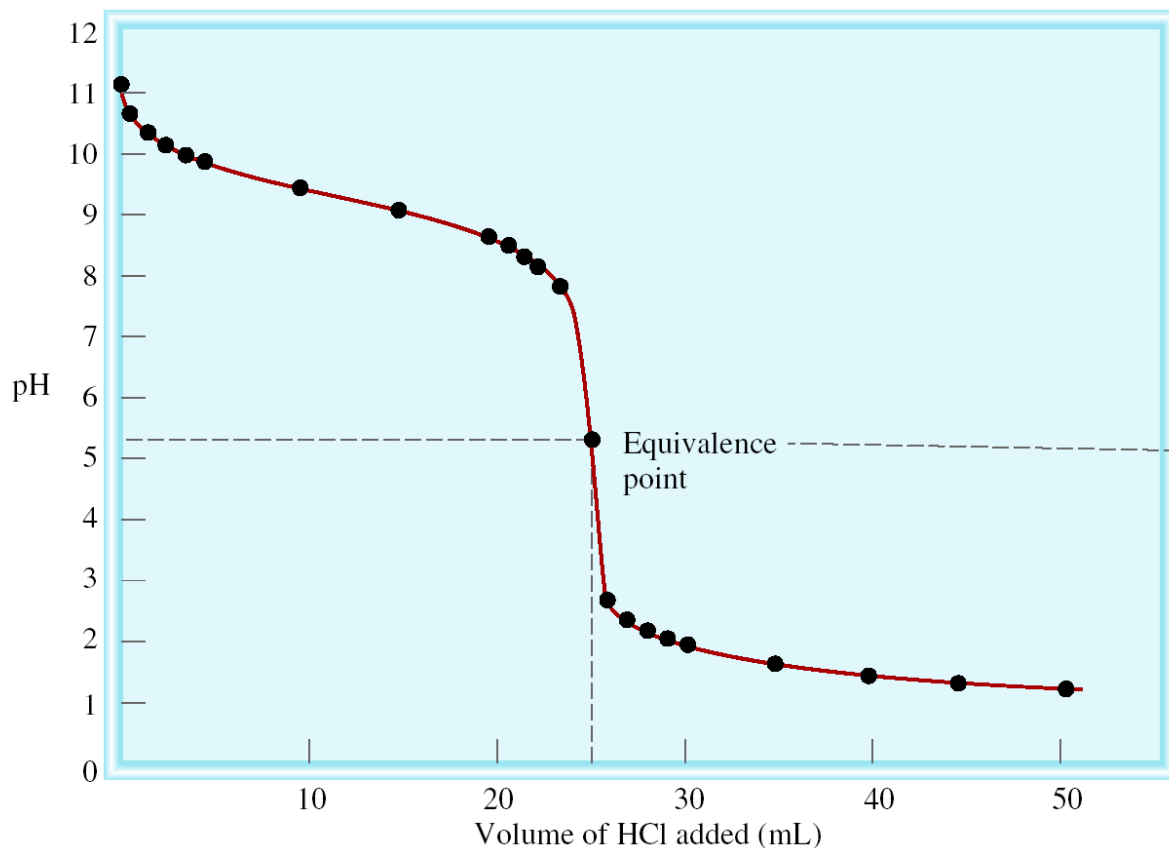


Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Strong Acid-Weak Base Titrations

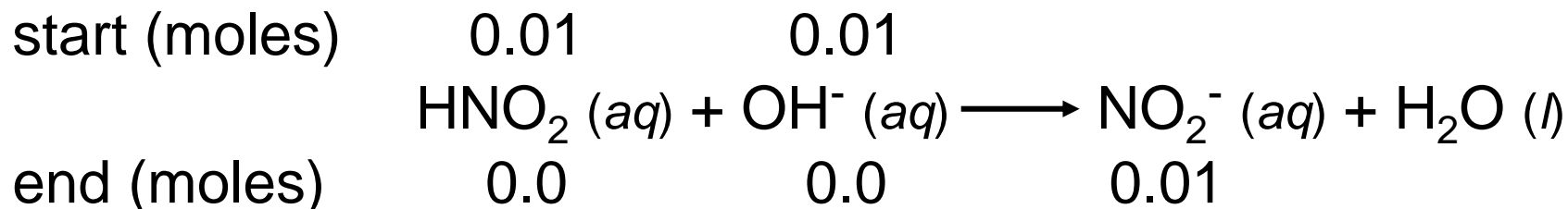


At equivalence point ($\text{pH} < 7$):



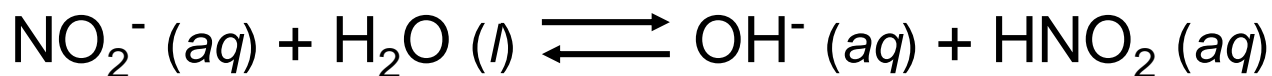
Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

Exactly 100 mL of 0.10 *M* HNO₂ are titrated with a 0.10 *M* NaOH solution. What is the pH at the equivalence point ?



Final volume = 200 mL

$$[\text{NO}_2^-] = \frac{0.01}{0.200} = 0.05 \text{ M}$$



Initial (<i>M</i>)	0.05	0.00	0.00
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Change (<i>M</i>)	- <i>x</i>	+ <i>x</i>	+ <i>x</i>
---------------------	------------	------------	------------

Equilibrium (<i>M</i>)	0.05 - <i>x</i>	<i>x</i>	<i>x</i>
--------------------------	-----------------	----------	----------

$$K_b = \frac{[\text{OH}^-][\text{HNO}_2]}{[\text{NO}_2^-]} = \frac{x^2}{0.05-x} = 2.2 \times 10^{-11} \quad \text{pOH} = 5.98$$

$$0.05 - x \approx 0.05 \quad x \approx 1.05 \times 10^{-6} = [\text{OH}^-] \quad \text{pH} = 14 - \text{pOH} = 8.02$$

Acid-Base Indicators



$\frac{[\text{HIn}]}{[\text{In}^-]} \geq 10$ Color of acid (HIn) predominates

$\frac{[\text{HIn}]}{[\text{In}^-]} \leq 10$ Color of conjugate base (In^-) predominates

TABLE 16.1 Some Common Acid-Base Indicators

Indicator	Color		pH Range*
	In Acid	In Base	
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

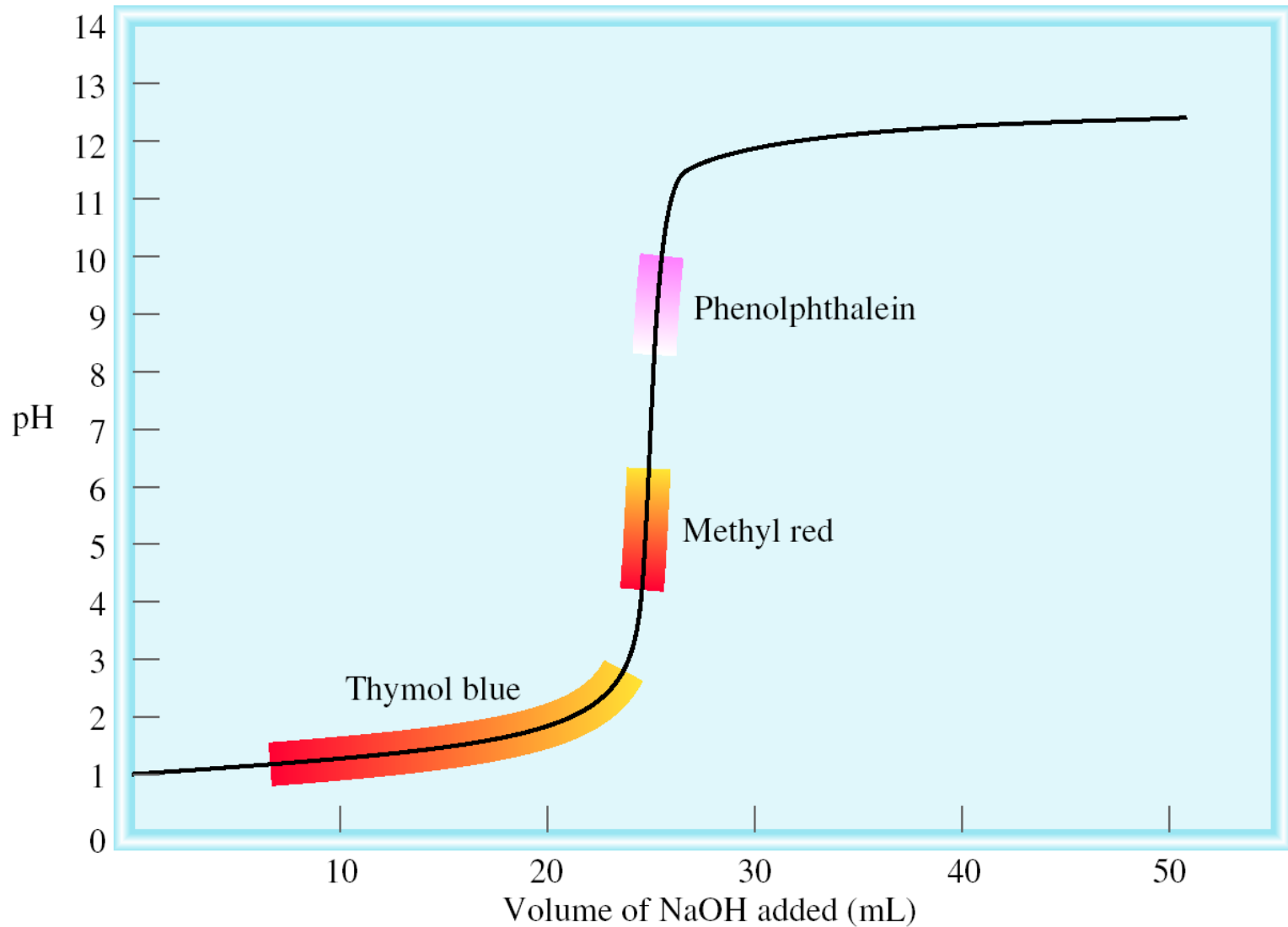
*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

Solutions of Red Cabbage Extract



———— pH —————→

The titration curve of a strong acid with a strong base.



Which indicator(s) would you use for a titration of HNO_2 with KOH ?

Weak acid titrated with strong base.

At equivalence point, will have conjugate base of weak acid.

At equivalence point, $\text{pH} > 7$

Use cresol red or phenolphthalein

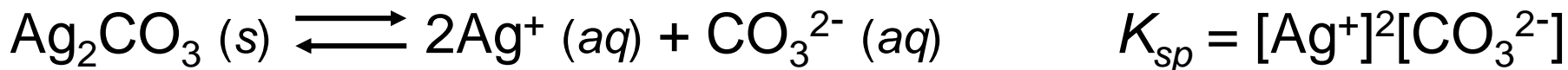
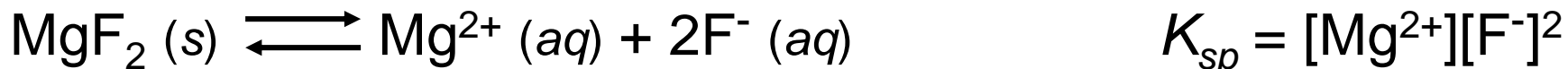
TABLE 16.1 Some Common Acid-Base Indicators			
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Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

Solubility Equilibria



$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$ K_{sp} is the ***solubility product constant***



Dissolution of an ionic solid in aqueous solution:

$Q < K_{sp}$ Unsaturated solution No precipitate

$Q = K_{sp}$ Saturated solution

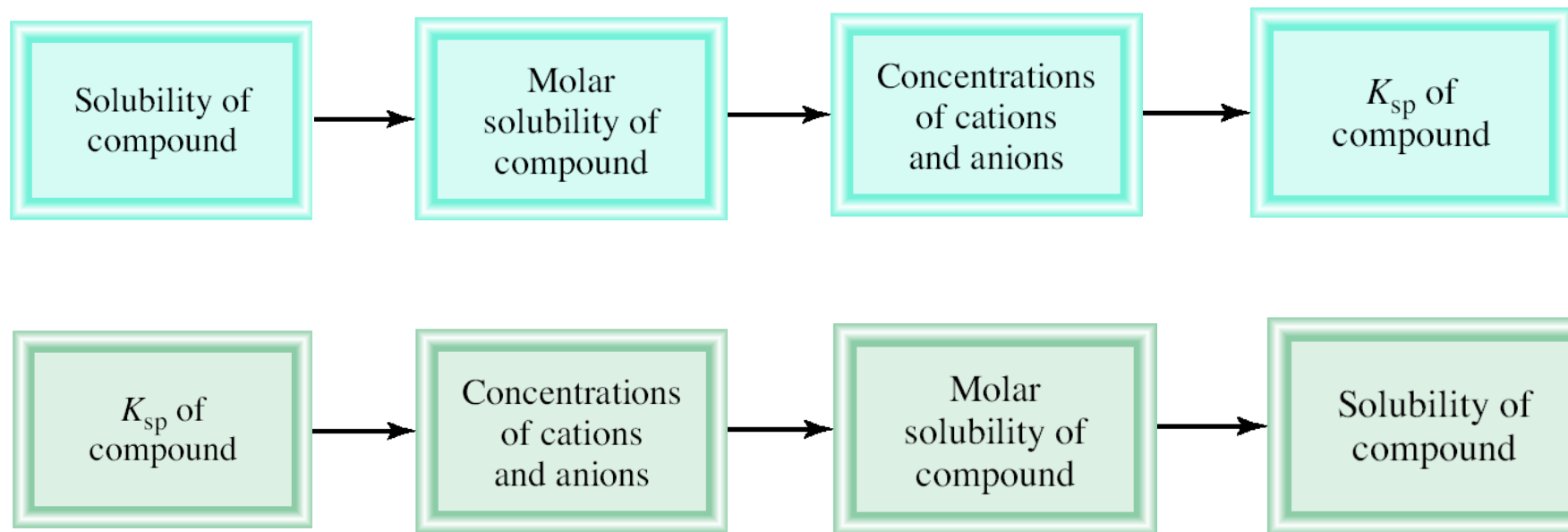
$Q > K_{sp}$ Supersaturated solution Precipitate will form

TABLE 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [Al(OH) ₃]	1.8×10^{-33}	Lead(II) chromate (PbCrO ₄)	2.0×10^{-14}
Barium carbonate (BaCO ₃)	8.1×10^{-9}	Lead(II) fluoride (PbF ₂)	4.1×10^{-8}
Barium fluoride (BaF ₂)	1.7×10^{-6}	Lead(II) iodide (PbI ₂)	1.4×10^{-8}
Barium sulfate (BaSO ₄)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi ₂ S ₃)	1.6×10^{-72}	Magnesium carbonate (MgCO ₃)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [Mg(OH) ₂]	1.2×10^{-11}
Calcium carbonate (CaCO ₃)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF ₂)	4.0×10^{-11}	Mercury(I) chloride (Hg ₂ Cl ₂)	3.5×10^{-18}
Calcium hydroxide [Ca(OH) ₂]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [Ca ₃ (PO ₄) ₂]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [Cr(OH) ₃]	3.0×10^{-29}	Silver bromide (AgBr)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag ₂ CO ₃)	8.1×10^{-12}
Copper(I) bromide (CuBr)	4.2×10^{-8}	Silver chloride (AgCl)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [Cu(OH) ₂]	2.2×10^{-20}	Silver sulfate (Ag ₂ SO ₄)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag ₂ S)	6.0×10^{-51}
Iron(II) hydroxide [Fe(OH) ₂]	1.6×10^{-14}	Strontium carbonate (SrCO ₃)	1.6×10^{-9}
Iron(III) hydroxide [Fe(OH) ₃]	1.1×10^{-36}	Strontium sulfate (SrSO ₄)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate (PbCO ₃)	3.3×10^{-14}	Zinc hydroxide [Zn(OH) ₂]	1.8×10^{-14}
Lead(II) chloride (PbCl ₂)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.



What is the solubility of silver chloride in g/L ?



Initial (<i>M</i>)	0.00	0.00	$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$
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Change (<i>M</i>)	+ <i>s</i>	+ <i>s</i>	$K_{sp} = s^2$
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Equilibrium (<i>M</i>)	<i>s</i>	<i>s</i>	$s = \sqrt{K_{sp}}$
--------------------------	----------	----------	---------------------

$$s = 1.3 \times 10^{-5}$$

$$[\text{Ag}^+] = 1.3 \times 10^{-5} \text{ M} \quad [\text{Cl}^-] = 1.3 \times 10^{-5} \text{ M}$$

$$\text{Solubility of AgCl} = \frac{1.3 \times 10^{-5} \cancel{\text{mol AgCl}}}{1 \text{ L soln}} \times \frac{143.35 \text{ g AgCl}}{1 \cancel{\text{mol AgCl}}} = 1.9 \times 10^{-3} \text{ g/L}$$

TABLE 16.3 Relationship Between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl	$[\text{Ag}^+][\text{Cl}^-]$	s	s	$K_{\text{sp}} = s^2; s = (K_{\text{sp}})^{\frac{1}{2}}$
BaSO ₄	$[\text{Ba}^{2+}][\text{SO}_4^{2-}]$	s	s	$K_{\text{sp}} = s^2; s = (K_{\text{sp}})^{\frac{1}{2}}$
Ag ₂ CO ₃	$[\text{Ag}^+]^2[\text{CO}_3^{2-}]$	$2s$	s	$K_{\text{sp}} = 4s^3; s = \left(\frac{K_{\text{sp}}}{4}\right)^{\frac{1}{3}}$
PbF ₂	$[\text{Pb}^{2+}][\text{F}^-]^2$	s	$2s$	$K_{\text{sp}} = 4s^3; s = \left(\frac{K_{\text{sp}}}{4}\right)^{\frac{1}{3}}$
Al(OH) ₃	$[\text{Al}^{3+}][\text{OH}^-]^3$	s	$3s$	$K_{\text{sp}} = 27s^4; s = \left(\frac{K_{\text{sp}}}{27}\right)^{\frac{1}{4}}$
Ca ₃ (PO ₄) ₂	$[\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$	$3s$	$2s$	$K_{\text{sp}} = 108s^5; s = \left(\frac{K_{\text{sp}}}{108}\right)^{\frac{1}{5}}$

If 2.00 mL of 0.200 M NaOH are added to 1.00 L of 0.100 M CaCl_2 , will a precipitate form?

The ions present in solution are Na^+ , OH^- , Ca^{2+} , Cl^- .

Only possible precipitate is $\text{Ca}(\text{OH})_2$ (solubility rules).

Is $Q > K_{sp}$ for $\text{Ca}(\text{OH})_2$?

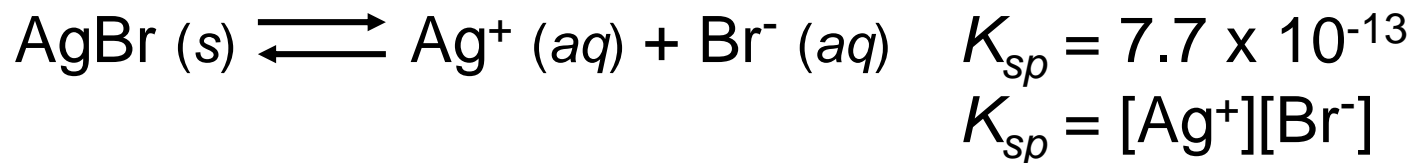
$$[\text{Ca}^{2+}]_0 = 0.100 \text{ M} \quad [\text{OH}^-]_0 = 4.0 \times 10^{-4} \text{ M}$$

$$Q = [\text{Ca}^{2+}]_0 [\text{OH}^-]_0^2 = 0.10 \times (4.0 \times 10^{-4})^2 = 1.6 \times 10^{-8}$$

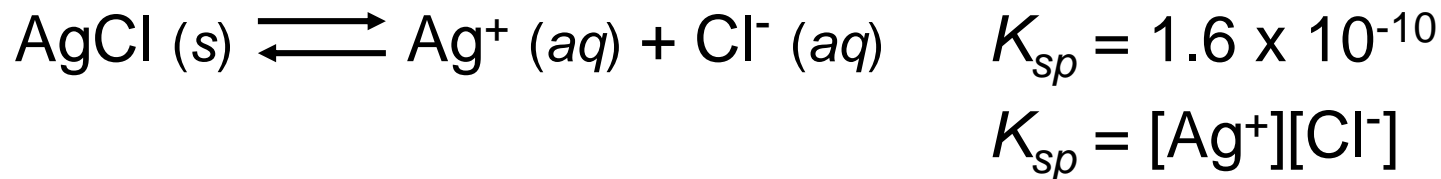
$$K_{sp} = [\text{Ca}^{2+}] [\text{OH}^-]^2 = 8.0 \times 10^{-6}$$

$$Q < K_{sp} \quad \text{No precipitate will form}$$

What concentration of Ag is required to precipitate ONLY AgBr in a solution that contains both Br⁻ and Cl⁻ at a concentration of 0.02 M?

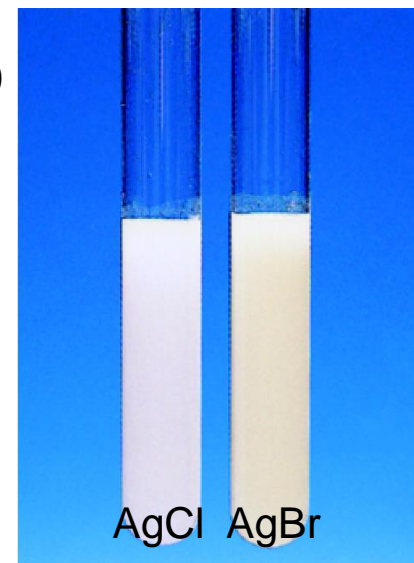


$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Br}^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11} \text{ M}$$



$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Cl}^-]} = \frac{1.6 \times 10^{-10}}{0.020} = 8.0 \times 10^{-9} \text{ M}$$

$$3.9 \times 10^{-11} \text{ M} < [\text{Ag}^+] < 8.0 \times 10^{-9} \text{ M}$$



The Common Ion Effect and Solubility

The presence of a common ion **decreases** the solubility of the salt.

What is the molar solubility of AgBr in (a) pure water and (b) 0.0010 M NaBr?



$$K_{sp} = 7.7 \times 10^{-13}$$

$$s^2 = K_{sp}$$

$$s = 8.8 \times 10^{-7}$$



$$[\text{Br}^-] = 0.0010 \text{ M}$$



$$[\text{Ag}^+] = s$$

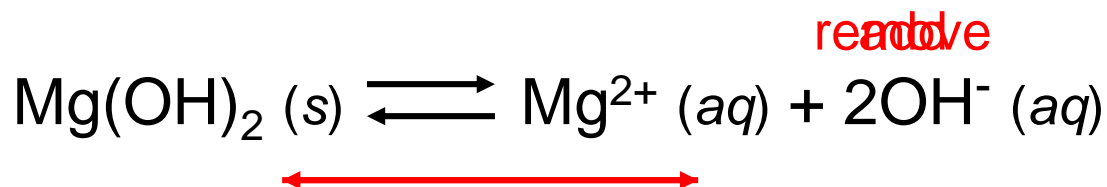
$$[\text{Br}^-] = 0.0010 + s \approx 0.0010$$

$$K_{sp} = 0.0010 \times s$$

$$s = 7.7 \times 10^{-10}$$

pH and Solubility

- The presence of a common ion **decreases** the solubility.
- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions



At pH less than 10.45

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11} \quad \text{Lower } [\text{OH}^-]$$

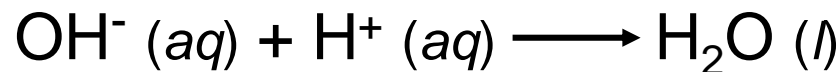
$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4s^3 = 1.2 \times 10^{-11}$$

$$s = 1.4 \times 10^{-4} \text{ M}$$

$$[\text{OH}^-] = 2s = 2.8 \times 10^{-4} \text{ M}$$

$$\text{pOH} = 3.55 \quad \text{pH} = 10.45$$



Increase solubility of Mg(OH)_2

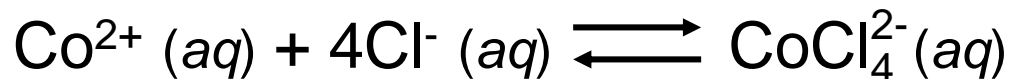
At pH greater than 10.45

Raise $[\text{OH}^-]$

Decrease solubility of Mg(OH)_2

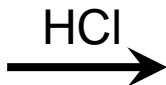
Complex Ion Equilibria and Solubility

A **complex ion** is an ion containing a central metal cation bonded to one or more molecules or ions.



The **formation constant or stability constant (K_f)** is the equilibrium constant for the complex ion formation.

$$K_f = \frac{[\text{CoCl}_4^{2-}]}{[\text{Co}^{2+}][\text{Cl}^{-}]^4}$$



$K_f \uparrow$

stability of complex \uparrow

Effect of Complexation on Solubility

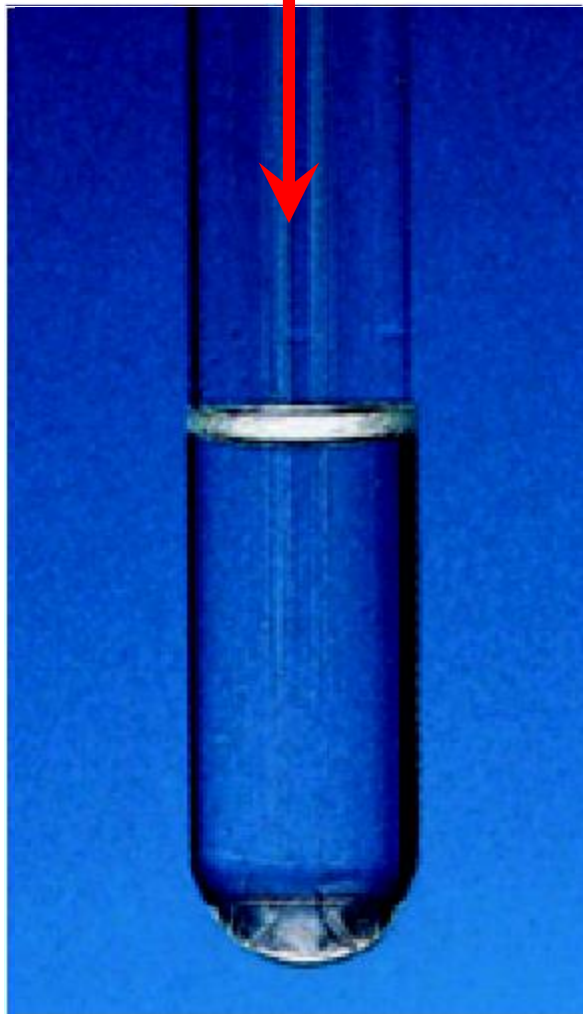


TABLE 16.4 **Formation Constants of Selected Complex Ions in Water at 25°C**

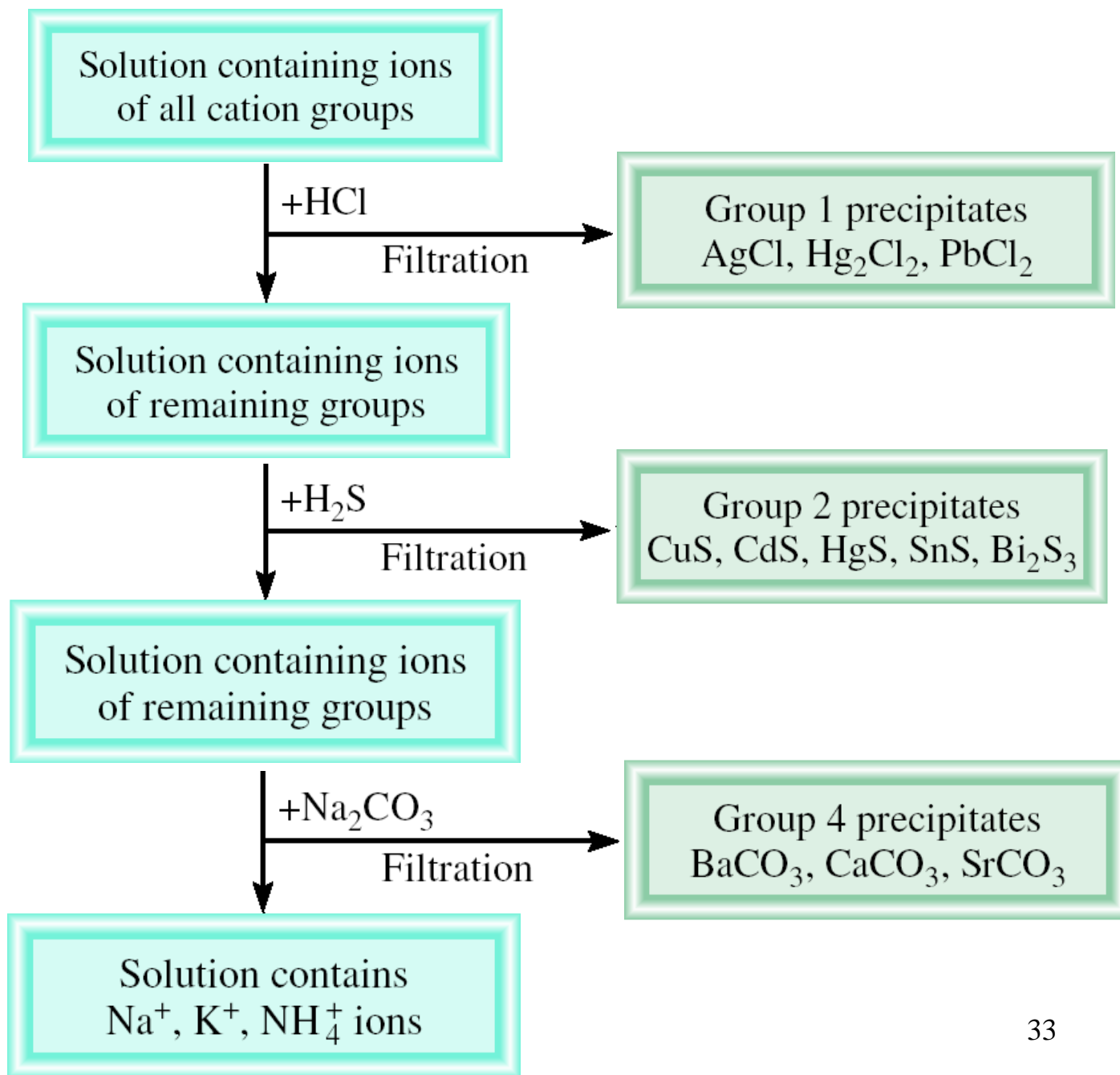
Complex Ion	Equilibrium Expression	Formation Constant (K_f)
$\text{Ag}(\text{NH}_3)_2^+$	$\text{Ag}^+ + 2\text{NH}_3 \rightleftharpoons \text{Ag}(\text{NH}_3)_2^+$	1.5×10^7
$\text{Ag}(\text{CN})_2^-$	$\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$	1.0×10^{21}
$\text{Cu}(\text{CN})_4^{2-}$	$\text{Cu}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cu}(\text{CN})_4^{2-}$	1.0×10^{25}
$\text{Cu}(\text{NH}_3)_4^{2+}$	$\text{Cu}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Cu}(\text{NH}_3)_4^{2+}$	5.0×10^{13}
$\text{Cd}(\text{CN})_4^{2-}$	$\text{Cd}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}$	7.1×10^{16}
CdI_4^{2-}	$\text{Cd}^{2+} + 4\text{I}^- \rightleftharpoons \text{CdI}_4^{2-}$	2.0×10^6
HgCl_4^{2-}	$\text{Hg}^{2+} + 4\text{Cl}^- \rightleftharpoons \text{HgCl}_4^{2-}$	1.7×10^{16}
HgI_4^{2-}	$\text{Hg}^{2+} + 4\text{I}^- \rightleftharpoons \text{HgI}_4^{2-}$	2.0×10^{30}
$\text{Hg}(\text{CN})_4^{2-}$	$\text{Hg}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Hg}(\text{CN})_4^{2-}$	2.5×10^{41}
$\text{Co}(\text{NH}_3)_6^{3+}$	$\text{Co}^{3+} + 6\text{NH}_3 \rightleftharpoons \text{Co}(\text{NH}_3)_6^{3+}$	5.0×10^{31}
$\text{Zn}(\text{NH}_3)_4^{2+}$	$\text{Zn}^{2+} + 4\text{NH}_3 \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+}$	2.9×10^9

TABLE 16.5

Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

Group	Cation	Precipitating Reagents	Insoluble Compound	K_{sp}
1	Ag^+	HCl ↓	AgCl	1.6×10^{-10}
	Hg_2^{2+}		Hg_2Cl_2	3.5×10^{-18}
	Pb^{2+}		PbCl_2	2.4×10^{-4}
2	Bi^{3+}	H_2S in acidic solutions ↓	Bi_2S_3	1.6×10^{-72}
	Cd^{2+}		CdS	8.0×10^{-28}
	Cu^{2+}		CuS	6.0×10^{-37}
	Hg^{2+}		HgS	4.0×10^{-54}
	Sn^{2+}		SnS	1.0×10^{-26}
	Al^{3+}		$\text{Al}(\text{OH})_3$	1.8×10^{-33}
3	Co^{2+}	H_2S in basic solutions ↓	CoS	4.0×10^{-21}
	Cr^{3+}		$\text{Cr}(\text{OH})_3$	3.0×10^{-29}
	Fe^{2+}		FeS	6.0×10^{-19}
	Mn^{2+}		MnS	3.0×10^{-14}
	Ni^{2+}		NiS	1.4×10^{-24}
	Zn^{2+}		ZnS	3.0×10^{-23}
	Ba^{2+}		BaCO_3	8.1×10^{-9}
	Ca^{2+}		CaCO_3	8.7×10^{-9}
4	Sr^{2+}	Na_2CO_3 ↓	SrCO_3	1.6×10^{-9}
	K^+		None	
	Na^+		None	
5	NH_4^+	No precipitating reagent	None	

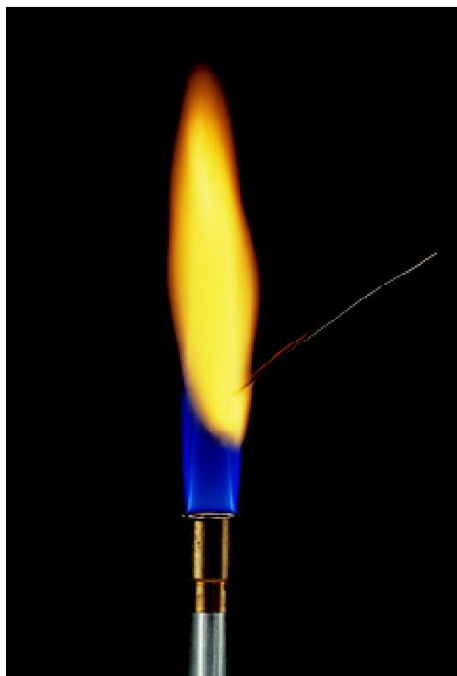
Qualitative Analysis of Cations



Flame Test for Cations



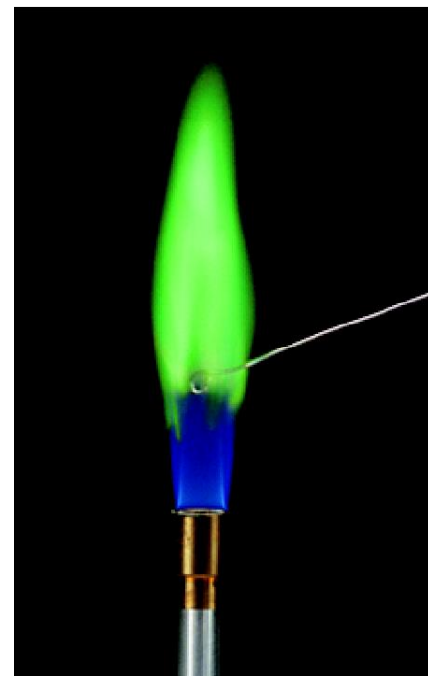
lithium



sodium

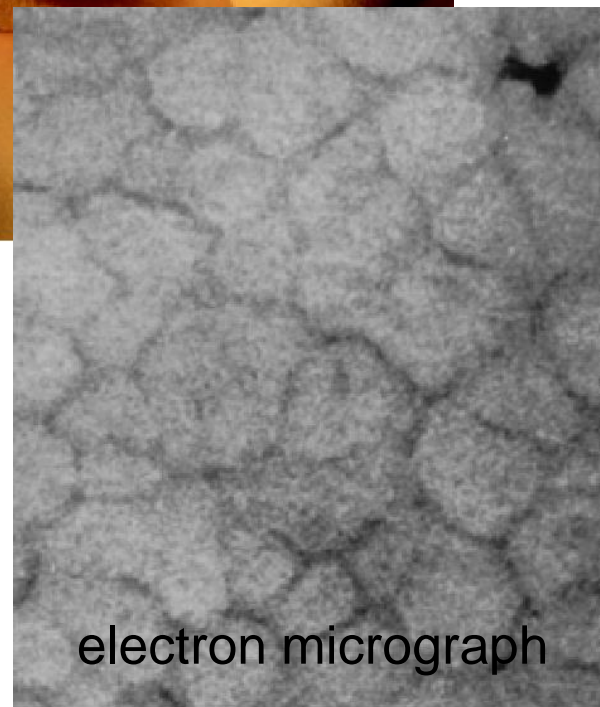
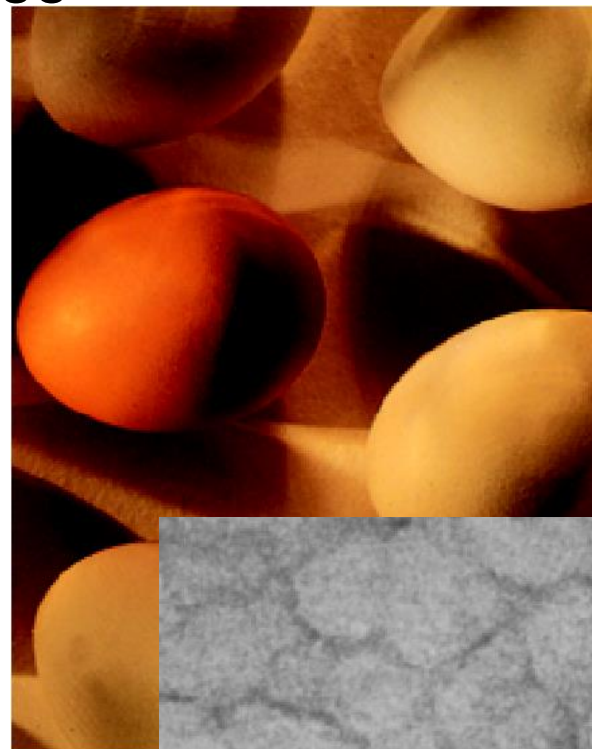
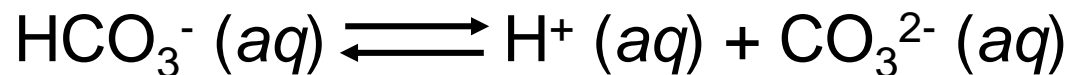
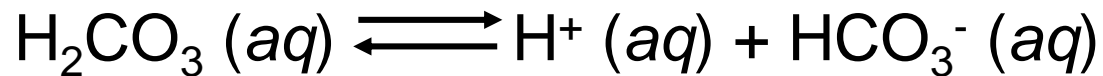
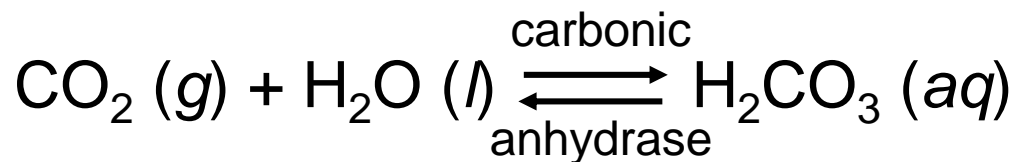
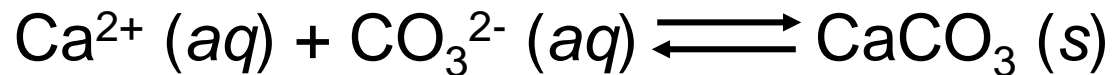


potassium



copper

Chemistry In Action: How an Eggshell is Formed



electron micrograph