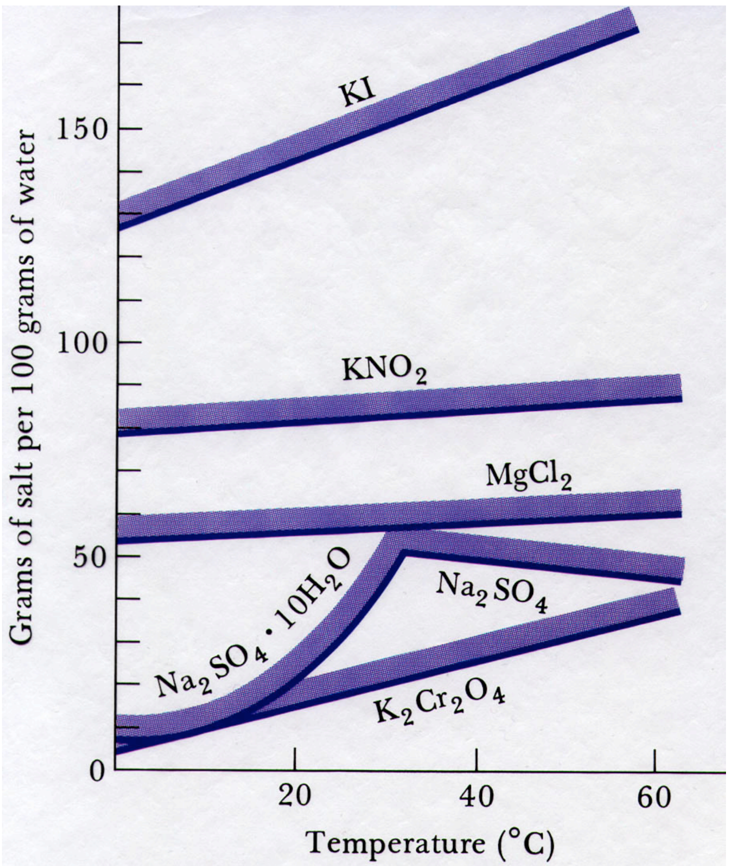
Soluble Salts in Water



- 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

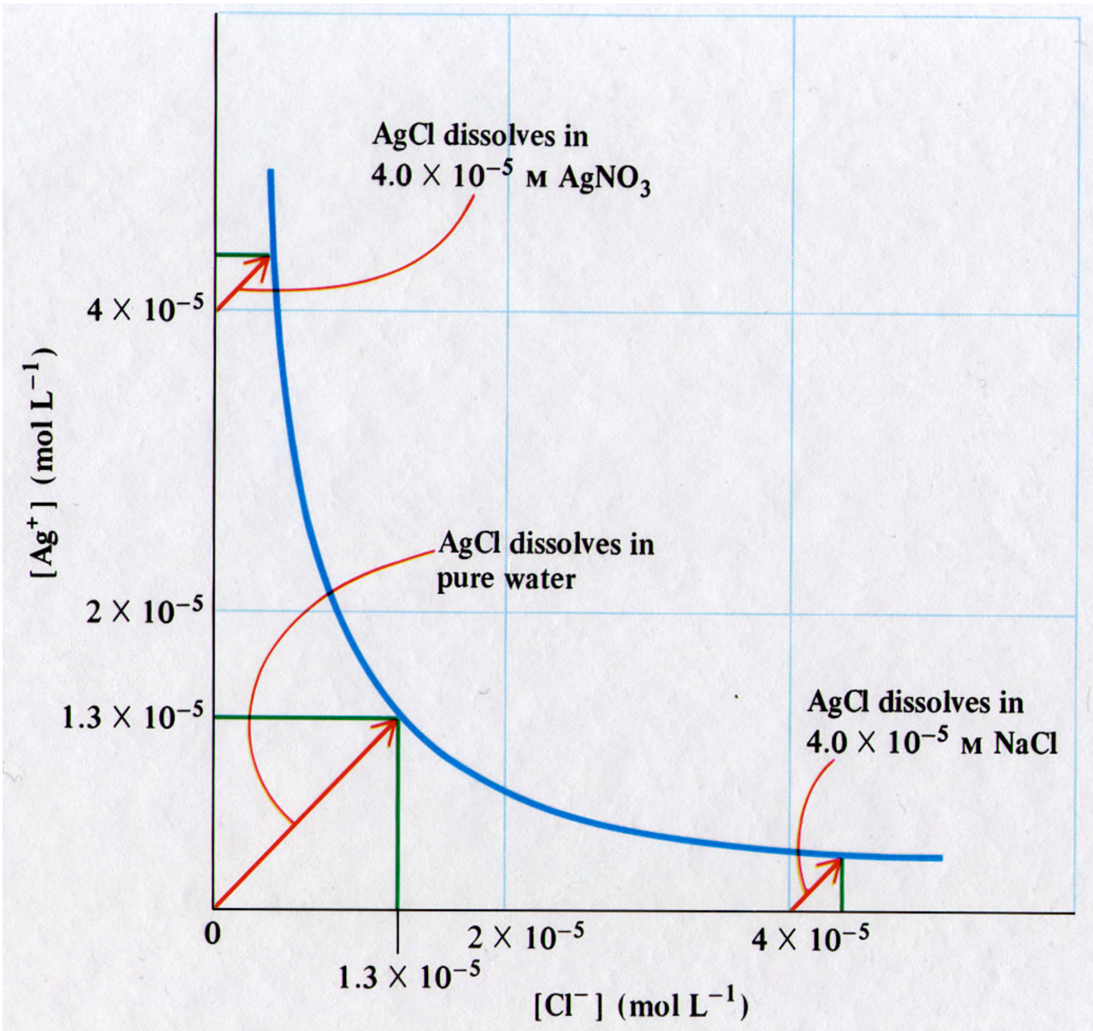
  $AgI(s) \rightleftharpoons Ag^+ + I^-$

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

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

- 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?

Dissolving Precipitates

- AgCl
  - Add ammonia
    - Forms soluble $Ag(NH_3)^{2+}$ complex
- AgBr
  - Add lots of ammonia
    - Forms soluble $Ag(NH_3)^{2+}$ complex
- AgI
  - Add cyanide ion
    - Forms soluble $Ag(CN_2)^{-}$ complex

Complex Ion Formation

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

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

- $Ag^{+}(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)^{2+}(aq)$

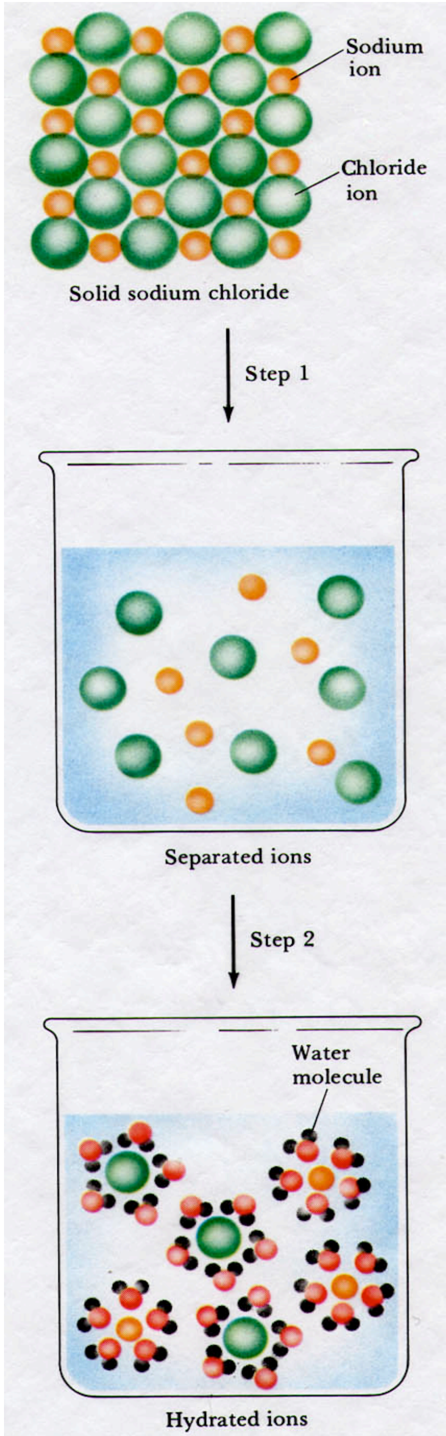
$$K_f = \frac{[Ag(NH_3)_2^{+}]}{[NH_3]^2[Ag^{+}]} \approx 10^{12}$$

- $AgI(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)^{2+}(aq) + I^{-}(aq)$

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

Complex ion formation demos

- AgCl ppt
- AgBr ppt
- AgI ppt
- Dissolve in ammonia and cyanide



Electrolytes

- Conductivity in water is due to *hydrated* 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

  $HCl \rightarrow H^+ + Cl^-$

  - Could not explain alkalinity of aqueous ammonia

- Brönsted

  $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

  $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

- Lewis

  $NH_3 + H^+ \rightarrow NH_4^+$

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…
  $[H_3O^+] = [OH^-] = 10^{-7}M$ and $pH = 7$

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

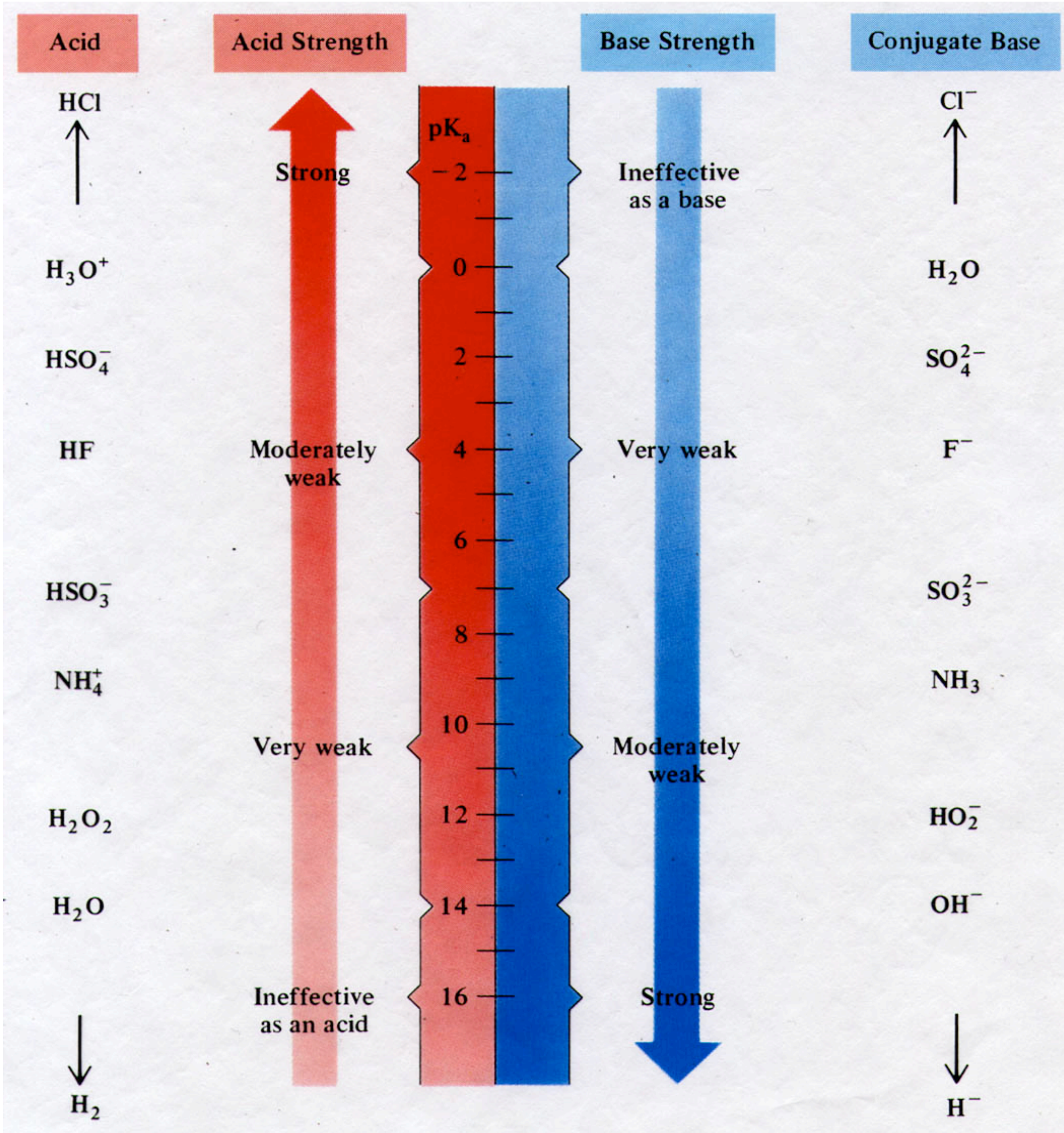
$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- For an acid of the general form HA

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

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

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


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

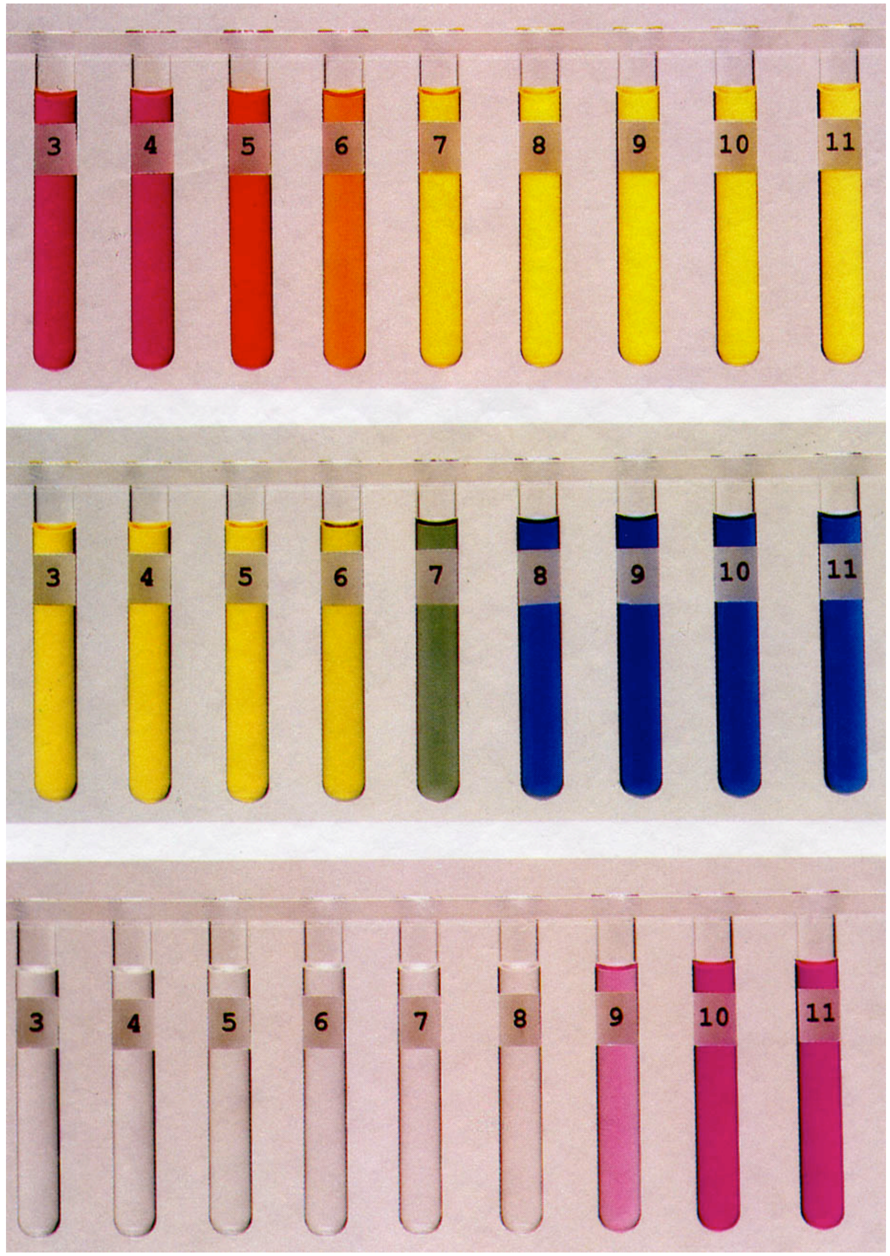
$$HInd + H_2O \rightleftharpoons H_3O^+ + Ind^-$$

- 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

$$Na_2O + H_2O \rightarrow 2NaOH$$

$$CaO + H_2O \rightarrow Ca(OH)_2$$

- Nonmetallic oxides

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$CO_2 + H_2O \rightarrow H_2CO_3$$

- Metal Hydrides

$$NaH + H_2O \rightarrow NaOH + H_2$$

For Strong Acids

- Aqueous hydrochloric acid solutions

  $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

- 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

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

  $k_a = 1.75 \times 10^{-5}$

  0.1M HOAc $\ll$ 0.1M H_3O+

  <u>*Incomplete*</u> dissociation: pH = 2.87

- Aqueous HF

  $HF + H_2O \rightleftharpoons H_3O^+ + F^-$

  $k_a = 7.2 \times 10^{-4}$ 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
NH_3	~10^{-16}	16	8

Indicators

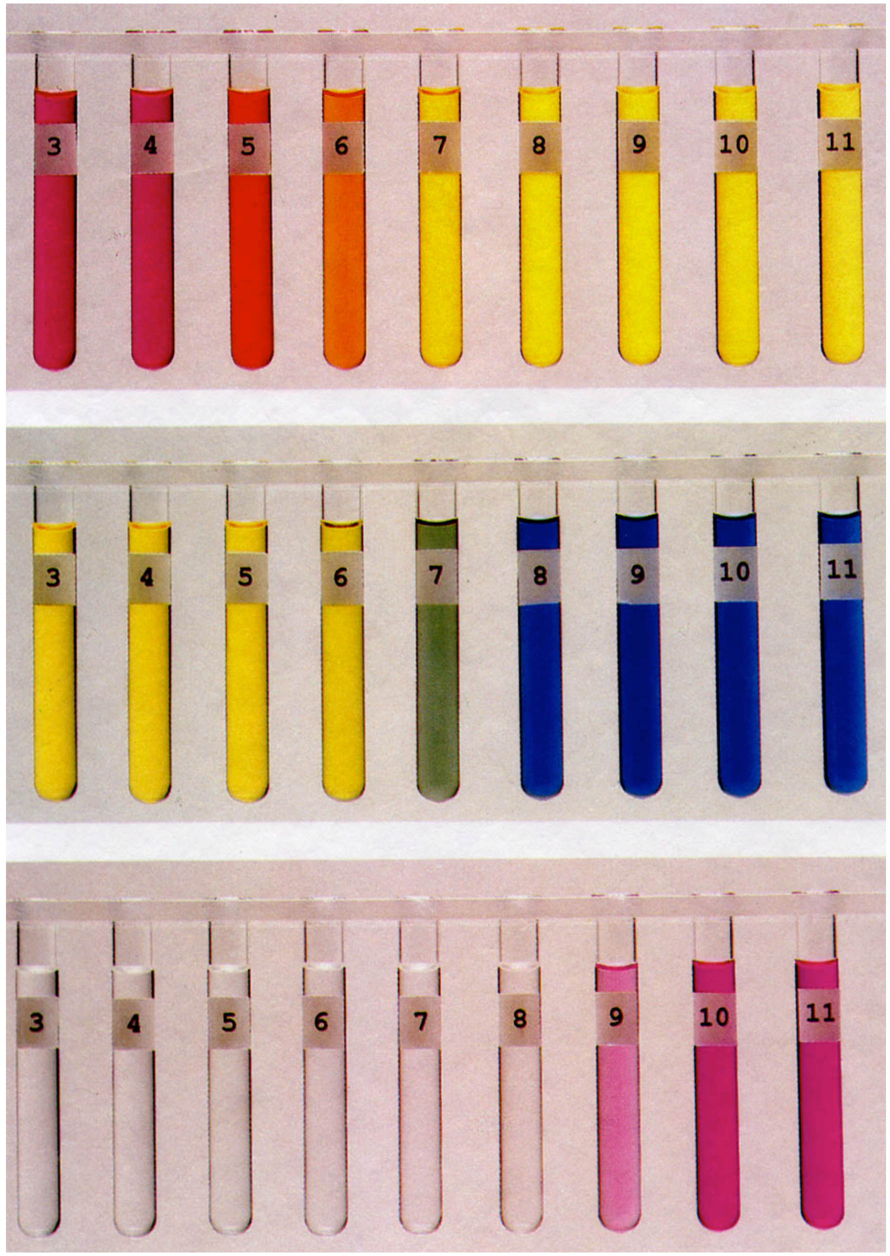
$$HInd + H_2O \rightleftharpoons H_3O^+ + Ind^-$$

- 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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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 from 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

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

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

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

- 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.

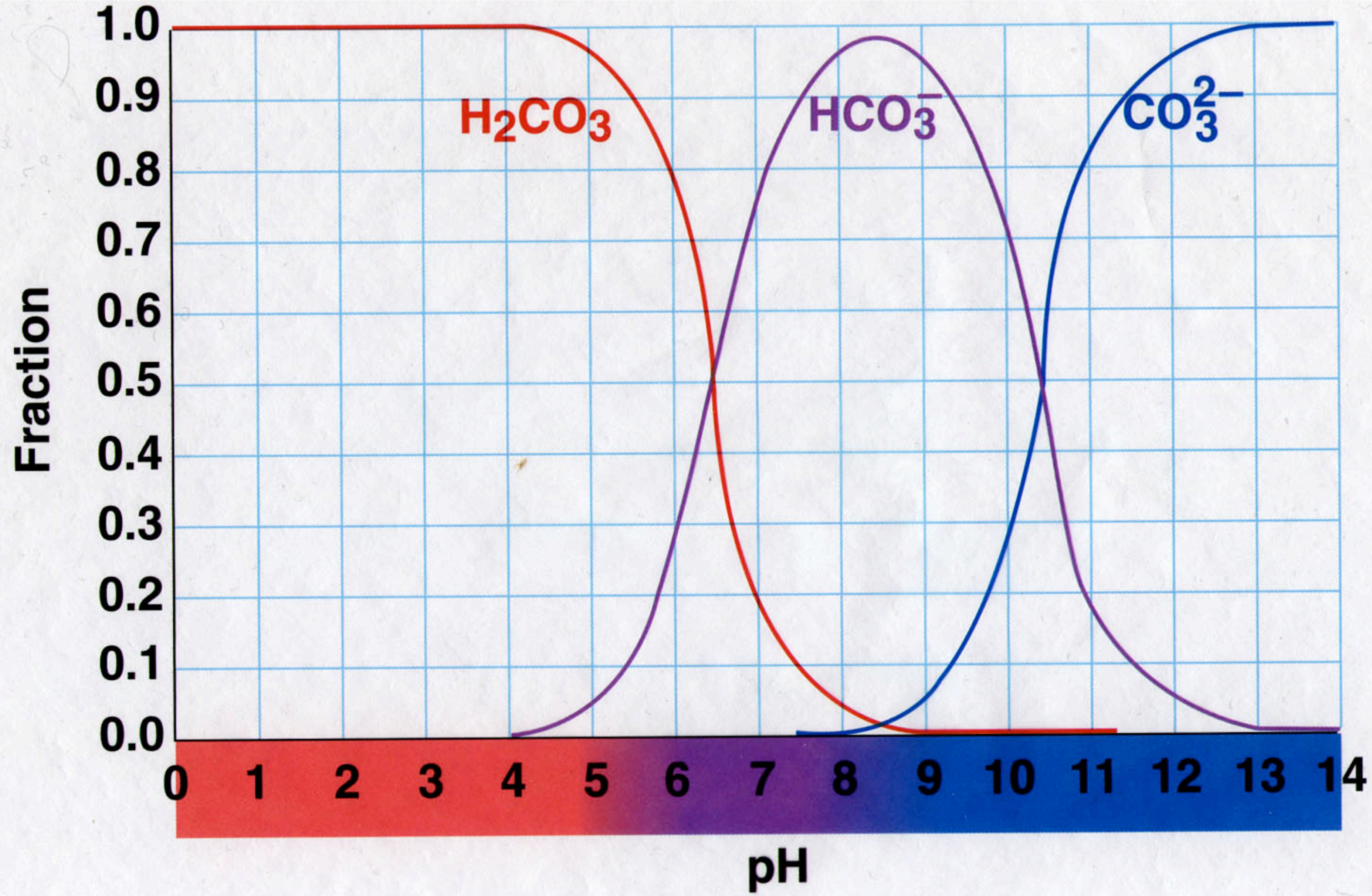
Polyprotic Acids

- Carbonic acid (H_2CO_3) K_a

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

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

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



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0.9
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0.6
0.5
0.4
0.3
0.2
0.1
0.0
Fraction
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

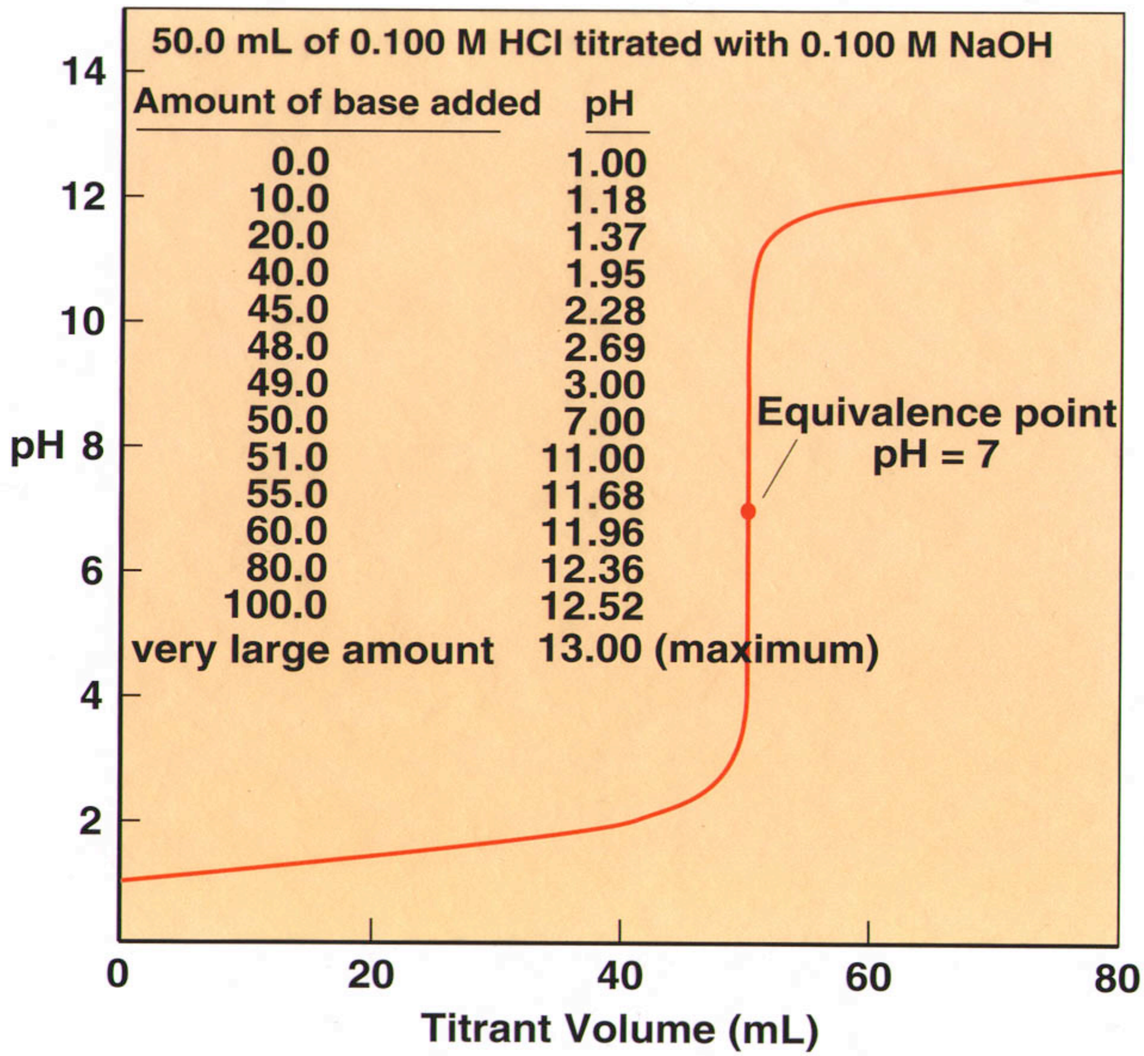
Reaction	pK_a
$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$	-5
$HSO_4^- + H_2O \rightleftharpoons H_3O^+ + SO_4^{2-}$	2

- Phosphoric acid (H_3PO_4) — pK_a

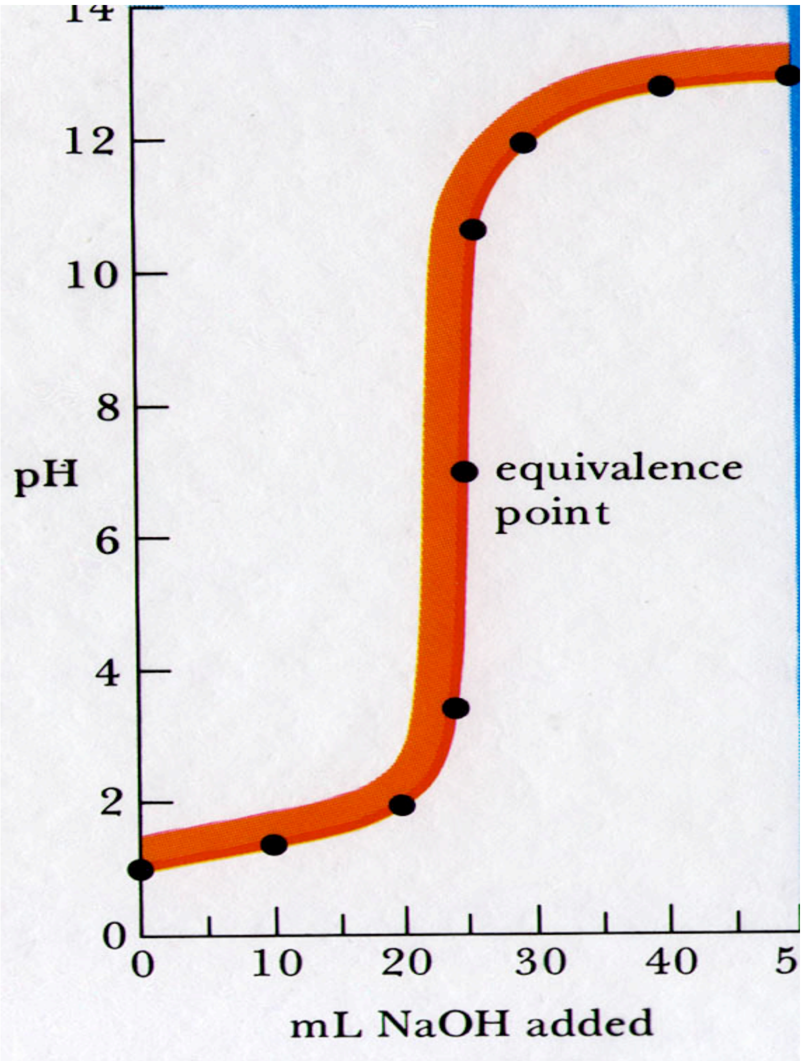
Reaction	pK_a
$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$	2.1
$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$	7.2
$HPO_4^- + H_2O \rightleftharpoons H_3O^+ + PO_4^{3-}$	12.3

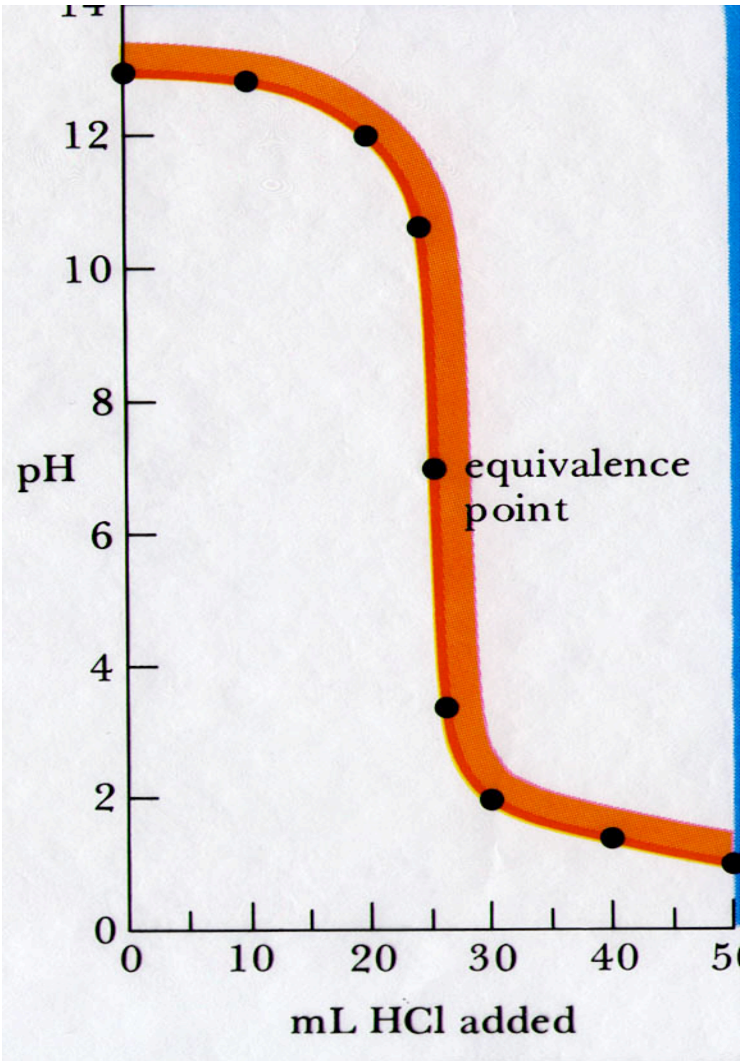
  - Note:K values are lower by several orders of magnitude due to increasing negative charge.

Titration curves

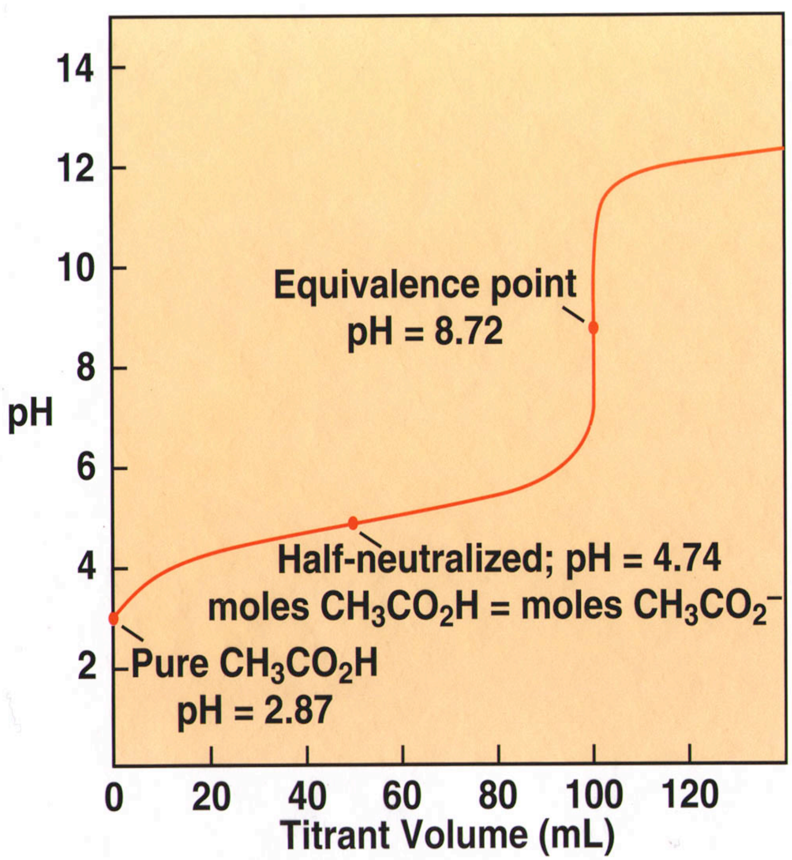


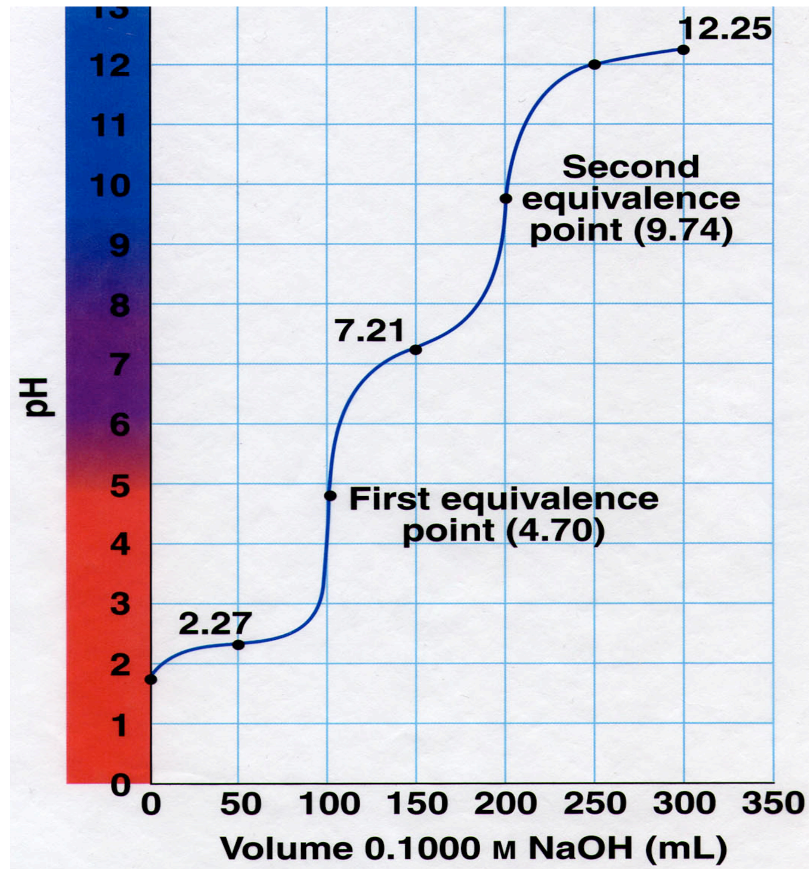
Titration curves





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