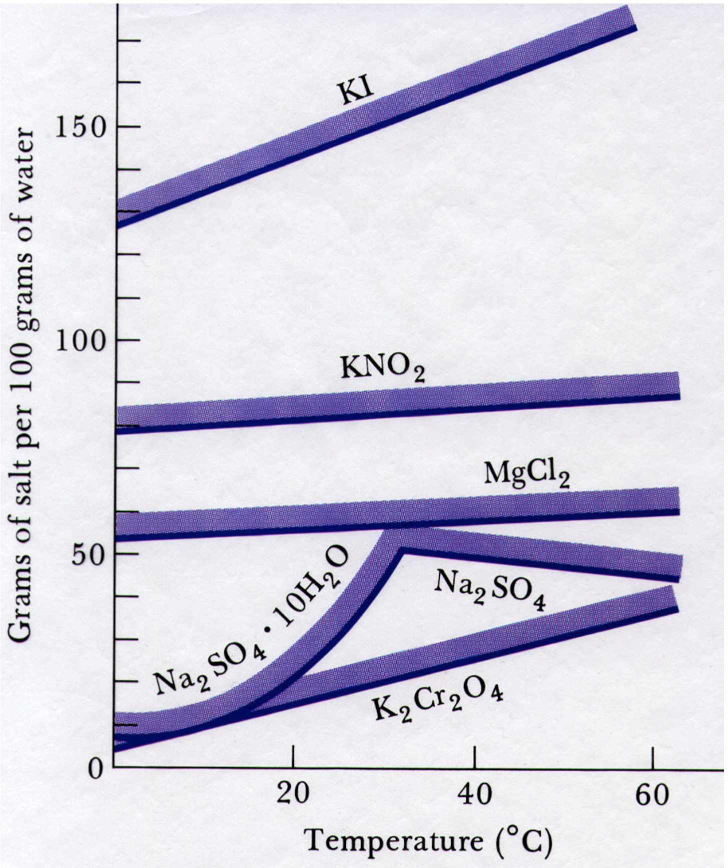
Soluble Salts in Water



- KI and K_2CrO_4:
  - Potassium iodide and potassium chromate are water-soluble.
- AgI and $PbCrO_4$
  - Silver iodide and lead chromate and are sparingly soluble:

    $K_{sp}(AgI)=8.5 \times 10^{-17}$

    $K_{sp}(PbCrO_4)=1.8 \times 10^{-14}$

TABLE 12–2 Solubility Product Constants at 25°C

Compound	K_{sp}	Compound	K_{sp}
AgBr	5.2×10^{-13}	$MgCO_3$	4.0×10^{-5}
AgCl	2.8×10^{-10}	$Mg(OH)_2$	1.2×10^{-11}
Ag_2CrO_4	1.9×10^{-12}	$Mn(OH)_2$	1.0×10^{-14}
AgI	8.5×10^{-17}	MnS	1.4×10^{-15}
Ag_2S	1.6×10^{-49}	$Ni(OH)_2$	1.6×10^{-16}
$Al(OH)_3$	1.8×10^{-33}	NiS	1.4×10^{-24}
$BaCO_3$	1.6×10^{-9}	$PbCO_3$	1.5×10^{-13}
$BaCrO_4$	8.5×10^{-11}	$PbCrO_4$	1.8×10^{-14}
BaF_2	1.7×10^{-6}	$Pb(OH)_2$	1.8×10^{-16}
$BaSO_4$	1.1×10^{-10}	PbS	3.4×10^{-28}
$CaCrO_4$	7.1×10^{-4}	$PbSO_4$	1.3×10^{-8}
CaF_2	1.7×10^{-10}	$Sn(OH)_2$	5×10^{-26}
$Ca_3(PO_4)_2$	1.3×10^{-32}	SnS	8×10^{-29}
$Cu(OH)_2$	1.6×10^{-19}	$SrCO_3$	1.6×10^{-9}
CuS	8.5×10^{-45}	SrF_2	2.8×10^{-9}
$Fe(OH)_2$	1.6×10^{-15}	$ZnCO_3$	2×10^{-10}
FeS	3.7×10^{-19}	$Zn(OH)_2$	4.5×10^{-24}
HgS	3×10^{-53}	ZnS	4.5×10^{-24}

Common Ion Effect

- Silver iodide

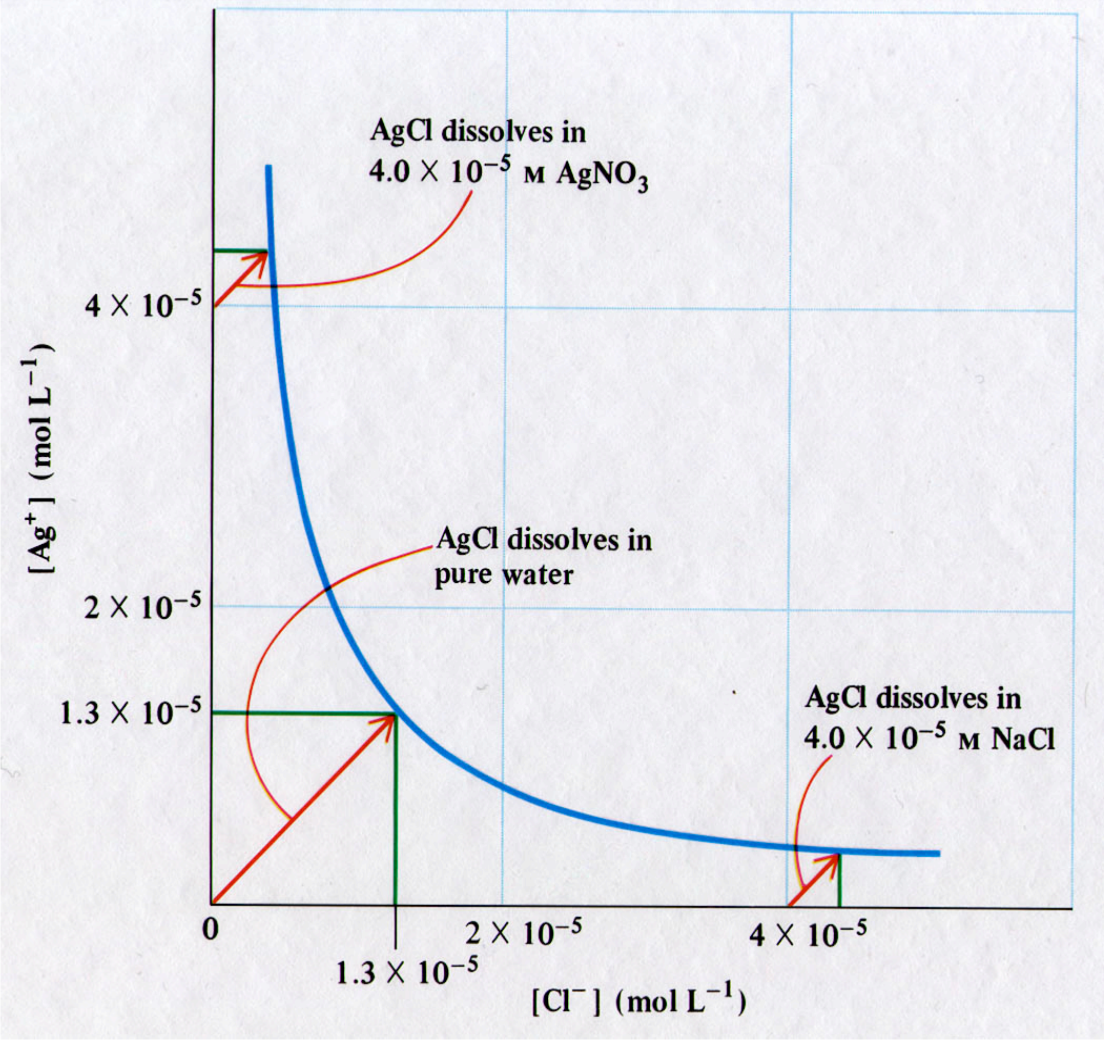
  $AgI(s) \rightleftharpoons Ag^+ + I^-$

  $K_{sp}=[Ag^+][I^-] = 8.5 \times 10^{-17}$

  $[Ag^+] = [I^-] = \text{solubility} = \sqrt{8.5x10^{-17}} = 9.2x10^{-9}$

- What if the solution were 0.1M in Ag^+ ions?
- What if the solution were 0.1M in I^- ions?

Common Ion Effect



Common Ion Effect

- Lead chromate

  $PbCrO_4(s) \rightleftharpoons Pb^{2+} + CrO_4^{2-}$

  $K_{sp}=[Pb^{2+}][CrO_4^{2-}] = 1.8 \times 10^{-14}$

  Let x = solubility of $[Pb^{2+}] = [CrO_4^{2-}]$
- What if $[Pb^{2+}] = 0.1M$?
- What if $[CrO_4^{2-}] = 0.1M$?
- What if $[Pb^{2+}]=[CrO_4^{2-}] = 0.1M$?

Common Ion Effect

- Calcium fluoride

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

$$K_{sp}=[Ca^{2+}][2F^-]^2 = 1.7 \text{ X } 10^{-10}$$

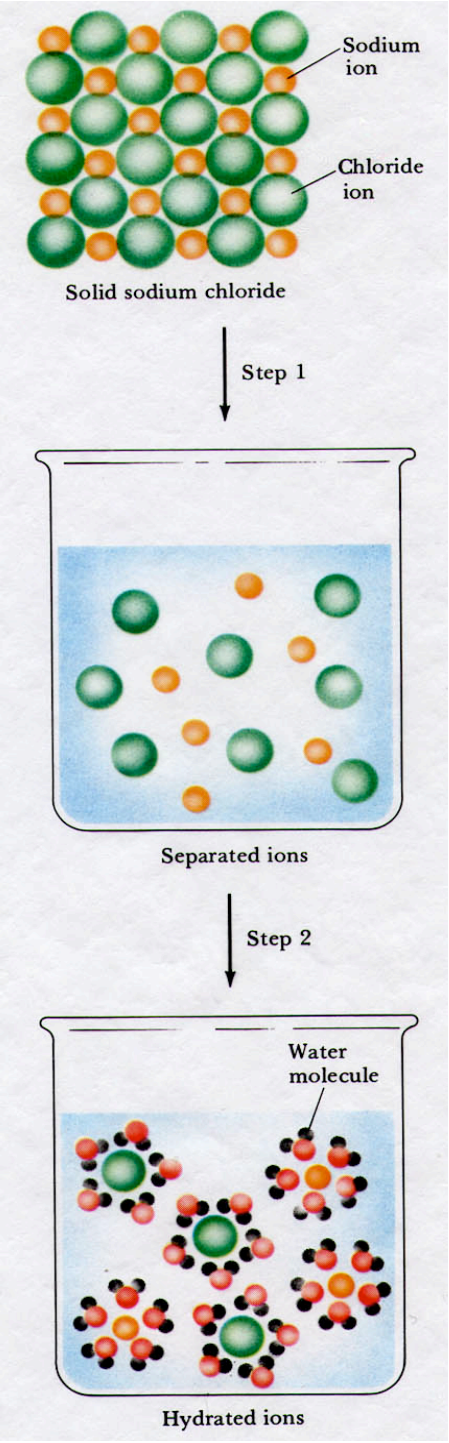
$$\text{Solubility} = x = [Ca^{2+}] = 5.6 \text{ X } 10^{-4}$$

$$K_{sp}=[Ca^{2+}]\ [2F^-]^2 = (x)(2x)^2 = 4x^3 = 1.7 \text{ X } 10^{-10}$$

$$K_{sp} = \sqrt[3]{4.25x10^{-11}} = 3.5x10^{-4}$$

Selective Precipitation

- A solution where $[Ba^{2+}] = [Ca^{2+}] = 0.1M$
  - Add sulfate ions:
    - $K_{sp}(BaSO_4) = 10^{-10}$; $K_{sp}(CaSO_4) = 10^{-5}$
    - Sparingly soluble $BaSO_4$ and $CaSO_4$ precipitate.
    - Which salt precipitates first?
    - How much of the first is left in solution when the second begins to precipitate?



Electrolytes

- Conductivity in water is due to <u>*hydrated*</u> ions moving about.
  - Water and aqueous sugar solutions
  - Acetic acid and vinegar
  - Aqueous salt solutions
- Experiments
  - Electrolytes
  - Nonelectrolytes

Autoionization of Water

- $H_2O(liq) + H_2O(liq) \rightleftharpoons H_3O^+ + OH^-$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_W = K[H_2O]^2 = [H_3O^+][OH^-] = 1.0x10^{-14}$$

$$[H_3O^+] = [OH^-] = \sqrt{K_W} = \sqrt{1.0x10^{-14}} = 1.0x10^{-7}\,M$$

Autoionization of Water

- $H_2O(liq) + H_2O(liq) \rightleftharpoons H_3O^+ + OH^-$

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

$$K_W = K[H_2O]^2 = [H_3O^+][OH^-] = 1.0x10^{-14}$$

$$[H_3O^+] = [OH^-] = x\,mol\;L^{-1}$$

$$K_W = [H_3O^+][OH^-] = (x)(x) = x^2 = 1.0x10^{-14}$$

$$x = \sqrt{K_W} = \sqrt{1.0x10^{-14}} = 1.0x10^{-7}\,M$$

Acid-Base Theories

- Arrhenius

  $HCl \quad \square \quad H^+ \; + \; Cl^-$

  - Could not explain alkalinity of aqueous ammonia
- Brönsted

  $NH_3 \; + \; H_2O \; \square \quad NH_4^+ \; + \; OH^-$

  $HCl \; + \; H_2O \; \square \quad H_3O^+ \; + \; Cl^-$
- Lewis

  $NH_3 \; + \; H^+ \; \square \; NH_4^+$

pH Scale

Measures *acidity* of Aqueous Solutions

$pH = -\log[H_3O^+]$
by definition

$pK_w = pH + pOH$
because.... $K_w=[H_3O^+][OH^-]$

For *neutral* solutions...
$[H_3O^+] = [OH^-]$
$= 10^{-7}M$

$pH = -\log[H_3O^+]$

$pH = 7$

TABLE 12–3 Approximate pH Values for Some Familiar Solutions

Solution	pH
1 M NaOH (lye)	14
1 M NH_3 (household ammonia)	11.6
saturated $Mg(OH)_2$ (milk of magnesia)	10.5
blood	7.3–7.5
saliva	6.5–7.5
urine	5.5–7.5
coffee	4.5–5.5
beer	4.0–5.0
tomato juice	4.0–4.4
wine	2.8–3.8
vinegar	2.4–3.4
lemon juice	2.2–2.4
gastric juice	1.0–3.0
battery acid	0.5
1 M HCl	0

pH of Aqueous Solutions

- If $[H_3O^+] = 5.25 \times 10^{-3}M$
  - Then pH = -log $5.25 \times 10^{-3} = 2.28$
- If pH = 5.25
  - Then $[H_3O^+] = 10^{-5.25} = 5.6 \times 10^{-6}M$
    - And $[OH^-] = Kw/[H_3O^+] = 1.78 \times 10^{-9}M$
    - So pOH = 8.75
    - And pH = 14 - 8.75 = 5.25

pH of Aqueous Solutions

- When pH is *low*……
    - $[H_3O^+] > [OH^-]$
- When pH is *neutral*…..
    - $[H_3O^+] = [OH^-]$
- When pH is *high*…..
    - $[H_3O^+] < [OH^-]$

Dissociation of HA in Water

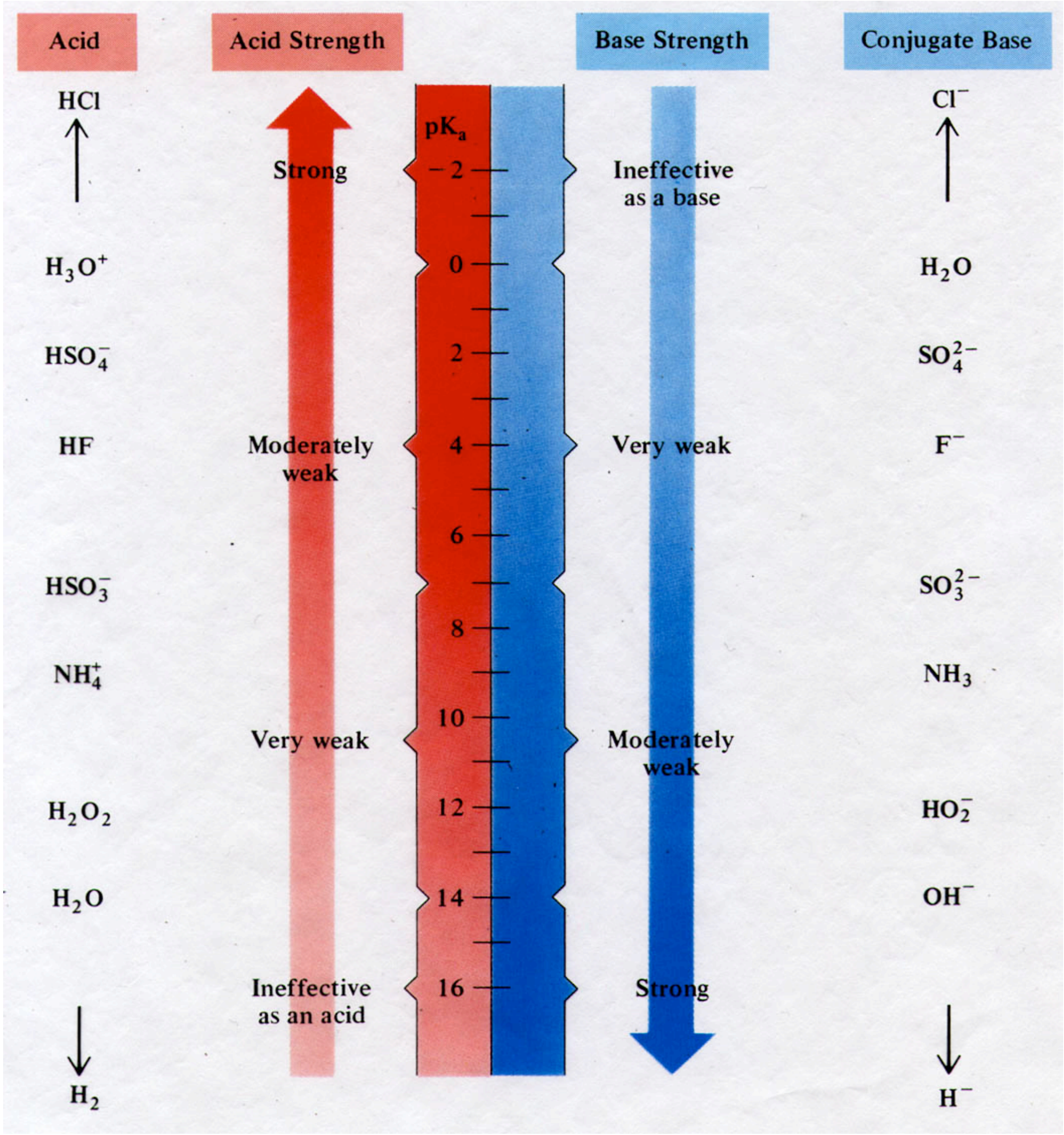
$HA + H_2O$ □ $H_3O^+ + A^-$

- For an acid of the general form HA

$$K_{HA} = \frac{[H_3O^+][A^{\square}]}{[HA]}$$

$$K_{HA}\frac{[HA]}{[A^{\square}]} = [H_3O^+]$$

$$pK_{HA} + \log\frac{[A^{\square}]}{[HA]} = pH$$



Acid	Acid Strength	pK_a	Base Strength	Conjugate Base
HCl				Cl^-
	Strong	−2	Ineffective as a base	
H_3O^+		0		H_2O
HSO_4^-		2		SO_4^{2-}
HF	Moderately weak	4	Very weak	F^-
		6		
HSO_3^-				SO_3^{2-}
		8		
NH_4^+				NH_3
	Very weak	10	Moderately weak	
H_2O_2		12		HO_2^-
H_2O		14		OH^-
	Ineffective as an acid	16	Strong	
H_2				H^-

Acid	K_a	Base	K_b
$HClO_4$	large	ClO_4^-	very small
H_2SO_4	large	HSO_4^-	very small
HCl	large	Cl^-	very small
HNO_3	large	NO_3^-	very small
H_3O^+	55.5	H_2O	1.8×10^{-16}
H_2SO_3	1.2×10^{-2}	HSO_3^-	8.3×10^{-13}
HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}
H_3PO_4	7.5×10^{-3}	$H_2PO_4^-$	1.3×10^{-12}
$Fe(H_2O)_6^{3+}$	6.3×10^{-3}	$Fe(H_2O)_5OH^{2+}$	1.6×10^{-12}
HF	7.2×10^{-4}	F^-	1.4×10^{-11}
HNO_2	4.5×10^{-4}	NO_2^-	2.2×10^{-11}
HCO_2H	1.8×10^{-4}	HCO_2^-	5.6×10^{-11}
$C_6H_5CO_2H$	6.3×10^{-5}	$C_6H_5CO_2^-$	1.6×10^{-10}
CH_3CO_2H	1.8×10^{-5}	$CH_3CO_2^-$	5.6×10^{-10}
$CH_3CH_2CO_2H$	1.3×10^{-5}	$CH_3CH_2CO_2^-$	7.7×10^{-10}
$Al(H_2O)_6^{3+}$	7.9×10^{-6}	$Al(H_2O)_5OH^{2+}$	1.3×10^{-9}
H_2CO_3	4.2×10^{-7}	HCO_3^-	2.4×10^{-8}
$Cu(H_2O)_6^{2+}$	1.6×10^{-7}	$Cu(H_2O)_5OH^+$	6.25×10^{-8}
H_2S	1×10^{-7}	HS^-	1×10^{-7}
$H_2PO_4^-$	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}

Acid	K_a	**Base**	K_b
HSO_3^-	6.2×10^{-8}	SO_3^{2-}	1.6×10^{-7}
$HClO$	3.5×10^{-8}	ClO^-	2.9×10^{-7}
$Pb(H_2O)_6^{2+}$	1.5×10^{-8}	$Pb(H_2O)_5OH^+$	6.7×10^{-7}
$Co(H_2O)_6^{2+}$	1.3×10^{-9}	$Co(H_2O)_5OH^+$	7.7×10^{-6}
$B(OH)_3(H_2O)$	7.3×10^{-10}	$B(OH)_4^-$	1.4×10^{-5}
NH_4^+	5.6×10^{-10}	NH_3	1.8×10^{-5}
HCN	4.0×10^{-10}	CN^-	2.5×10^{-5}
$Fe(H_2O)_6^{2+}$	3.2×10^{-10}	$Fe(H_2O)_5OH^+$	3.1×10^{-5}
HCO_3^-	4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}
$Ni(H_2O)_6^{2+}$	2.5×10^{-11}	$Ni(H_2O)_5OH^+$	4.0×10^{-4}
HPO_4^{2-}	3.6×10^{-13}	PO_4^{3-}	2.8×10^{-2}
H_2O	1.8×10^{-16}	OH^-	55.5
HS^-	1×10^{-19}	S^{2-}	1×10^5
C_2H_5OH	very small	$C_2H_5O^-$	large
NH_3	very small	NH_2^-	large
H_2	very small	H^-	large
CH_4	very small	CH_3^-	large

Indicators

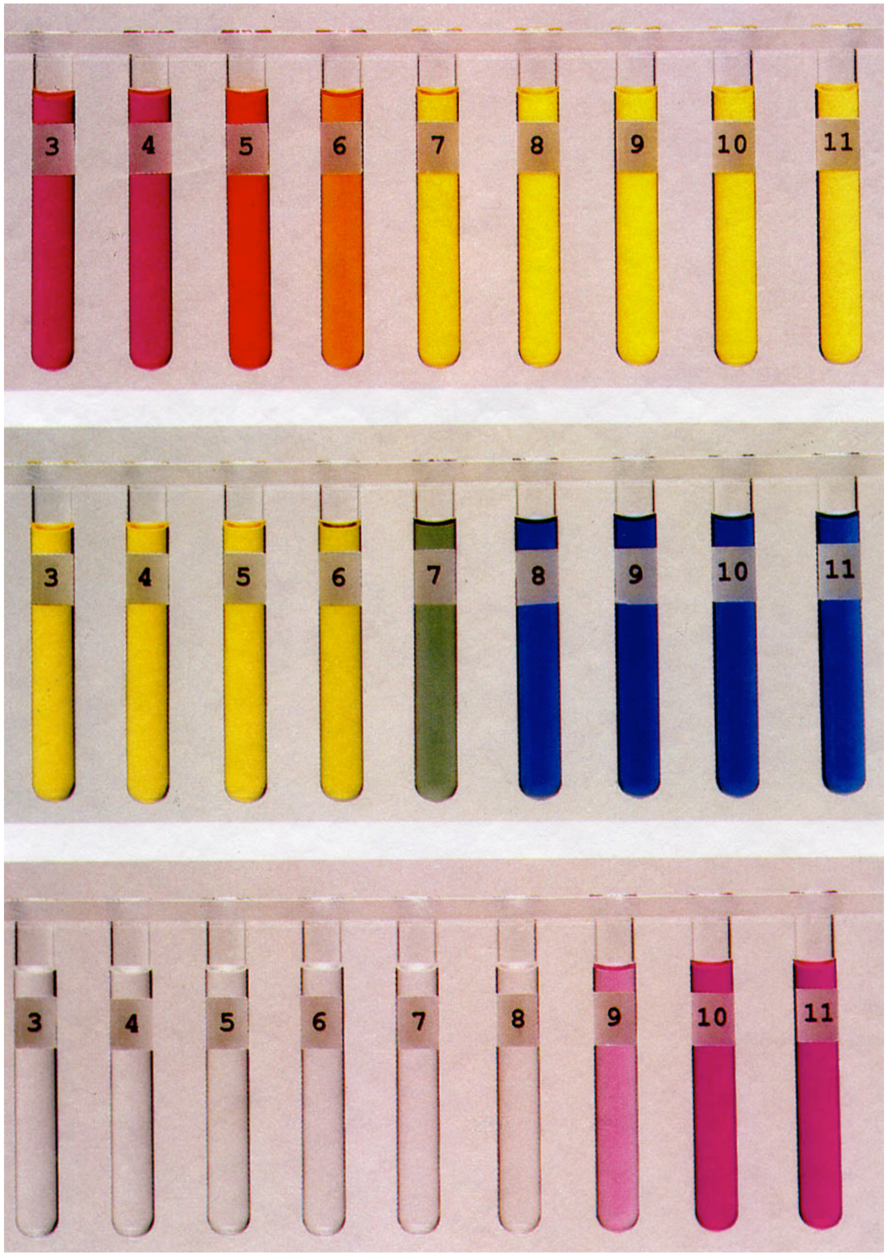
$$HInd + H_2O \rightleftharpoons H_3O^+ + Ind^-$$

- Indicator equation

$$K_{HInd} = \frac{[H_3O^+][Ind^-]}{[HInd]}$$

$$K_{HInd}\frac{[HInd]}{[Ind^-]} = [H_3O^+]$$

$$pK_{HInd} + \log\frac{[Ind^-]}{[HInd]} = pH$$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Oxides and Hydrides

- Metallic oxides

$Na_2O + H_2O \;\square\; 2NaOH$

$CaO + H_2O \;\square\; Ca(OH)_2$

- Nonmetallic oxides

$SO_2 + H_2O \;\square\; H_2SO_3$

$CO_2 + H_2O \;\square\; H_2CO_3$

- Metal Hydrides

$NaH + H_2O \;\square\; NaOH + H_2$

For Strong Acids

- Aqueous hydrochloric acid solutions

  $HCl + H_2O$ □ $H_3O^+ + Cl^-$
- $0.1M\ HCl = 0.1M\ H_3O^+$
  - Presumption is complete dissociation
  - pH = 1
- Add 10 mL to 990 mL of H_2O
  - pH change is… huge!

For Weak Acids

- Aqueous acetic acid solutions

  HOAc + H_2O □ H_3O^+ + OAc^-

  k_a=1.75 X 10^{-5}

  0.1M HOAc << 0.1M H_3O+

  Incomplete dissociation: pH = 2.87

- Aqueous HF

  HF + H_2O □ H_3O^+ + F^-

  k_a=7.2 X 10^{-4} and pH = ?

For Very Weak Acids

- Aqueous hydrogen cyanide solutions

  $$HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$$

- 0.1M HCN <<< 0.1M H_3O^+
  - $K_a = 4.0 \times 10^{-10}$ and pH = 5.2
- 0.1M NaCN pH = ?
- 0.1M NaF pH = ?
- 0.1M NaOAc pH = ?

0.10M Solutions of HA

	K_a	pK_a	pH
HCl	~10^7	-7	1
HOAc	~10^{-5}	5	3
HCN	~10^{-11}	11	6
H_2O	~10^{-14}	14	7

0.10M Solutions of B

	K_b	pK_b	pOH
NH_3	~10^{-5}	5	3

Solvolysis/Hydrolysis

- For a weak acid HA…..
  - the anion is strong and reacts with the solvent in a proton-transfer reaction:

$$A^- + H_2O \rightleftharpoons HA + OH^-$$

- For a weak base B…..
  - the cation ion is strong and reacts with the solvent in a proton-transfer reaction:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+$$

Hydrolysis

- Alkaline solutions: NaOAc, NaF, NaCN
- Acidic solutions: NH_4Cl
- Neutral solutions: NH_4OAc
- NaCN and Na_2CO_3 solutions?
- $AlCl_3$ and $Fe(NO_3)_3$ solutions?
- NH_4CN solutions?

pH of 0.10M Aqueous NaOAc

- NaOAc(s) $\rightarrow$ $Na^+(aq)$ + $OAc^-(aq)$
- OAc- + H_2O $\rightleftharpoons$ HOAc + OH^-

$$K_b = \frac{K_w}{K_a} = \frac{[H_3O^+][OH^-]}{\frac{[H_3O^+][OAc^-]}{[HOAc]}} = \frac{[HOAc][OH^-]}{[OAc^-]} = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$10^{-9} = \frac{(x)(x)}{(.1 - x)} \approx \frac{x^2}{.1} and \;\; x = [OH^-] = 10^{-5} M$$

- pOH = 5 and pH =14 - 5 = 9

Buffers

- Solutions of a weak acid and its conjugate base:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- Solutions of a weak base and its conjugate acid:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

Buffers

- Buffers act across an [A-]/[HA] range of 10/1 to 1/10 … or 2 pH units:

$$K_{HA} = \frac{[H_3O^{+}][A^{-}]}{[HA]}$$

$$K_{HA}\frac{[HA]}{[A^{-}]} = [H_3O^{+}]$$

$$pK_{HA} + \log\frac{[A^{-}]}{[HA]} = pH$$

Buffers

- Aqueous acetic acid solutions

  $$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$$

  - For 0.1M HOAc: pH = 2.87
  - For HOAc/NaOAc buffer: pH = pKa = 4.76
  - PROBLEM: Add 50mL 0.10M HCl to 950 mL H_2O containing 0.050 mole HOAc and 0.050 mole NaOAc.
    - Buffer soaks up the acid
    - pH change is relatively small.

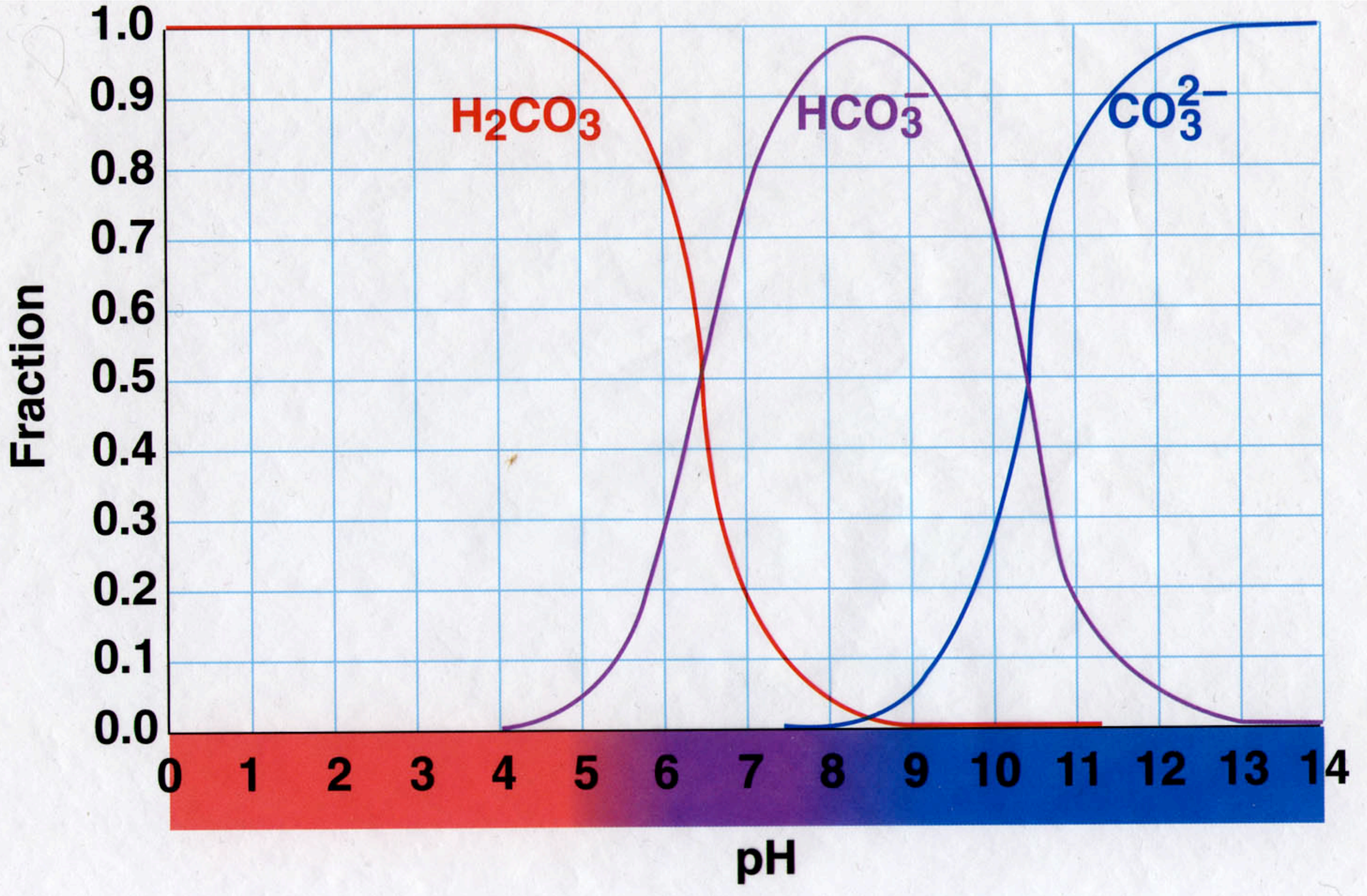
Polyprotic Acids

- Carbonic acid (H_2CO_3) K_a

  $H_2CO_3 + H_2O \ \square \ H_3O^+ + HCO_3^-$ 10^{-7}

  $HCO_3^- + H_2O \ \square \ H_3O^+ + CO_3^{2-}$ 10^{-11}

  - Acidity is essentially supplied by $K_a(1)$
  - Blood is buffered by $[CO_2]/[HCO_3^-]$



Fraction
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
H_2CO_3
HCO_3^-
CO_3^{2-}
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH

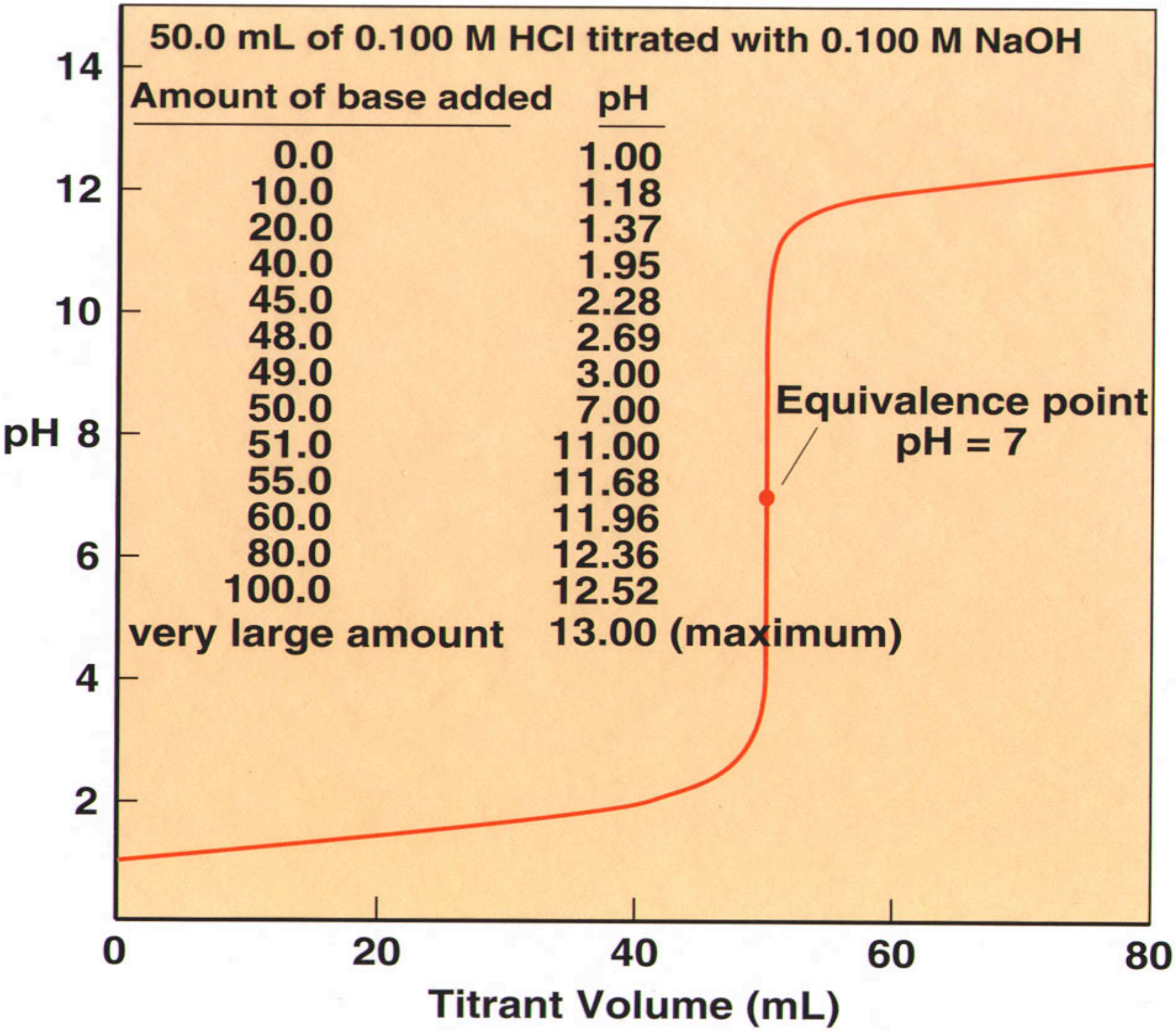
Polyprotic Acids

– Sulfuric acid (H_2SO_4)	pK_a
$H_2SO_4 + H_2O \square H_3O^+ + HSO_4^-$	-5
$HSO_4^- + H_2O \square H_3O^+ + SO_4^{2-}$	2

– Phosphoric acid (H_3PO_4)	pK_a
$H_3PO_4 + H_2O \square H_3O^+ + H_2PO_4^-$	2.1
$H_2PO_4^- + H_2O \square H_3O^+ + HPO_4^{2-}$	7.2
$HPO_4^- + H_2O \square H_3O^+ + PO_4^{3-}$	12.3

- Note:K values are lower by several orders of magnitude due to increasing negative charge.

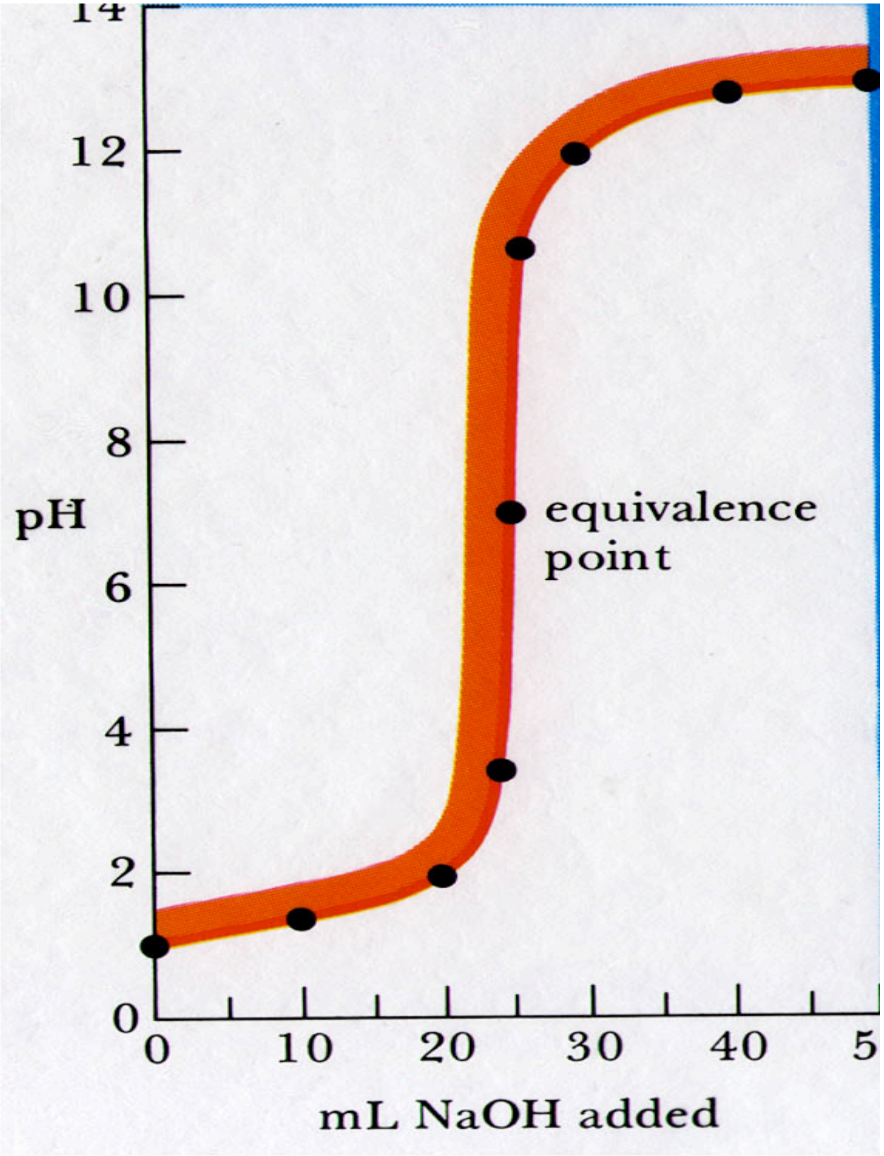
Titration curves

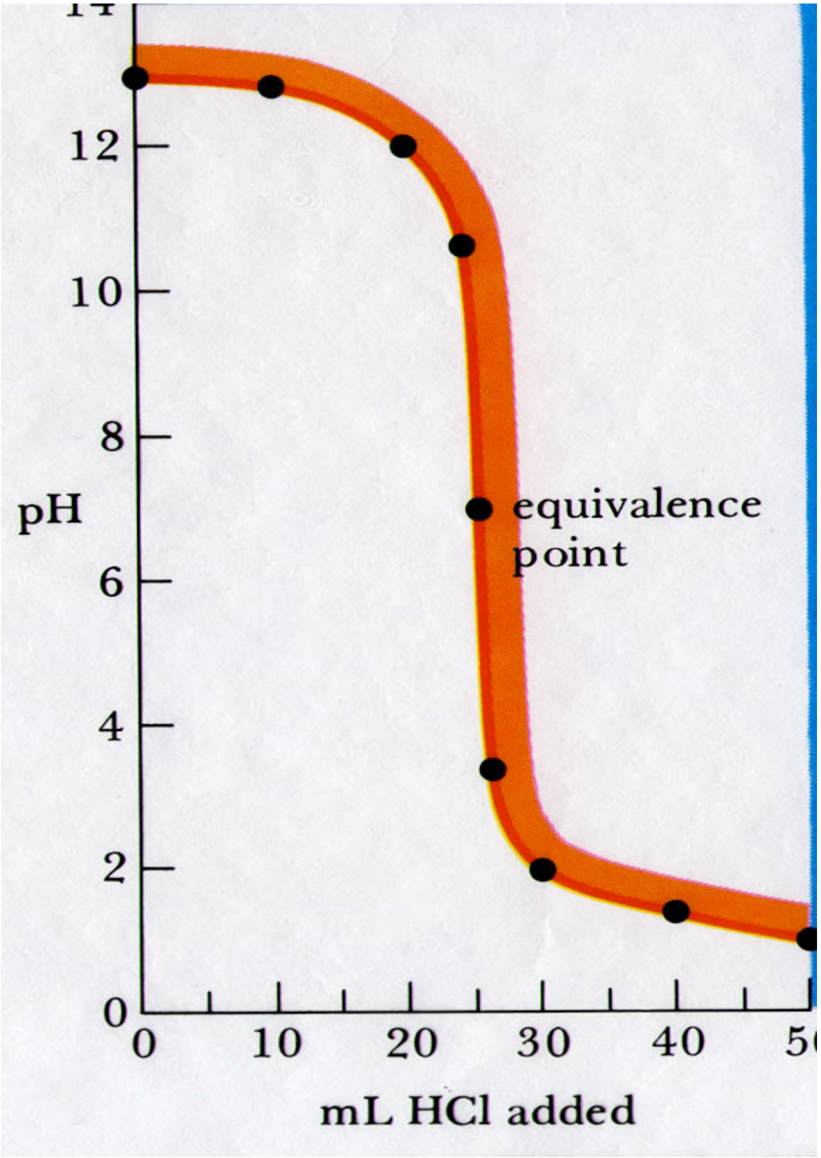


50.0 mL of 0.100 M HCl titrated with 0.100 M NaOH

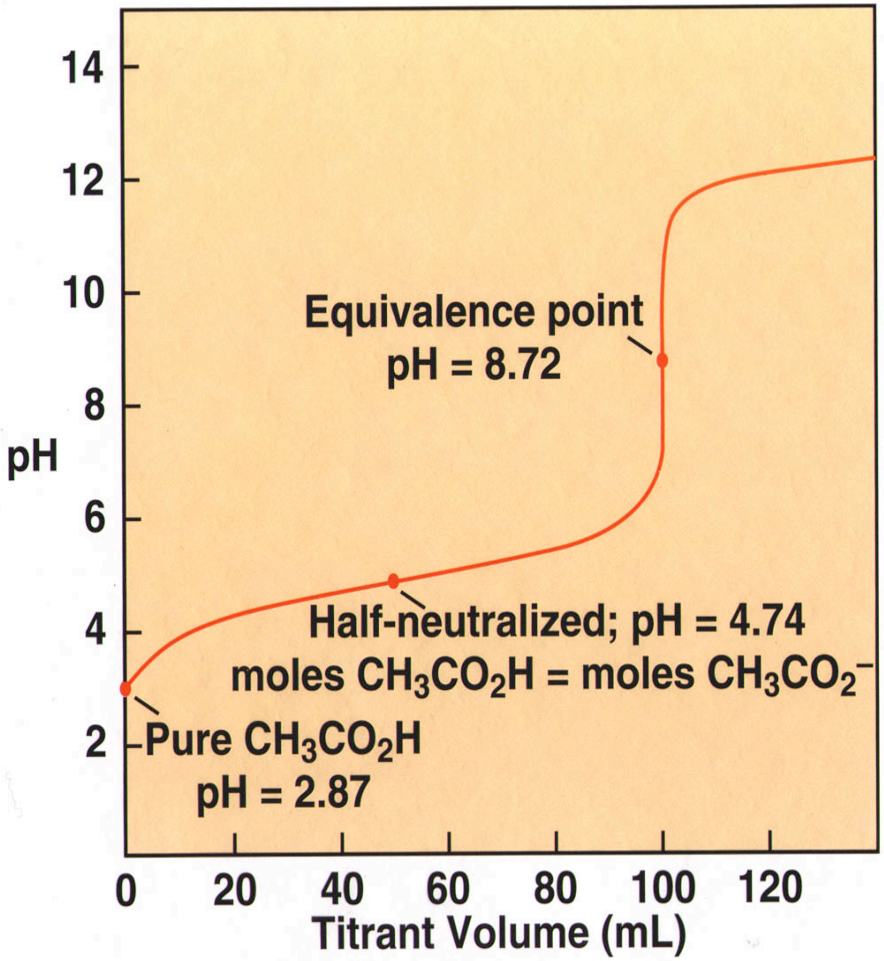
Amount of base added	pH
0.0	1.00
10.0	1.18
20.0	1.37
40.0	1.95
45.0	2.28
48.0	2.69
49.0	3.00
50.0	7.00
51.0	11.00
55.0	11.68
60.0	11.96
80.0	12.36
100.0	12.52
very large amount	13.00 (maximum)

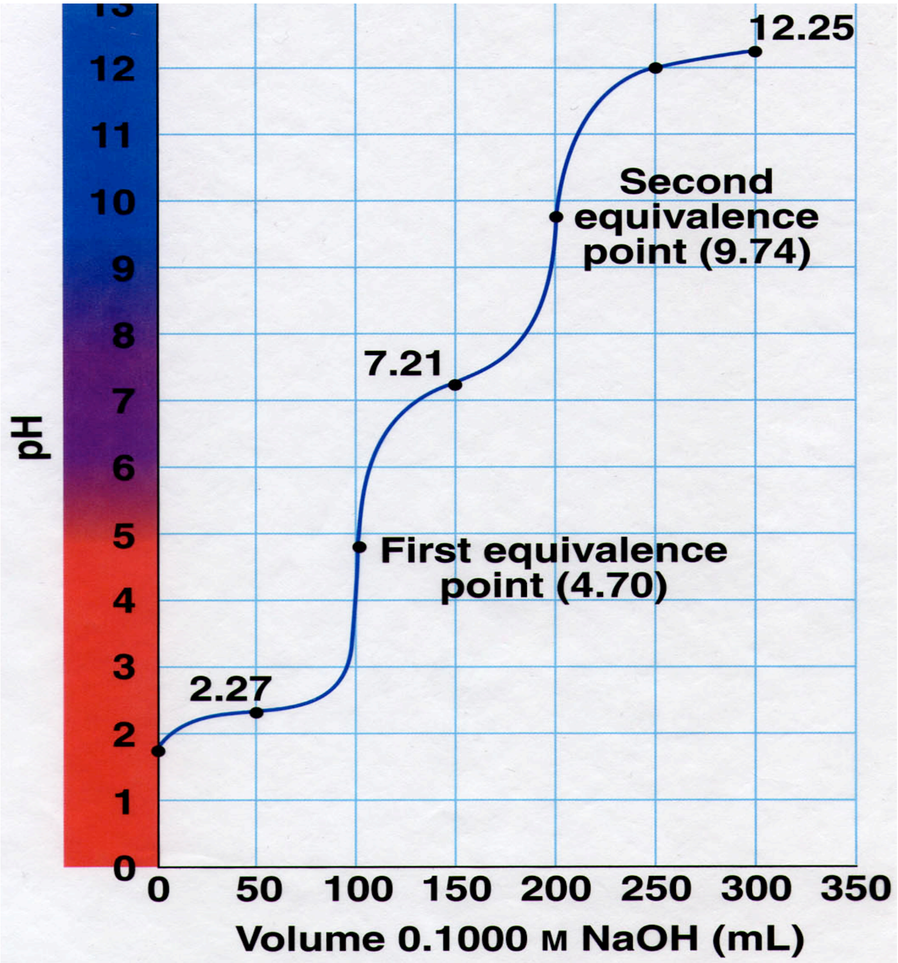
Titration curves





Titration curves





Finding K_a for Weak Acids

- For a monoprotic acid, at the mid-point,

[HA] = [A-]

pH = pKa

$$K_{HA} = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_{HA}\frac{[HA]}{[A^-]} = [H_3O^+]$$

$$pK_{HA} + \log\frac{[A^-]}{[HA]} = pH$$

ACID/BASE ISSUES

- Acid rain and coal mine run-off:
  - Kentucky, West Virginia, Indiana, Illinois, Minnesota… many places.
- Industrial acid/base run-off in rivers:
  - Raritan River is one of many.
- Acid rain and steel manufacture Acid:
  - Adirondks and Great Smokys
  - Illinois and Indiana mills

ACID/BASE ISSUES

- Corrosion
  - N and S oxides
  - Acidic oxides
- Particulates in the air:
  - Donora, Pennsylvania
  - Dupont “nylon” in downtown Chicago

Lessons from History

The disadvantage of men not knowing the past is that they do not know the present.

- G. K. Chesterton

Complex Ion Formation

1) $AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$

$$K_{sp} = [Ag^+][I^-] = 10^{-16}$$

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

$$K_f = \frac{[Ag(NH_3)_2^+]}{[NH_3]^2[Ag^+]} \approx 10^{12}$$

3) $AgI(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + I^-(aq)$

$$K_{sp}K_f = \frac{[Ag(NH_3)_2^+][I^-]}{[NH_3]^2} \approx (10^{12})(10^{-16}) = 10^{-4}$$

Complex ion formation

- AgCl ppt dissolves in aq. NH_3
- AgBr ppt dissolves in aq. NH_3 but with difficulty
- AgI ppt does not dissolve in aq. NH_3 but does dissolve in aq. CN^-

Dissolving Precipitates

- AgCl
  - Add ammonia
    - Forms soluble $Ag(NH_3)^+$ complex
- AgBr
  - Add lots of ammonia
    - Forms soluble $Ag(NH_3)^+$ complex
- AgI
  - Add cyanide ion
    - Forms soluble $Ag(CN)_2^-$ complex