화학 General Chemistry
034.020-005

2018 Spring Semester

Tue/Thr 9:30~10:45
Building 028-302

송윤주 woonjusong@snu.ac.kr

The Nature of Acids and Bases

11.1 Acids and Bases

◈ Arrhenius definition

acid: a substance that dissociates in water to form H^+

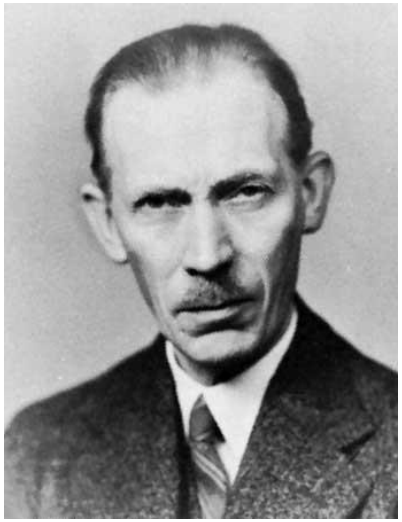
base: a substance that dissociates in water to form OH^-

Acid: HCl, H_2SO_4, HNO_3

Base: NaOH, KOH, LiOH, $Mg(OH)_2$

Svante Arrhenius (1859 –1927)

◈ Brønsted-Lowry definition (1923)



1879 –1947

1874 -1936

acid: **proton** donor

base: **proton** acceptor

→ general theory *for any solvent* or *no solvent at all*

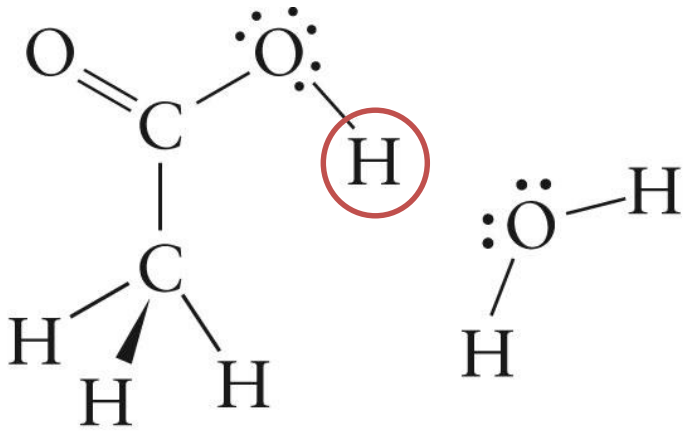
* Conjugate acid-base pair in *proton transfer reactions*.

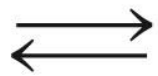
Acid (*proton donor*) → deprotonation → conjugate base

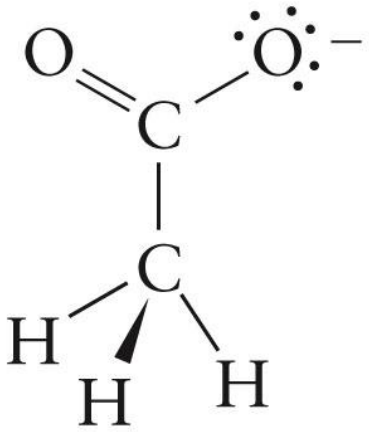
Base (*proton acceptor*) → protonation → conjugate acid

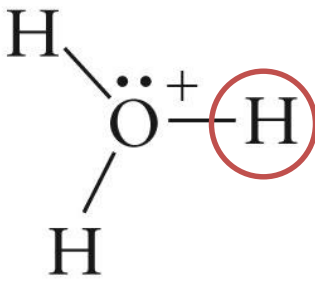
acid: **proton** donor

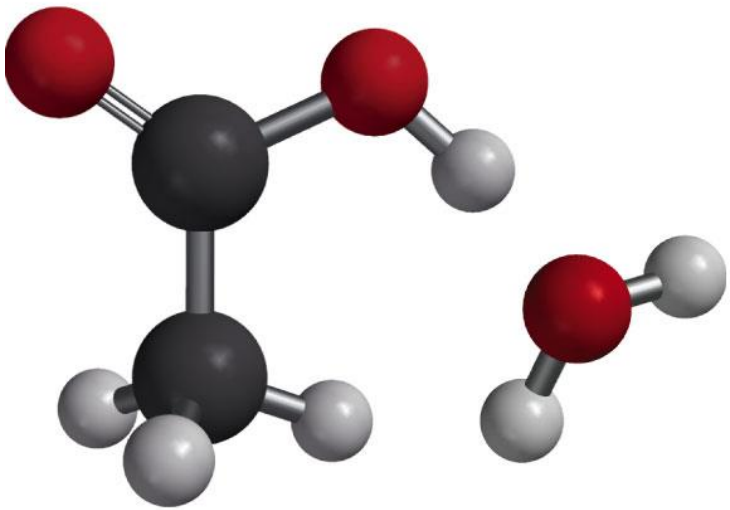
base: **proton** acceptor

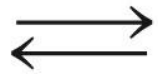


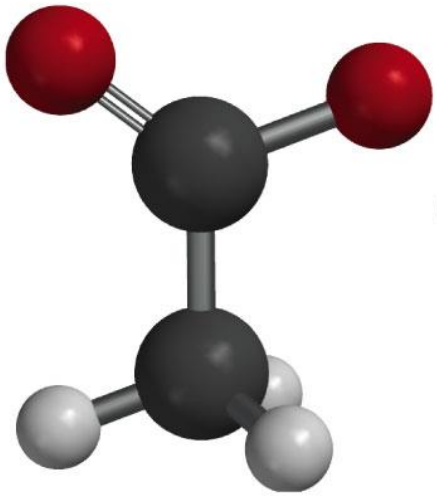


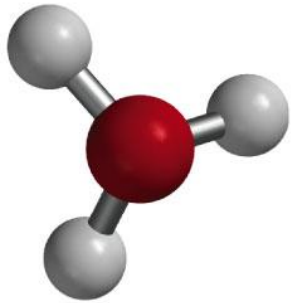












Acid

Base

Conjugate Base

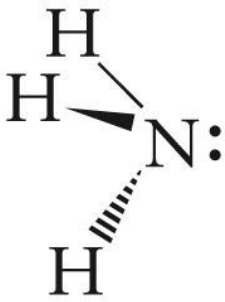
Conjugate Acid

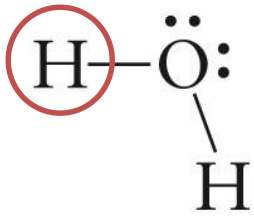
Acetic acid

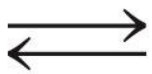
acetate

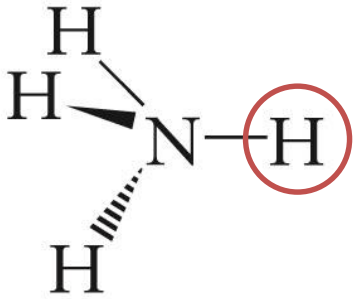
acid: proton donor

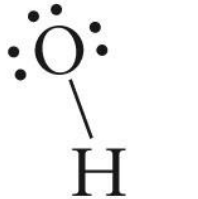
base: proton acceptor

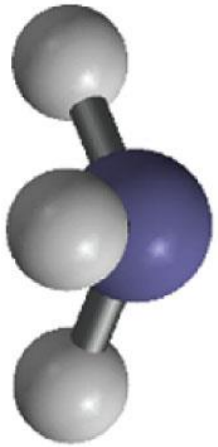


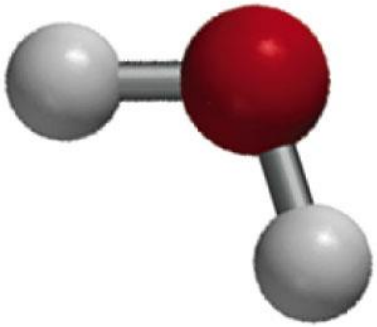


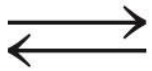


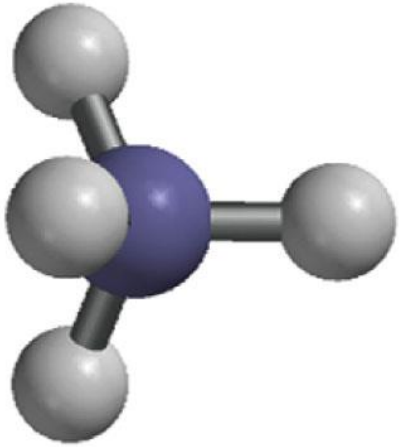












Base

Ammonia

Acid

Conjugate Acid

Ammonium cation

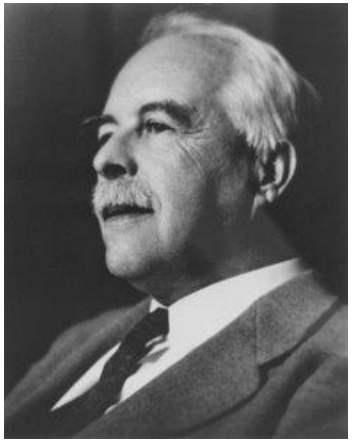
Conjugate Base

◈ Lewis definitions (most general theory)

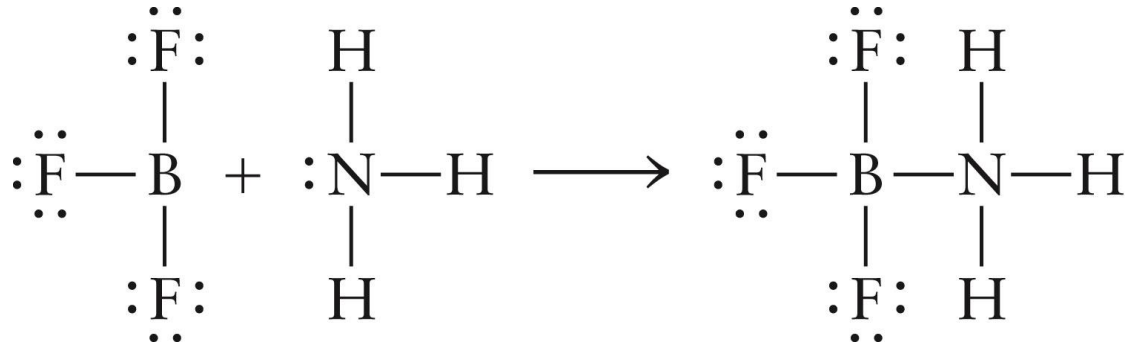
Lewis acid: an **electron pair** acceptor

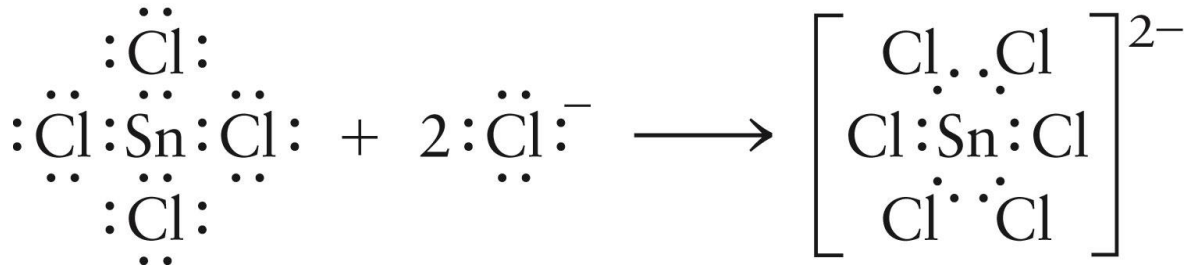
Lewis base: an **electron pair** donor

→ Proton transfer (Brønsted-Lowry theory) is a special type of Lewis acid-base reaction



Gilbert N. Lewis
(1875 –1946)



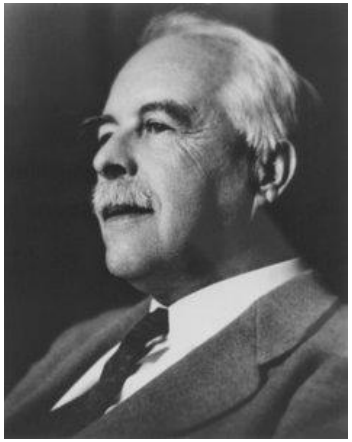


◈ Lewis definitions (most general theory)

Lewis acid: an electron pair acceptor

Lewis base: an electron pair donor

→ Proton transfer (Brønsted-Lowry theory) is a special type of Lewis acid-base reaction



Gilbert N. Lewis
(1875 –1946)

◈ Acidic, Basic and Amphoteric Oxides

1. **Non-metal oxides** (CO_2, SO_3, Cl_2O_7, N_2O_5 ···)

   : Generally tend to act as **Lewis Acids** and react with **water** to form a Brønsted Acid → called acidic oxide

   : React with bases to form a salt and water

   : Not Brønsted Acids

2. **Metal oxides** (CaO, Na_2O, MgO ···)

   : Generally tend to act as **Lewis Bases** and react with **water** to form a Brønsted base → called basic oxide

   : React with acids to form a salt and water

   : Not Brønsted Bases

Non-obvious cases of acids and bases

Aq. Solutions of some compounds that do not appear as acids and bases can act as acids and bases.

Acid anhydrides

-Dehydrates (-remove H_2O) of oxy-acids.

Oxyacid Acid anhydride

$H_2CO_3 \rightarrow CO_2$

-When CO_2 dissolves in water, it produces H_2CO_3: it acts as an acid.

-More examples

$N_2O_5\,(s) + H_2O(l) \rightarrow 2HNO_3(aq) \rightarrow 2H^+ + 2NO_3^-\,(aq)$

$SO_3(g) + H_2O\,(l) \rightarrow H_2SO_4\,(aq) \rightarrow H^+ + HSO_4^-.\,(aq)$

3. **Amphoteric oxides** (Al_2O_3, SnO_2, ZnO ⋯)

: Exhibit **both acid and base** characters and react with both acids and bases

$$Al_2O_3\ (s) + 6\ \boldsymbol{H_3O^+}\ (aq) \leftrightarrow 2\ Al(H_2O)_6{}^{3+}\ (aq) + 3\ H_2O\ (l)$$

$$Al_2O_3\ (s) + 2\ \boldsymbol{OH^-}\ (aq) + 3\ H_2O\ (l) \leftrightarrow 2\ Al(OH)_4{}^-\ (aq)$$

Increasing acidity →

I	II	III	IV	V	VI	VII
Li_2O	BeO	B_2O_3	CO_2	N_2O_5	(O_2)	OF_2
Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
K_2O	CaO	Ga_2O_3	GeO_2	As_2O_5	SeO_3	Br_2O_7
Rb_2O	SrO	In_2O_3	SnO_2	Sb_2O_5	TeO_3	I_2O_7
Cs_2O	BaO	Tl_2O_3	PbO_2	Bi_2O_5	PoO_3	At_2O_7

← Increasing basicity

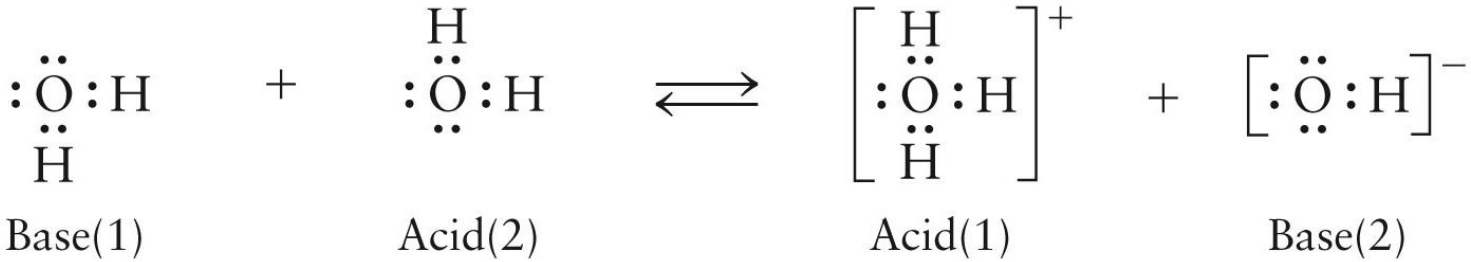
Increasing acidity →

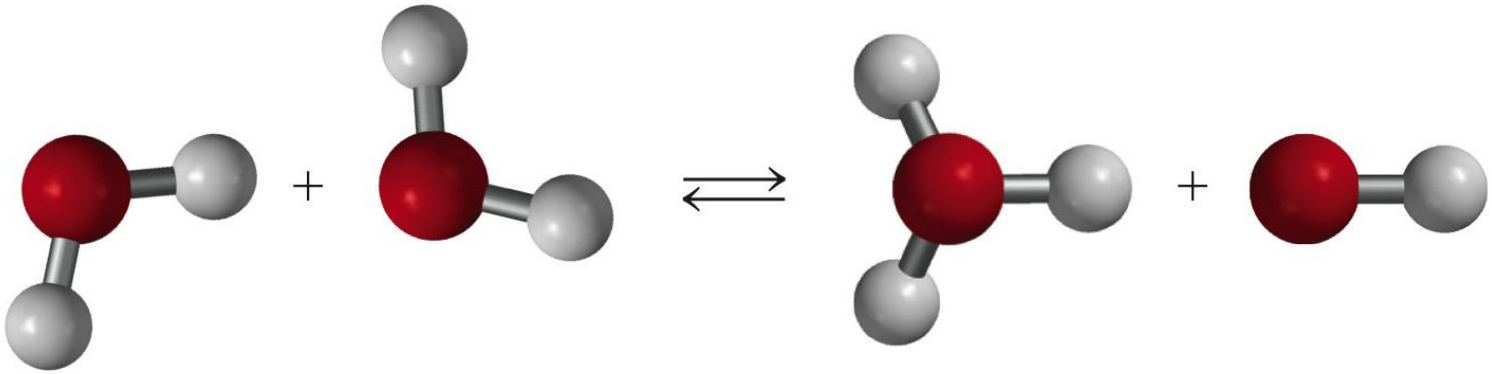
← Increasing basicity

11.2. Acid and Base in Aqueous Phase

◈ **Autoprotolysis (autoionization)** of water

: Amphiprotic species (H_2O, NH_3 ⋯) act as either a Brønsted acid (proton donor) or a Brønsted base (proton acceptor)





* Autoionization constant, K_w

$$K_w = \frac{a_{H_3O^+} \cdot a_{OH^-}}{(a_{H_2O})^2} \approx [H_3O^+] \cdot [OH^-] = 1.0 \times 10^{-14} \text{ at 298 K}$$

-Equilibrium constant from ΔG^o ??

Example 1

What are the $[H_3O^+]$ and $[OH^-]$

in the 0.0030 M $Ba(OH)_2$ aqueous solution

at 298 K?

TABLE 15.1

Temperature Dependence of K_w

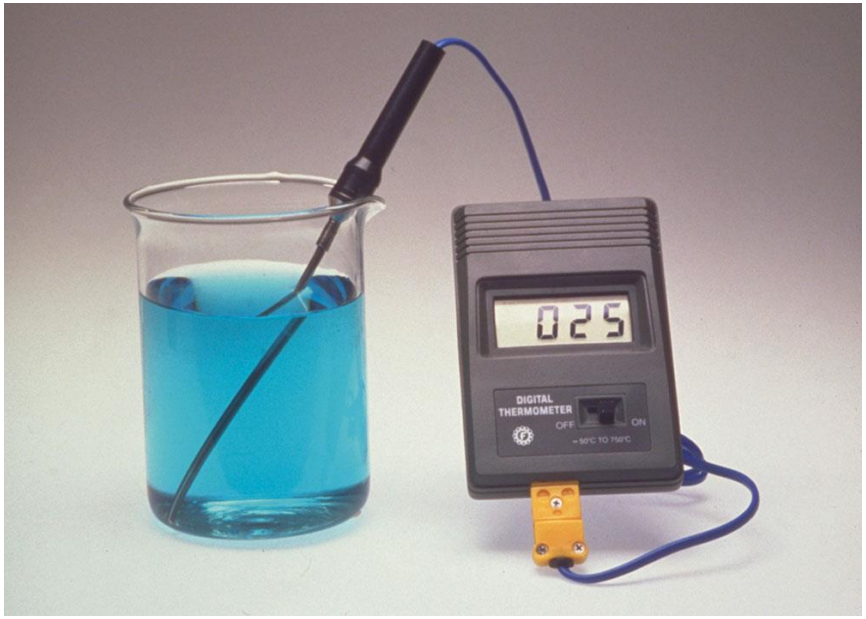
T(°C)	K_w	pH of Water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

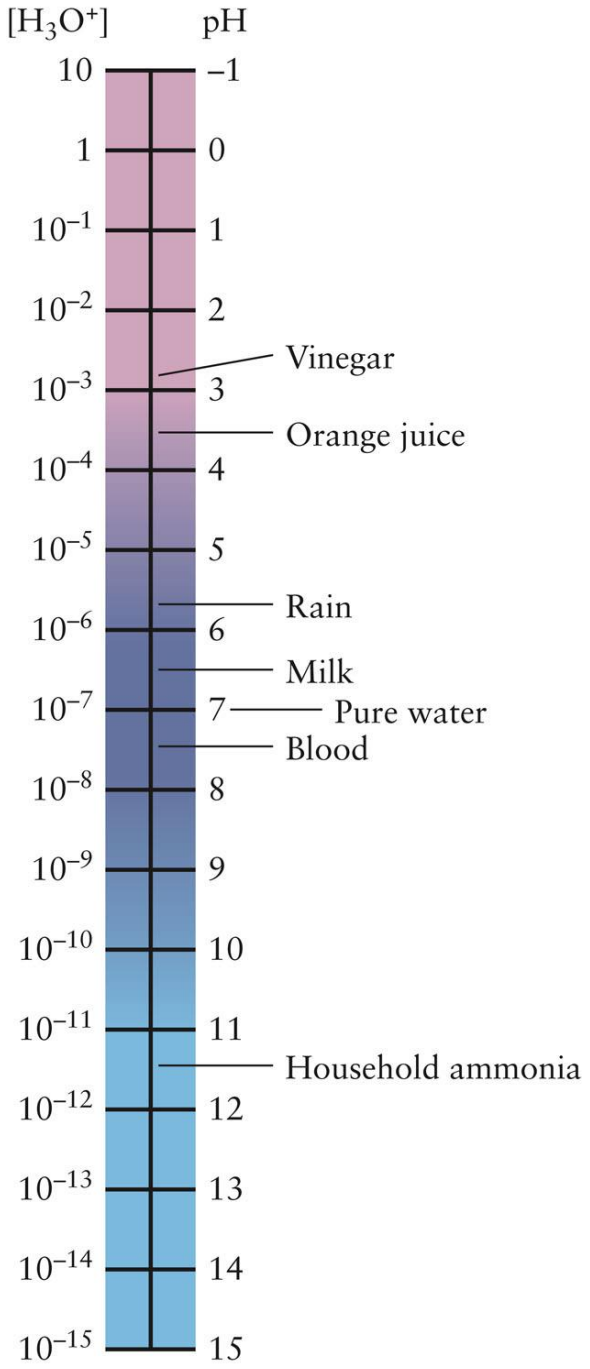
◈ The pH Scale

- Measure of acidity or basicity

$$pH \equiv -\log a_{H_3O^+}$$

In general, $pH = -\log[H_3O^+]$





$$pH \equiv -\log a_{H_3O^+}$$

◈ The pOH Scale

- Generalized expression

$$pX \equiv -\log X$$

- pOH

$$pOH \equiv -\log a_{OH^-}$$

In general, $pH = -\log[OH^-]$ (dimensionless)

$$pH + pOH = 14 \ (at\ 298\ K)$$

$$pH + pOH = const \ (at\ constant\ T)$$

$2H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + OH^-\ (aq)$

$K = [H_3O^+][OH^-] = 10^{-14}\ (at\ 298\ K)$

For neutral water , $[H_3O^+] = [OH^-] = x$

$K = [H_3O^+][OH^-] = x^2 = 10^{-14}$

Therefore, $[H_3O^+]=[OH^-]= 10^{-7}$ M

11.3. Strong/Weak Acids and Bases

◈ Strong acids and bases → reaction goes to almost completion

$$\boldsymbol{HBr}\,(aq) + H_2O\,(l) \rightarrow H_3O^+\,(aq) + \boldsymbol{Br}^-\,(aq)$$

$$\boldsymbol{NH_2}^-\,(aq) + H_2O\,(l) \rightarrow \boldsymbol{NH_3}\,(aq) + OH^-\,(aq)$$

Thus,

0.1 M HCl (aq) soln. → $pH = -\log[H_3O^+] = 1$

1.0 M HCl (aq) soln. → $pH = -\log[H_3O^+] = 0$

0.1 M KOH (aq) soln. → $pH = -\log[H_3O^+] = 13$

1.0 M KOH (aq) soln. → $pH = -\log[H_3O^+] = 14$

$$pH + pOH = 14\ (at\ 298\ K)$$

◈ **Weak acids and bases** → chemical **equilibrium** is established

- Approach from the equilibrium constant K

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

$$K = K_a = \frac{a_{H_3O^+} \cdot a_{A-}}{a_{HA} \cdot a_{H2O}} \approx \frac{[H_3O^+][A^-]}{[HA]}$$ = acidity constant

$$pK_a = -\log K_a$$

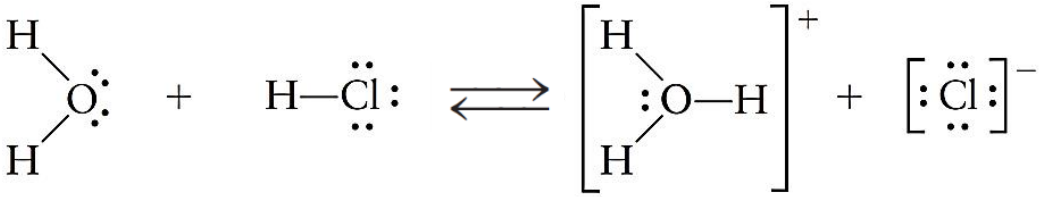
- For base,

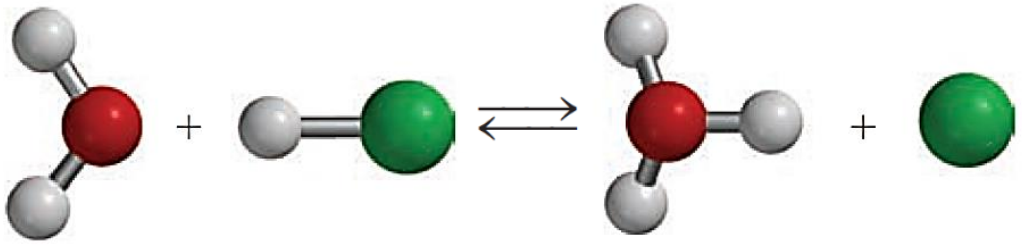
$$B\,(aq) + H_2O\,(l) \leftrightarrow BH^+\,(aq) + OH^-\,(aq)$$

$$K = K_b = \frac{a_{BH^+} \cdot a_{OH-}}{a_B \cdot a_{H2O}} \approx \frac{[BH^+][OH^-]}{[B]}$$ = basicity constant

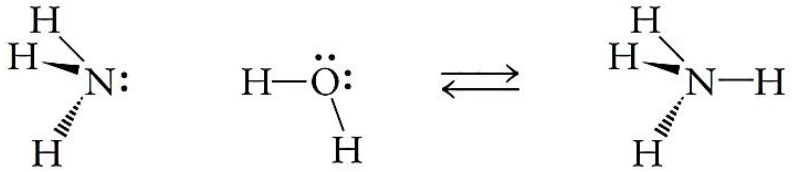
$$pK_b = -\log K_b$$

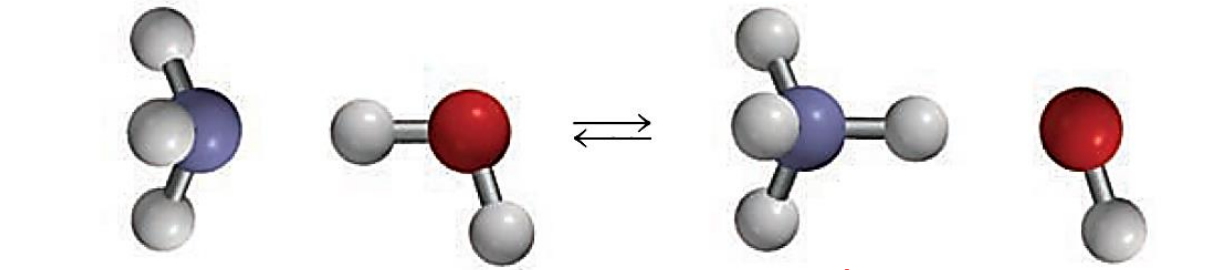
◈ Conjugate seesaw





Weak B Strong A Strong A Weak B





Strong B Weak A Weak A Strong B

* Quantitatively,

$$HA\,(aq) + H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + A^-\,(aq) \qquad K_a(HA) = \frac{[H_3O^+][A^-]}{[HA]}$$

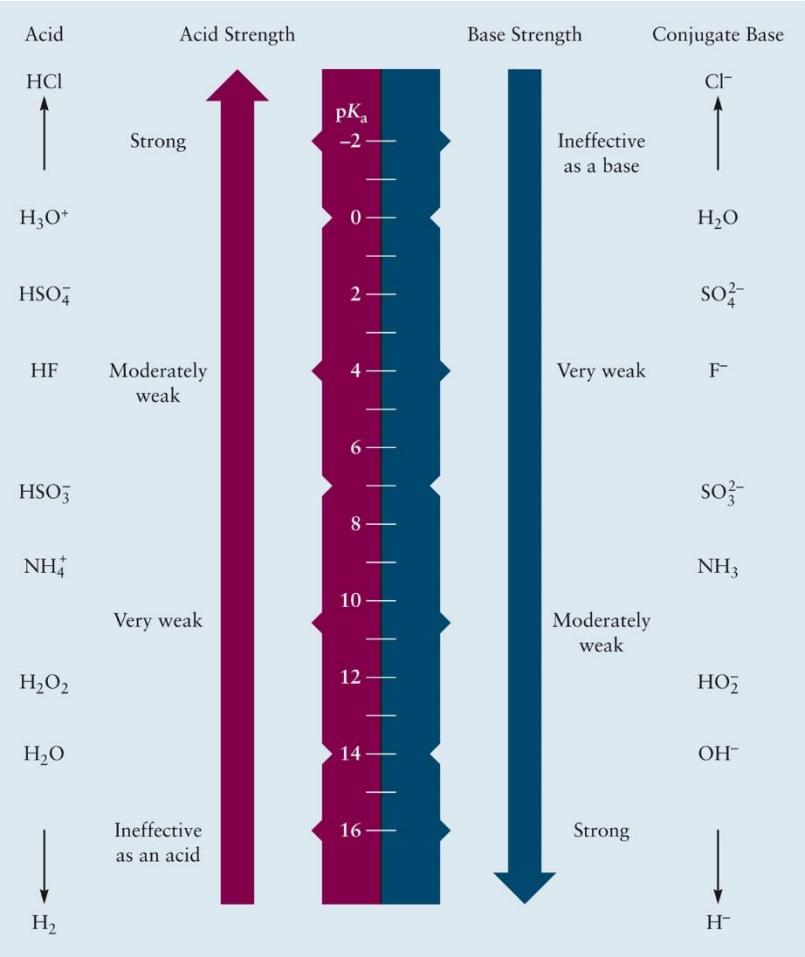
$$A^-\,(aq) + H_2O\,(l) \leftrightarrow HA\,(aq) + OH^-\,(aq) \qquad K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$$

$$2\,H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + OH^-\,(aq) \qquad K = K_a \times K_b = K_w$$

$$pK_a(HA) + pK_b(A^-) = pK_w = const.$$

How about strong acid such as HCl, HBr or HNO_3 ?

(stronger proton donor than H_3O^+; $K_a > 1$; $pK_a < 0$)



$$pK_a(HA) + pK_b(A^-) = pK_w = const.$$

TABLE 15.1

Temperature Dependence of K_w

T(°C)	K_w	pH of Water
0	0.114×10^{-14}	7.47
10	0.292×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.47×10^{-14}	6.63
60	9.61×10^{-14}	6.51

Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of H^+ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

11.4. Molecular Structure and Acid Strength

Acid Strength-Difficult to predict only with the structure because it is dependent on Gibbs free energy! (Entropy included!) and is dependent on the interaction with solvent.

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

$$\Delta H = -\Delta_{solv}(HA) + \Delta H_B(H\text{-}A) + I(H) - E_a(A) + \Delta H_{hyd}(H^+) + \Delta H_{hyd}(A^-)$$

Example 2

(1) HF, HCl, HBr, HI

(2) CH_4, NH_3, H_2O, HF

(3) HClO, HBrO, HIO

(4) HClO, $HClO_2$, $HClO_3$, $HClO_4$

$$HA\ (g) \rightarrow HA\ (aq)$$

$$HA\ (g) \rightarrow H(g) + A(g)$$

$$H(g) \rightarrow H^+(g) + e^-\ (g)$$

$$A(g) + e^-\ (g) \rightarrow A^-(g)$$

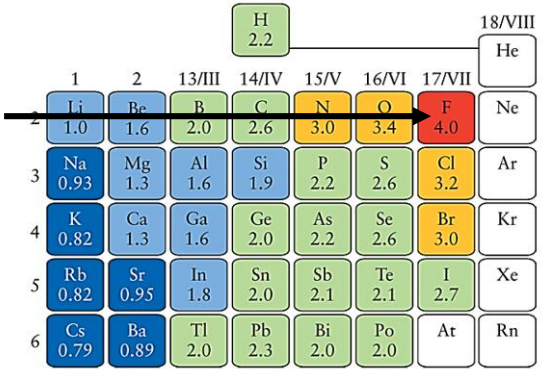
$$H^+(g) + H_2O\ (l) \rightarrow H_3O^+\ (aq)$$

$$A^-(g) \rightarrow A^-\ (aq)$$

1. Polar H-A bonds have more ionic character and show more acidity
   Ionic character in AB is increased if the electronegativity difference between A and B are increased.
   → More electronegative A in HA produce stronger acid.

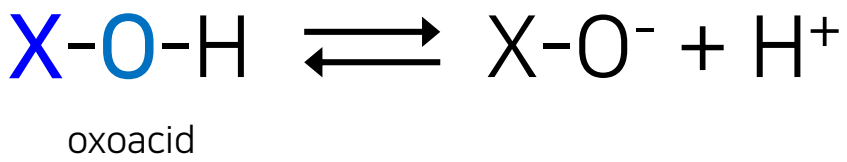
HF vs **NH_3**

HCl vs H_2O



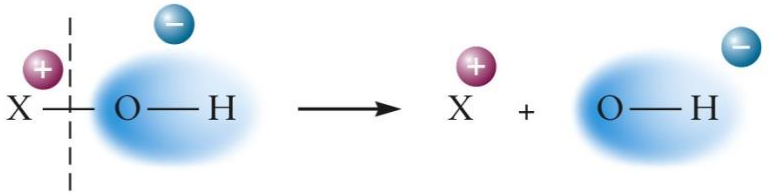
2. Bond strength: weaker the H-A bond, stronger the acidity.
(HA is energetically unstable): compare ΔH_B(H-A)
HF* << HCl < HBr < HI
$H_2O < H_2S < H_2Se < H_2Te$

Electronegativity of neighboring atoms



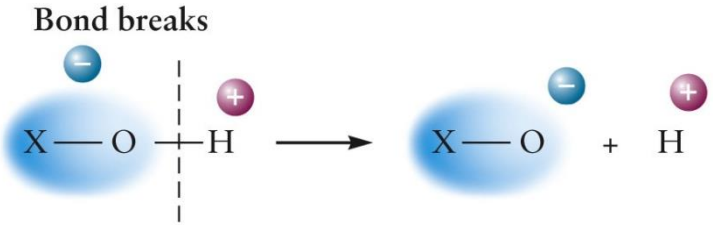
X = electro-positive element (Na in Na-O-H)

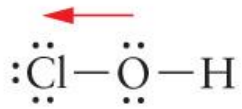
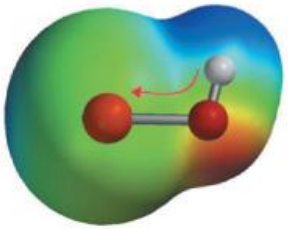
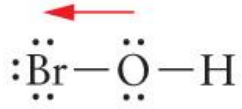
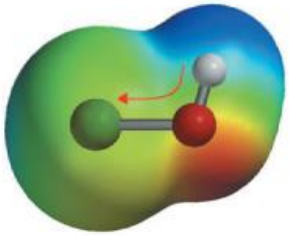
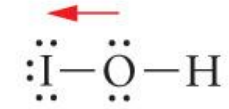
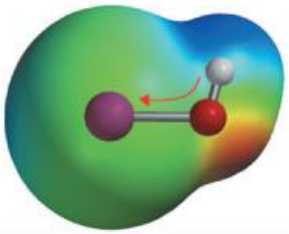
X-O bond is **ionic**:
→ Acts as a base



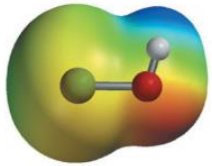
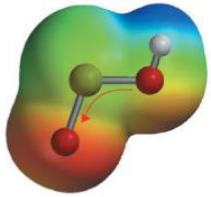
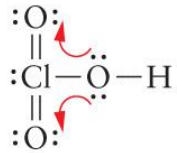
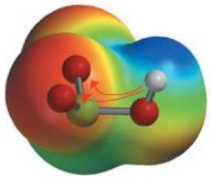
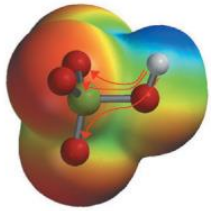
X = electro-negative element (B, C, P, or Br)

X-O bond is **covalent**
→ Acts as an acid



Acid, HXO	Structure*	Electronegativity of atom X	pK_a	
hypochlorous acid, HClO		3.2	7.53	
hypobromous acid, HBrO		3.0	8.69	
hypoiodous acid, HIO		2.7	10.64	

*The red arrows indicate the direction of the shift of electron density away from the O—H bond.

Acid	Structure*	Oxidation number of Cl atom	pK_a	
hypochlorous acid, HClO		+1	7.53	
chlorous acid, $HClO_2$		+3	2.00	
chloric acid, $HClO_3$		+5	strong	
perchloric acid, $HClO_4$		+7	strong	

*The red arrows indicate the direction of the shift of electron density away from the O—H bond. The Lewis structures shown are the ones with the most favorable formal charges, but it is unlikely that the bond orders are as high as these structures suggest.

Carboxylic acids

	pK_a
CH_3COOH	4.76
$CH_2ClCOOH$	2.86
$CHCl_2COOH$	1.29
CCl_3COOH	0.65

	pK_a
CH_2FCOOH	2.66
$CH_2ClCOOH$	2.86
$CH_2BrCOOH$	2.90
CH_2ICOOH	3.17

	pK_a
$CH_3CH_2CH_2COOH$	4.82
$CH_3CH_2CHClCOOH$	2.84
$CH_3CHClCH_2COOH$	4.06
$CH_2ClCH_2CH_2COOH$	4.52

	pK_a
$HCOOH$	3.75
CH_3COOH	4.76
CH_3CH_2COOH	4.87
$CH_3CH_2CH_2COOH$	4.82

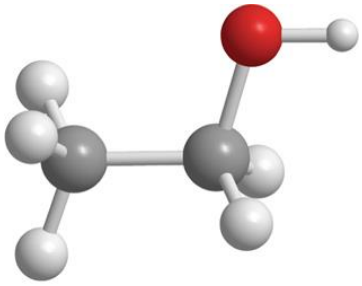
Resonance stabilization of A^- leads to stronger acid

Alcohols (R-OH) : in general, very weak acid because RO^- is very unstable.

C_2H_5OH (pKa = 15.9 (water)), ClC_2H_4OH (pKa = 14.3(water))
(In water, they show no acidity)

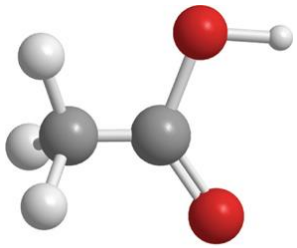
Phenol (C_6H_5-OH) is an alcohol, but it shows unusual acidity because C_6H_5O- anion is very stable due to the resonance stabilization.

Carboxylic acid: structurally similar to alcohols but they show significant acidity because of resonance stabilization of carboxylate anions.

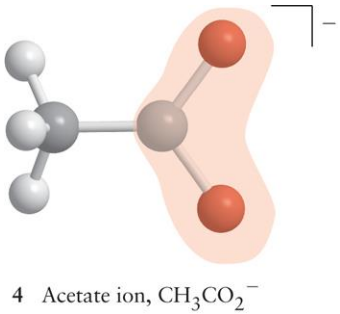


2 Ethanol, CH_3CH_2OH

pK_a = 15.9



3 Acetic acid, CH_3COOH



4 Acetate ion, $CH_3CO_2^-$

pK_a = 4.7

Strong acid:

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

1 M of HCl in water

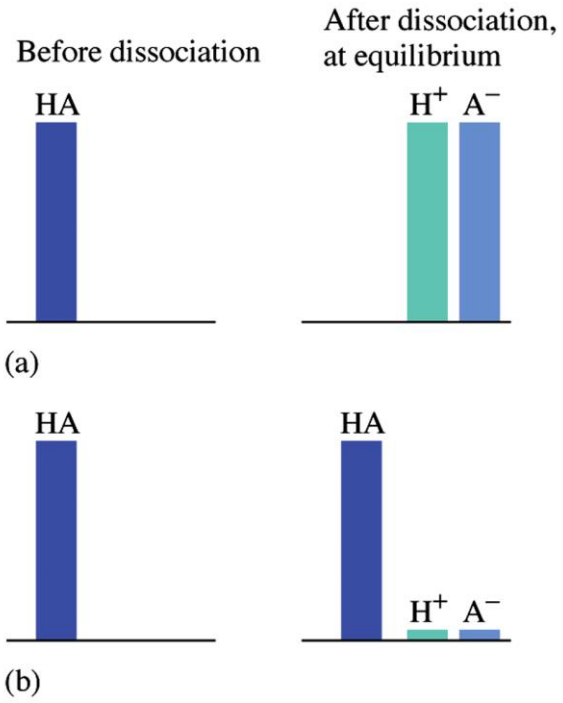
→ Mostly Cl^- and H^+

Weak acid:

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

1 M of Acetic acid in water

→ Mostly CH_3COOH in water



How much will be ionized?

For Acetic acid (CH_3COOH= AcH)

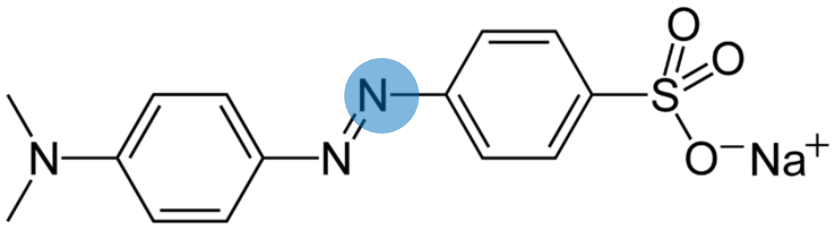
K_a= 1.75 x 10^{-5} or pK_a =-logK_a = 4.757

For 1 M of AcH in water,

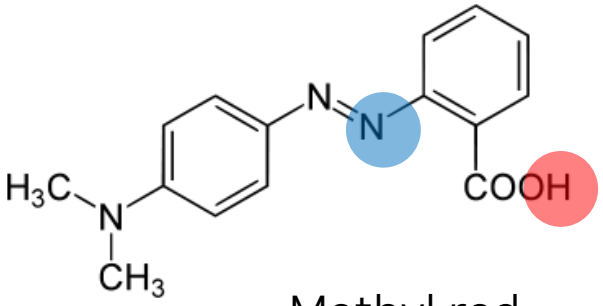
	AcH	Ac-	H+
Initial	1	0	0
Final	1-x	x	x

11.5. Acid-Base Indicators

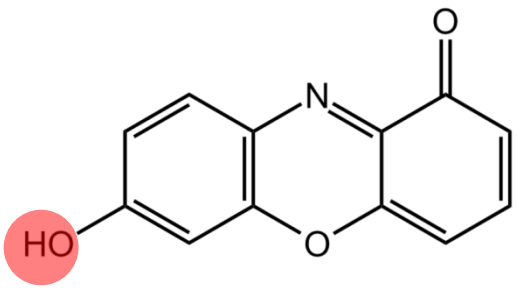
A weak acid that has one color in its acid form (HIn) and another color in its conjugate base form (In^-)



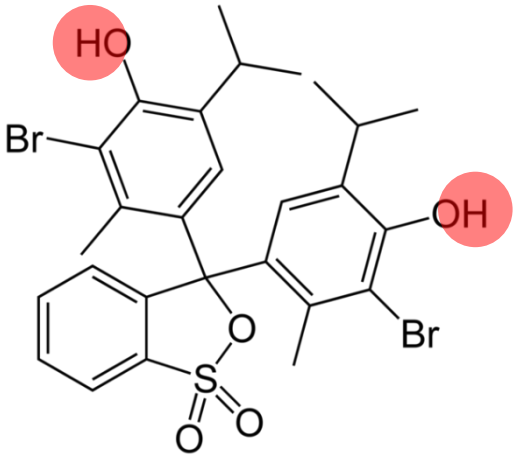
Methyl orange



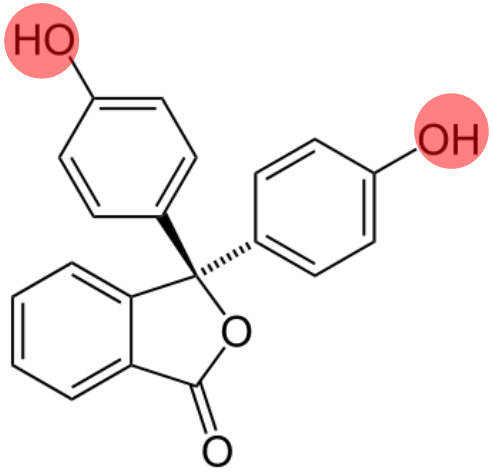
Methyl red



Litmus



Bromothymol blue



Phenolphthalein

$$HIn\,(aq) + H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + In^-\,(aq)$$

$$K_{In} = K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

- End Point

: the point at which the conc. of its acid and base forms are equal

$$[HIn] = [In^-]$$

$$\therefore K_{In} = [H_3O^+], i.e.\, pK_{In} = pH$$

pH of mixed acids and bases

A mixture of acids, HA (a M), HB (b M)

$HA \leftrightarrow H^+ + A^-,\ K_{a1}$

$HB \leftrightarrow H^+ + B^-,\ K_{a2}$

What is the pH of this mixture?

$$K_{a1} = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]x}{a-x} = \frac{(x+y)x}{a-x}$$

$$K_{a2} = \frac{[H^+][B^-]}{[HB]} = \frac{[H^+]y}{b-y} = \frac{(x+y)y}{b-y}$$

$$[H^+] = x + y = ?$$

Two coupled quadratic equations with unknown x and y.
→ Not easy to solve with hand

Solution: dominating equilibrium

- For a mixture of HA and HB,
  the reaction that provides more H^+ dominates the equilibrium:

1. Stronger acid determines pH.

2. If the pK_a's are about the same, the reaction with stronger concentration determines pH.

- AcH in Water

(AcH is a weak acid, but H_2O is a very weak acid):

$AcH \leftrightarrows H^+ + Ac^-$ $K_a = 10^{-5}$

$H_2O \leftrightarrows H^+ + OH^-$ $K_w = 10^{-14}$

Disregard the 2nd equation.

- 1 M of AcH + 0.1 M of HCl

$AcH \leftrightarrows H^+ + Ac^-$ $K_{a1} = 10^{-5}$

$HCl \leftrightarrows H^+ + Cl^-$ K_{a2} = Large number (>1)

What is the concentration of Ac^-?

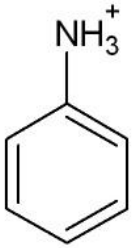
Most of the H^+ comes from HCl. Therefore,
$[H^+] = 0.1$ M, pH = -log 0.1= 1

$$K_{a1} = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(0.1)x}{1-x} = 10^{-5}$$

- pH of a mixture solution containing
1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$)

11.7. The pH of Salt Solutions

◈ Cations



- Acidic cations

  : The conjugate acids of weak bases (ex. NH_4^+, $C_6H_5NH_3^+$)

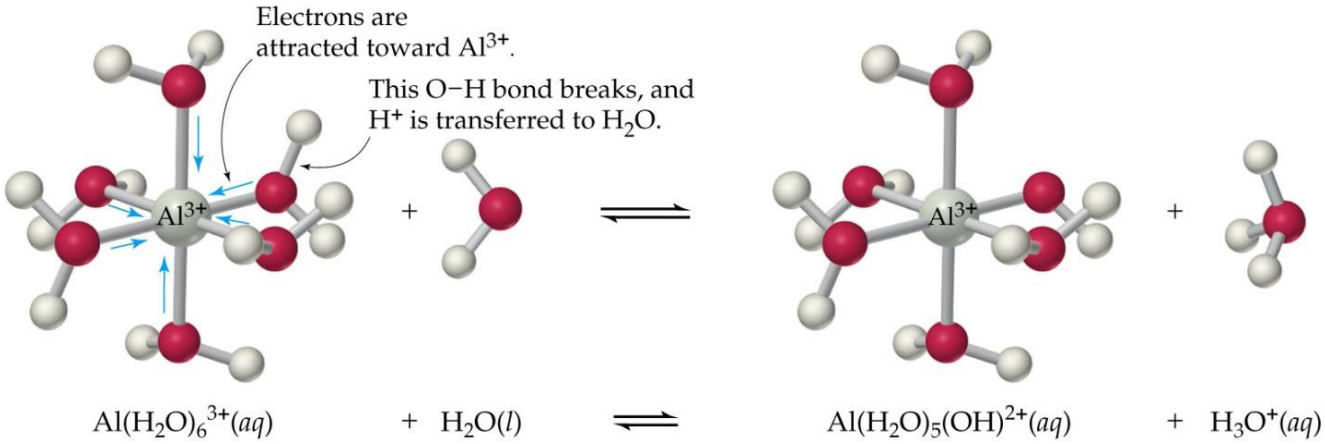
  : Certain small, highly charged metal cations (ex. Fe^{3+}, Cu^{2+})

- Neutral cations

  : group 1 and 2 cations, cations with +1 charge (ex. Li^+, Mg^{2+} Ag^+)

- Basic cations

  : none



Character	Examples	K_a	pK_a
Acidic			
conjugate acids of weak bases	Anilinium ion, $C_6H_5NH_3^+$	2.3×10^{-5}	4.64
	Pyridinium ion, $C_5H_5NH^+$	5.6×10^{-6}	5.24
	Ammonium ion, NH_4^+	5.6×10^{-10}	9.25
	Methylammonium ion, $CH_3NH_3^+$	2.8×10^{-11}	10.56
small, highly charged metal cations	Fe^{3+} *as* $Fe(H_2O)_6^{3+}$	3.5×10^{-3}	2.46
	Cr^{3+} *as* $Cr(H_2O)_6^{3+}$	1.3×10^{-4}	3.89
	Al^{3+} *as* $Al(H_2O)_6^{3+}$	1.4×10^{-5}	4.85
	Cu^{2+} *as* $Cu(H_2O)_6^{2+}$	3.8×10^{-8}	7.49
	Ni^{3+} *as* $Ni(H_2O)_6^{2+}$	9.3×10^{-10}	9.03
	Fe^{2+} *as* $Fe(H_2O)_6^{2+}$	8.0×10^{-11}	10.10
Neutral			
group 1 and 2 metal cations	$Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ag^+ \cdots$		
Basic	none		

◈ Anions

- Acidic anions

  : very few (ex. HSO_4^-, $H_2PO_4^-$)

- Neutral anions

  : conjugate bases of strong acid (ex. Cl^-, ClO_4^-, NO_3^-)

- Basic anions

  : Conjugate bases of weak acids (ex. CH_3COO^-, F^-, S^{2-})

Character	Examples
Acidic	
very few	$HSO_4^-, H_2PO_4^-$
Neutral	
conjugate bases of strong acids	$Cl^-, Br^-, I^-, NO_3^-, ClO_4^-$
Basic	
conjugate bases of weak acids	$F^-, O^{2-}, OH^-, S^{2-}, HS^-, HCO_3^-, PO_4^{3-}$ CH_3COO^-, and other carboxylic ions

Example) Estimate the pH of 0.15 M **NH_4Cl** (aq). Using $K_b = 1.8 \times 10^{-5}$ for NH_3.

$$NH_4{}^+ (aq) + H_2O (l) \leftrightarrow H_3O^+ (aq) + NH_3 (aq)$$

Example Estimate the pH of 0.15 M **$Ca(CH_3CO_2)_2$** (aq). Using $K_a = 1.8 \times 10^{-5}$ for CH_3COOH.

$$CH_3COO^- (aq) + H_2O (l) \leftrightarrow CH_3COOH (aq) + OH^- (aq)$$

$$CH_3COOH (aq) + H_2O (l) \leftrightarrow CH_3COO^- (aq) + H_3O^+ (aq)$$

11.8. Very Dilute Soln. of Strong A and B

- Very dilute solution **less than 10^{-6} M**

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

$$2H_2O\ (l) \rightarrow H_3O^+\ (aq) + OH^-\ (aq)$$

3 equations

1. Autoprotolysis equilibrium: $\boldsymbol{K_w} = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$
2. Charge Balance: $[H_3O^+] = [OH^-] + [A^-]$
3. Material Balance:

$$[A^-] = [HA]_{initial} \text{ (strong acid)}$$

$$\therefore K_w = [H_3O^+]\,([H_3O^+] - [HA]_{initial})$$

Example 11.13. what is the pH of $8.0*10^{-8}$ M HCl (aq)?

11.9. Very Dilute Soln. of Weak A and B

Very similar to the case with strong acid/base except that….

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

$$2H_2O\,(l) \rightarrow H_3O^+\,(aq) + OH^-\,(aq)$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

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

$$[A^-] \neq [HA]_{initial}$$

$$[HA]_{initial} = [HA] + [A^-]$$

$$K_a = [H_3O^+][A^-]/([HA]_{initial} - [A^-])$$

$$K_a = [H_3O^+]([H_3O^+] - K_w/[H_3O^+])/([HA]_{initial} - [H_3O^+] + K_w/[H_3O^+])$$

$$K_a =\sim [H_3O^+]^2/([HA]_{initial} - [H_3O^+])$$

11.10. The pH of a Polyprotic Acid Solution

Polyprotic acids: species that can donate more than one proton

$$H_2CO_3\,(aq) + H_2O\,(l) \leftrightarrow HCO_3^-\,(aq) + H_3O^+\,(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2O\,(l) \leftrightarrow CO_3^{2-}(aq) + H_3O^+\,(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$

$$K_{a1} \gg K_{a2} \gg K_{a3} \gg \cdots$$

Acid	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}
H_2SO_4	Strong		1.2×10^{-2}	1.92		
$(COOH)_2$	5.9×10^{-2}	1.23	6.5×10^{-5}	4.19		
H_3PO_3	1.0×10^{-2}	2.00	2.6×10^{-7}	6.59		
H_3PO_4	7.6×10^{-3}	2.12	6.2×10^{-8}	7.21	2.1×10^{-13}	12.68
H_2CO_3	4.3×10^{-7}	6.37	5.6×10^{-11}	10.25		
H_2S	1.3×10^{-7}	6.89	7.1×10^{-15}	14.15		
$H_3C_6H_5O_7$	7.1×10^{-4}	3.15	1.7×10^{-5}	4.77	6.4×10^{-6}	5.19
$H_2C_6H_6O_6$	7.9×10^{-5}	4.10	1.6×10^{-12}	11.80		

- Sulfuric acid is the only common polyprotic acid for which the first deprotonation is complete.

Example: Calculate the pH of 0.010 M H_2SO_4 (aq)

$$H_2SO_4 + H_2O\ (l) \leftrightarrow H_3O^+ + HSO_4^-$$

$$\underset{0.01-x}{HSO_4^-} + H_2O\ (l) \leftrightarrow \underset{0.01+x}{H_3O^+} + \underset{x}{SO_4^{2-}}; \quad (0.01+x)*x/(0.01-x) = 0.012$$

Example: Calculate the pH of 0.20 M H_3PO_4 (aq).

$$H_3PO_4\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+ + H_2PO_4^-$$

$$H_2PO_4^-\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+ + HPO_4^{2-}$$

$$HPO_4^{2-}\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+ + PO_4^{3-}$$

Assumption

1. The polyprotic acid is the species present in **largest amount.**
2. Only the **first deprotonation** contributes significantly to $[H_3O^+]$
3. The autoprotolysis of water does **not** contribute significantly to $[H_3O^+]$ or $[OH^-]$

0.034M H_2CO_3 equilibrium concentrations of H_2CO_3, HCO_3^-, CO_3^{2-}, H^+?

$K_{a1} >> K_{a2}$: consider the first ionization

	$H_2CO_3(aq)$	→	$H^+(aq)$ +	$HCO_3^-(aq)$
initial:	0.034		0	0
equilibrium:	0.034-x		x	x

checking assumption: $[HCO_3^-] >> [CO_3^{2-}]$

little effect of second ionization on concentrations of $[H_3O^+]$ and $[HCO_3^-]$

$[H_3O^+] >> 1 \times 10^{-7}$: negligible contribution from autoionization of water

11.11. Solutions of Salts of Polyprotic Acids

amphiprotic

- Reasonable assumption

$$pH \approx \frac{1}{2}(pK_{a1} + pK_{a2})$$

: Valid if $\boldsymbol{s} \gg \frac{K_w}{K_{a2}}$ and $\boldsymbol{s} \gg K_{a1}$ (s = the initial conc. of the salt)

: **independent** of the concentration of the anion

$$H_2PO_4^-\,(aq) + H_2O\,(l) \leftrightarrow H_3O^+\,(aq) + HPO_4^{2-}\,(aq)\ K_{a2}$$

$$H_2PO_4^-\,(aq) + H_2O\,(l) \leftrightarrow OH^-\,(aq) + H_3PO_4\,(aq)\ K_{b1} = K_w/K_{a1}$$

$$H_3PO_4\,(aq) + H_2O\,(l) \leftrightarrow H_2PO_4^-\,(aq) + H_3O^+\,(aq)\ K_{a1}$$

Example

Estimate the pH of (a) 0.20 M NaH_2PO_4 (aq); (b) 0.20 M $Na_2HC_6H_5O_7$ (aq), a salt of citric acid, $H_3C_6H_5O_7$.

11.12. Composition and pH

- Concentrations of the several solution species vary with the pH of the solution. As the pH is increased, the fraction of deprotonated species increases. (consistency with Le Chatelier's principle)

Example

Calculate the fraction of carbonate present as H_2CO_3, HCO_3^-, CO_3^{2-} at pH 10.00.

$$c.f.) \quad f(H_2CO_3) = \frac{[H_2CO_3]}{[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]}$$

$$H_2CO_3\,(aq) + H_2O\,(l) \leftrightarrow HCO_3^-\,(aq) + H_3O^+\,(aq) \qquad K_{a1} = 4.3 \times 10^{-7}$$

$$HCO_3^-\,(aq) + H_2O\,(l) \leftrightarrow CO_3^{2-}(aq) + H_3O^+\,(aq) \qquad K_{a2} = 5.6 \times 10^{-11}$$

$$[HCO_3^-][H_3O^+]/[H_2CO_3] = 4.3 \times 10^{-7}$$

$$[CO_3^{2-}][H_3O^+]/[HCO_3^-] = 5.6 \times 10^{-11}$$

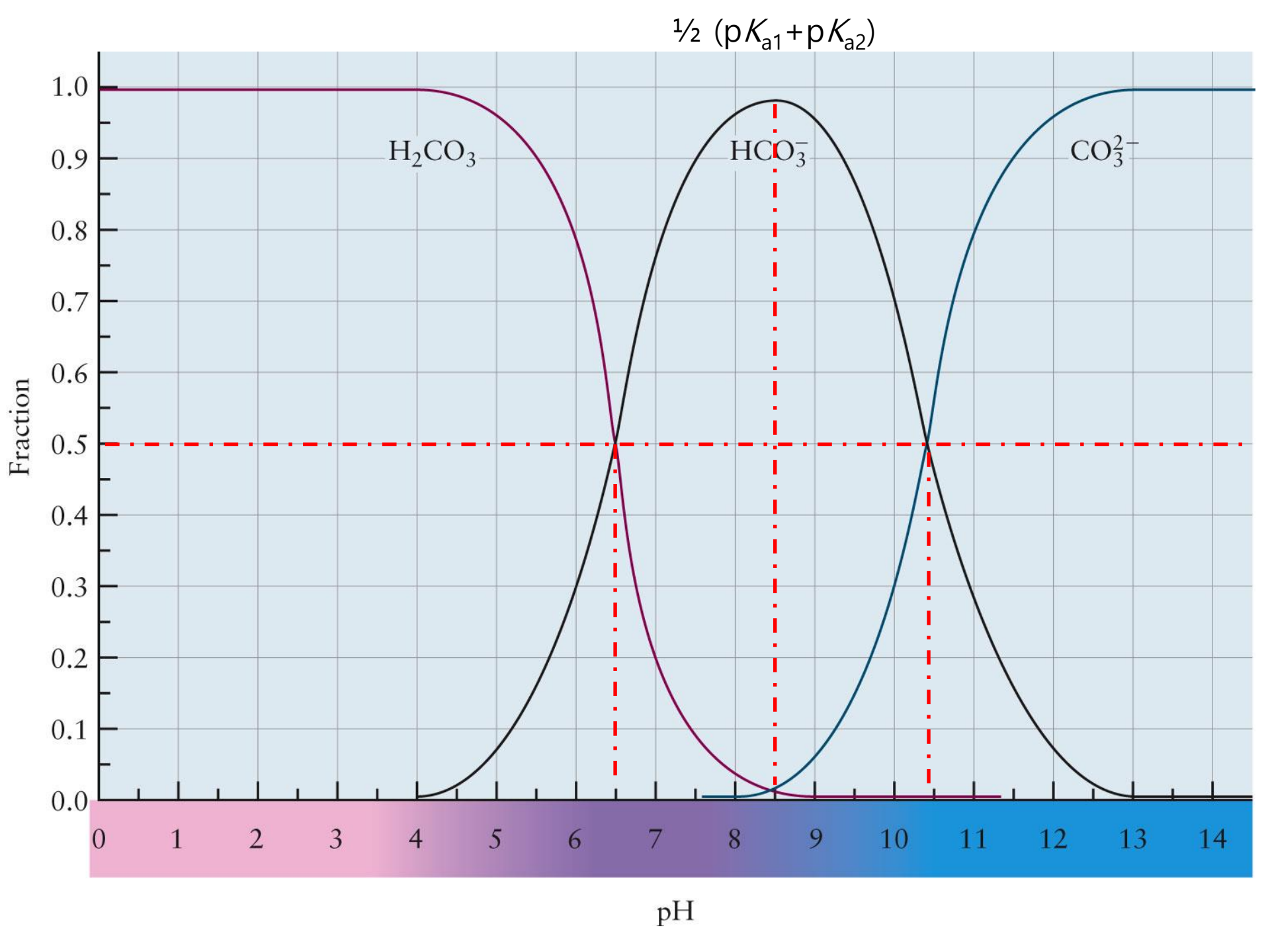
$$[H_2CO_3] = [HCO_3^-][H_3O^+]/4.3 \times 10^{-7}$$

$$[CO_3^{2-}] = 5.6 \times 10^{-11}\,][HCO_3^-]/[H_3O^+]$$

$$f(H_2CO_3) = \frac{[H_2CO_3]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]} = \frac{[H_3O^+]^2}{[H_3O^+]^2+[H_3O^+]K_{a1}+K_{a1}K_{a2}}$$

$$f(HCO_3^-) = \frac{[HCO_3^-]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]} = \frac{[H_3O^+]K_{a1}}{[H_3O^+]^2+[H_3O^+]K_{a1}+K_{a1}K_{a2}}$$

$$f(CO_3^{2-}) = \frac{[CO_3^{2-}]}{[H_2CO_3]+[HCO_3^-]+[CO_3^{2-}]} = \frac{K_{a1}K_{a2}}{[H_3O^+]^2+[H_3O^+]K_{a1}+K_{a1}K_{a2}}$$


½ (pKa1+pKa2)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
Fraction
H2CO3
HCO3−
CO3 2−
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
pH

12.1. Buffer Solution

◈ Buffer

: A mixed solution containing **weak conjugate acid-base** pairs that stabilize the pH of a solution.

→ provides a source and a sink for protons.

- Acid Buffer

: consists of a **weak acid** and its **conjugate base** provided as a salt

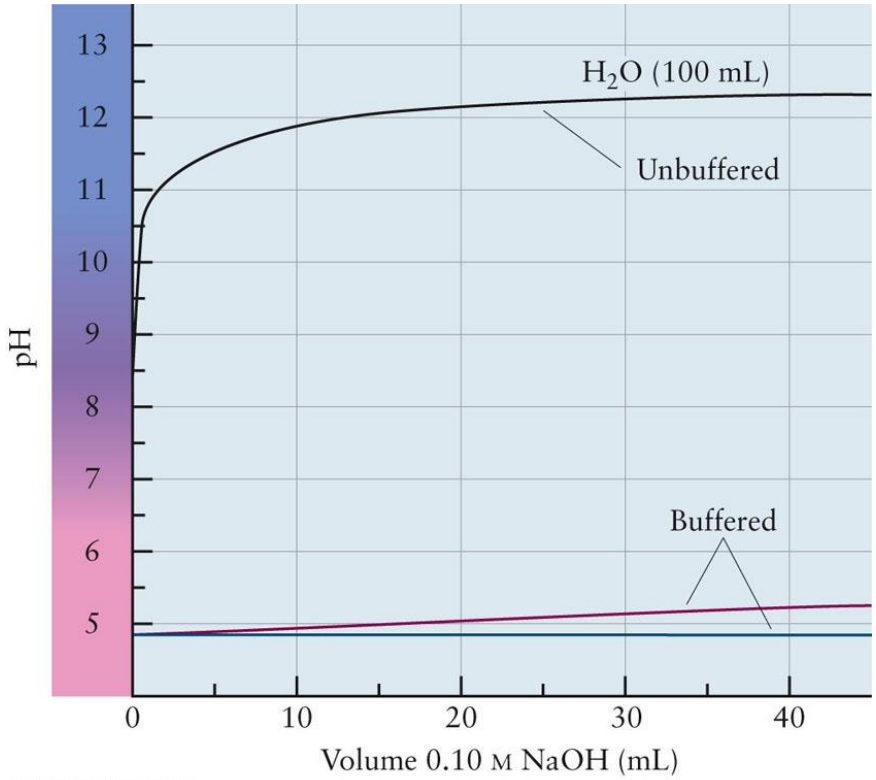
Ex) 0.05 M CH_3COOH (aq) + 0.05 M CH_3COONa (aq)

- Base Buffer

: consists of a **weak base** and its **conjugate acid** provided as a salt

Ex) 0.05 M NH_3 (aq) + 0.05 M NH_4Cl (aq)

- Buffer solution: equal mixture of a weak acid and its conjugate base.
- The mixture resists the change of pH, and it acts to stabilize the pH of solution. All of the living organisms have buffer solutions.
- Such buffering capability is greater with higher concentrations of HA and MA.



© 2007 Thomson Higher Education

Mixture of weak acid and its conjugate base

Very weak acid: $pK_a > 14$ **Weak acid**: $0 < pK_a < 14$

Conjugate base of a weak acid is a weak base.

*Weak acid only: most of weak acid (HA) exist as HA

$$HA \leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{(10^{-7} + x)x}{1.0 - x} \cong \frac{x^2}{1.0 - x} \cong x^2 / 1.0 = 10^{-5}$$

*Conjugate base (MA) only: most of salt exist as A^-.

$$K_b = \frac{[HAc][\mathrm{OH}^-]}{[\mathrm{Ac}^-]} = \frac{y(10^{-7} + y)}{1.0 - y} \cong \frac{y^2}{1.0} = 10^{-9}$$

*Mixture of weak acid (HA) and conjugate base (MA) with comparable concentrations:

With a M of HA and b M of B^-, the equilibrium concentrations are almost the same as those of the initial concentrations of HA and MA.

$$K_a \cong \frac{[H^+][A^-]_0}{[HA]_0} = \frac{[H^+]b}{a} \qquad pH = pK_a + \log\left(\frac{b}{\mathrm{a}}\right)$$

X and y will be small number. In fact they will be even smaller than in the case of pure
HA or pure MA cases because of Le Chatlier principle. The difference, x-y will be also small number.

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](b - y + x)}{a - x + y} = \frac{[H^+](b + (x - y))}{a - (x - y))} \cong \frac{[H^+]b}{a}$$

Acetic acid (AcH) + Sodium Acetate CH_3COOH, CH_3COONa = (CH_3COO^- + Na^+)

$$K_a \cong \frac{[H^+][A^-]_0}{[HA]_0} = \frac{[H^+]b}{a}$$

Consider equimolar (1 M) conc. Of AcH and AcNa.

$$-\log[K_a] = pK_a = -\log\left(\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{AcH}]}\right) = pH - \log\left(\frac{[\mathrm{Ac^-}]}{[\mathrm{AcH}]}\right)$$

$$\therefore pH = pK_a + \log\left(\frac{[\mathrm{Ac^-}]}{[\mathrm{AcH}]}\right) \qquad \therefore pH = pK_a$$

$$\therefore pH = pK_a + \log\left(\frac{[\mathrm{Ac^-}]}{[\mathrm{AcH}]}\right) = pK_a + \log\left(\frac{1.00\ \mathrm{M}}{1.00\ \mathrm{M}}\right) = pK_a$$

Addition of strong acid (such as HCl) with concentration 0.01 M.

$$\therefore pH = pK_a + \log\left(\frac{1.00 - 0.01}{1.00 + 0.01}\right) \approx pK_a$$

$HA \leftrightarrow H^+ + A^-$

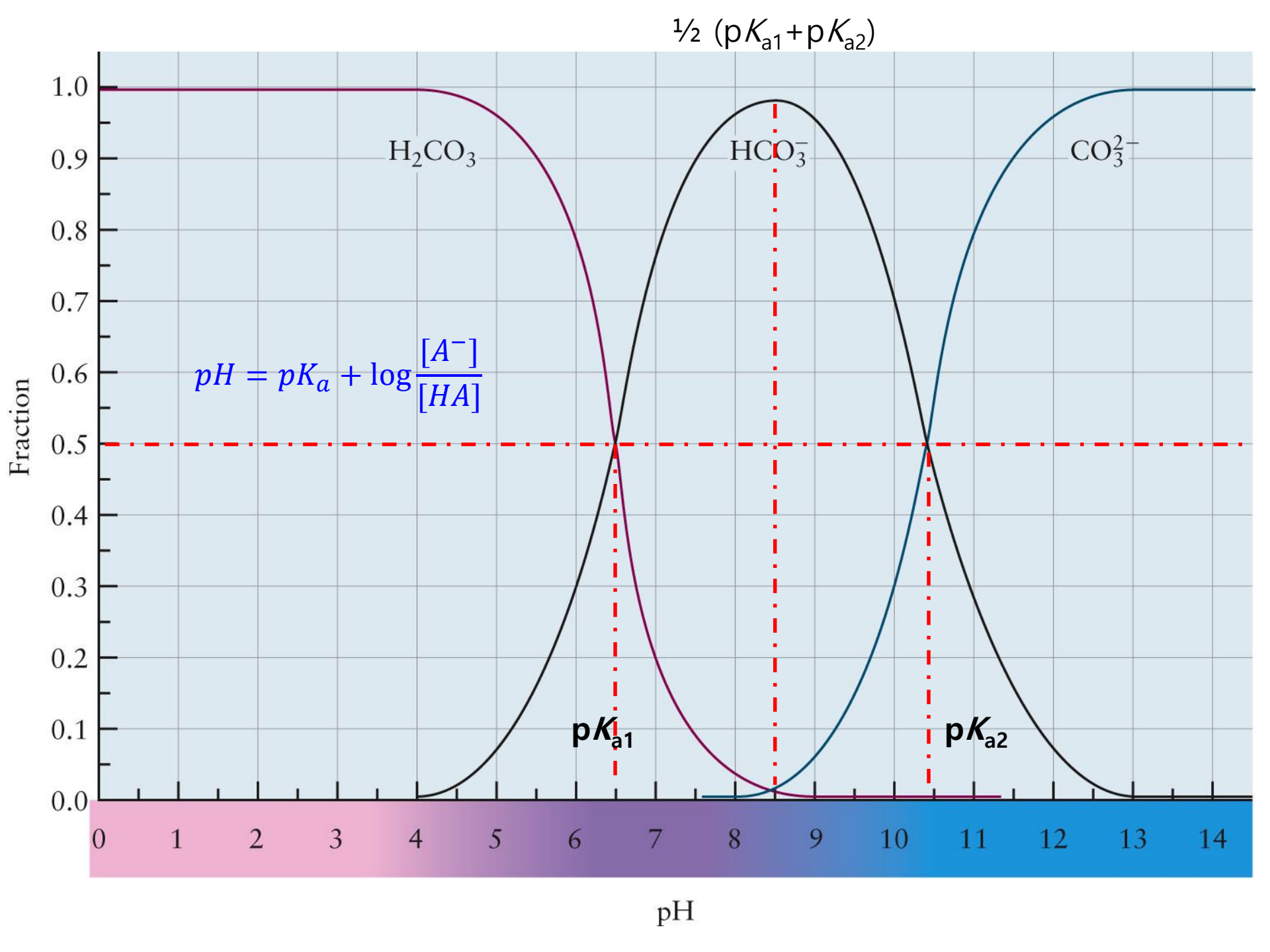
Mixture of HA (weak acid) and XA
= resist the change of pH!!! (BUFFER SOLUTION)

◈ Quantitative Approach

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

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

$$\therefore pH = pK_a + \log\frac{[A^-]}{[HA]} \approx pK_a + \log\frac{[A^-]_{initial}}{[HA]_{initial}}$$


½ (pK$_{a1}$+pK$_{a2}$)
H_2CO_3
HCO_3^-
CO_3^{2-}
$pH = pK_a + \log\frac{[A^-]}{[HA]}$
pK$_{a1}$
pK$_{a2}$
Fraction
pH
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

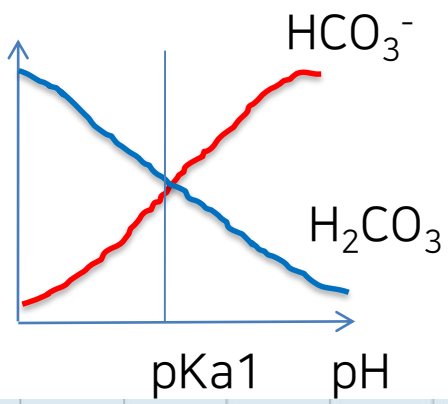
Influence of pH on H_2CO_3, HCO_3^-, CO_3^{2-}

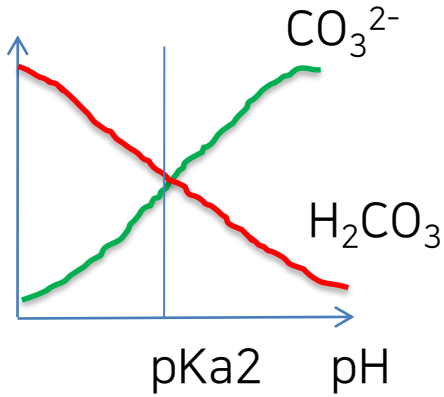
$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_{a1}}{[H^+]}$$

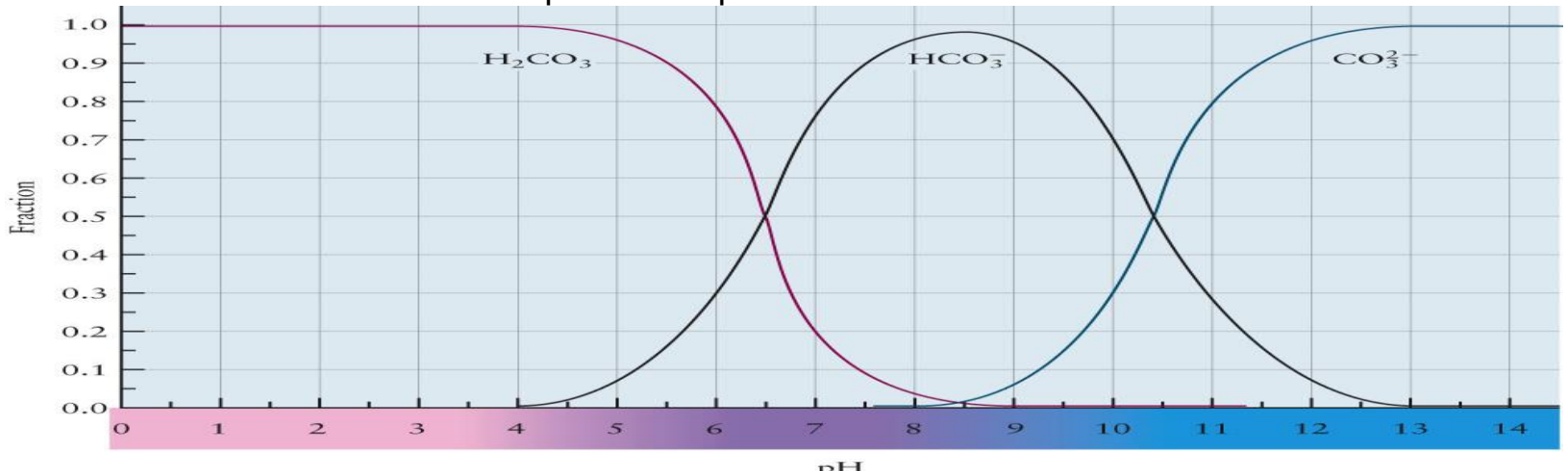
$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_{a2}}{[H^+]}$$

$$\log\left(\frac{[HCO_3^-]}{[H_2CO_3]}\right) = pH - pK_{a1}$$

$$\log\left(\frac{[CO_3^{2-}]}{[HCO_3^-]}\right) = pH - pK_{a2}$$





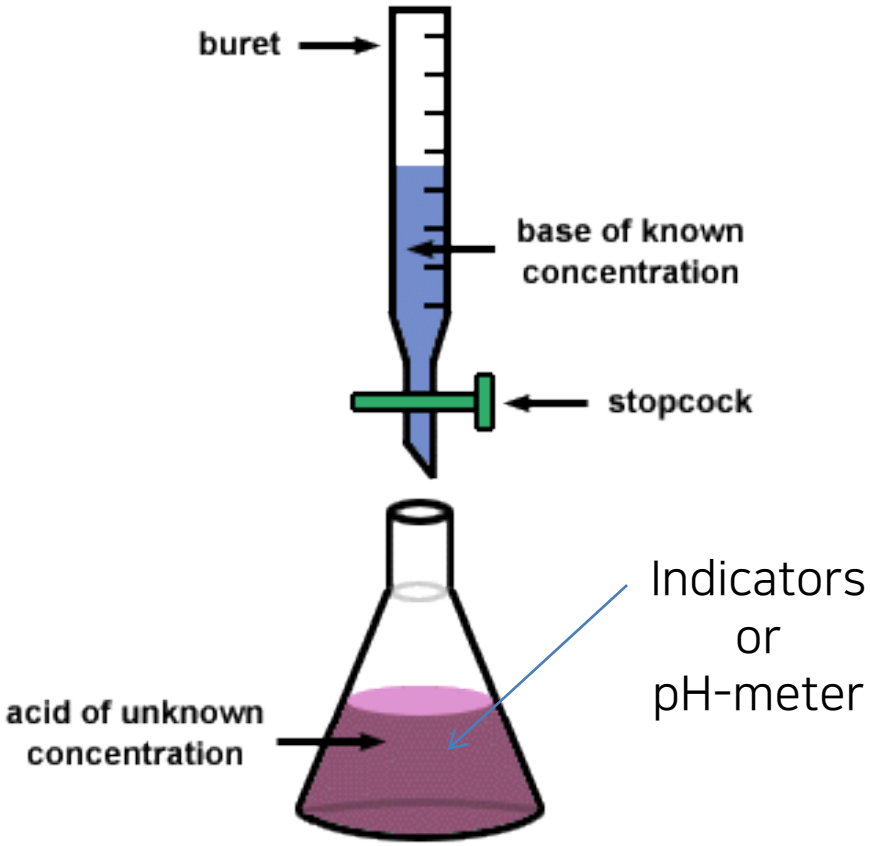


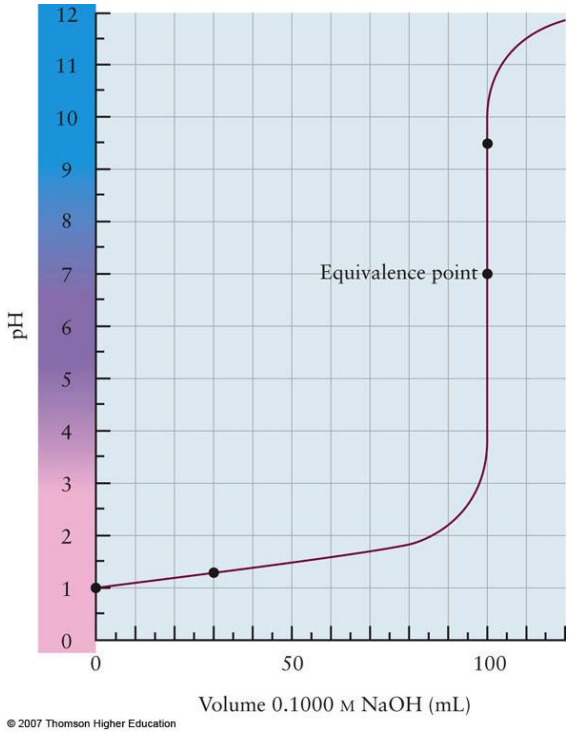
Example We prepare a buffer solution that is 0.040 M CH_3COONa (aq) and 0.080 M CH_3COOH (aq) at 25 ^oC. What is the pH of the solution?

$$pH = pK_a + \log\left(\frac{[Ac^-]}{[AcH]}\right)$$

Example Suppose we dissolve 1.2 g of NaOH (0.030 mol) in 500 mL of the buffer solution above. Calculate the pH of resulting solution.

Acid-base titration





1. Concentration of analyte
2. pH change during the acid-base titration

$$C_a V_a = C_b V_b$$

unknown — known — measure

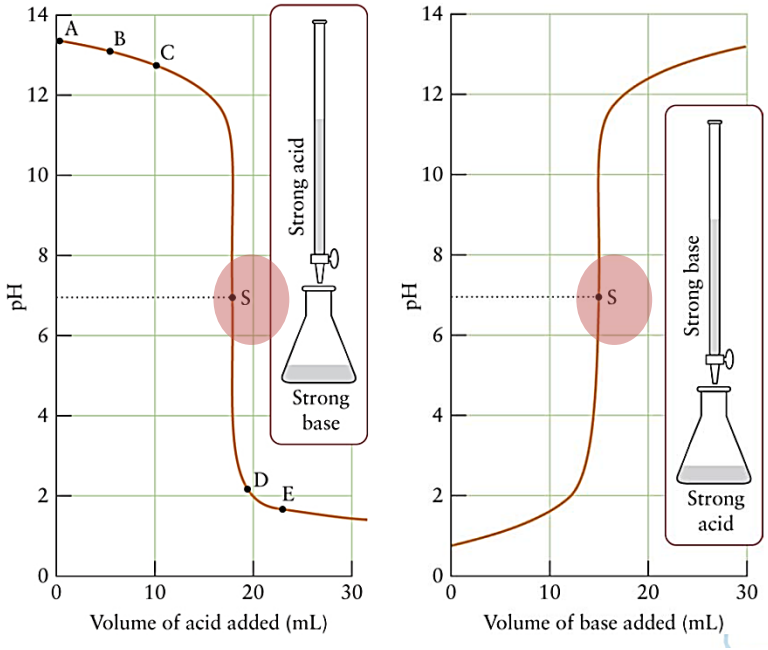
We can solve the coupled equations to precisely predict pH of the solution. However, we will use simple approximations.

12.2. Strong Acid-Strong Base Titration

- pH curve: a plot of the pH of the analyte solution against the volume of titrant added during a titration

Ex) $2\,HCl\,(aq) + Ca(OH)_2 \rightarrow\ CaCl_2\,(aq) + 2\,H_2O\,(l)$

Example Suppose we are carrying out a titration in which the analyte initially consists of 25.00 ml of 0.250 M NaOH (aq) and the **titrant** is 0.340 M HCl (aq). Calculate (a) the pH of the original analyte solution and (b) the new pH after the addition of 5.00 mL of the acid titration.



(a) pOH = -log [OH-], (b) [OH-]= OH- mol/total volume L

Strong-acid and strong base

- 0.1 M, 100.0 mL of HCl (analyte) + 0.1 M V_b mL, NaOH (titrant)

  - Originally, we have $[H^+]$=0.1 M, moles of H^+ = 0.1 M * 100.0 mL

  - V_b = 30.00 mL:

  Moles of NaOH added = 0.1 M * 30.0 mL

  Moles of H^+ remaining = 0.1 M * 100.0 mL -0.1 M * 30.0 mL = 10-3 = 7 mmoles.

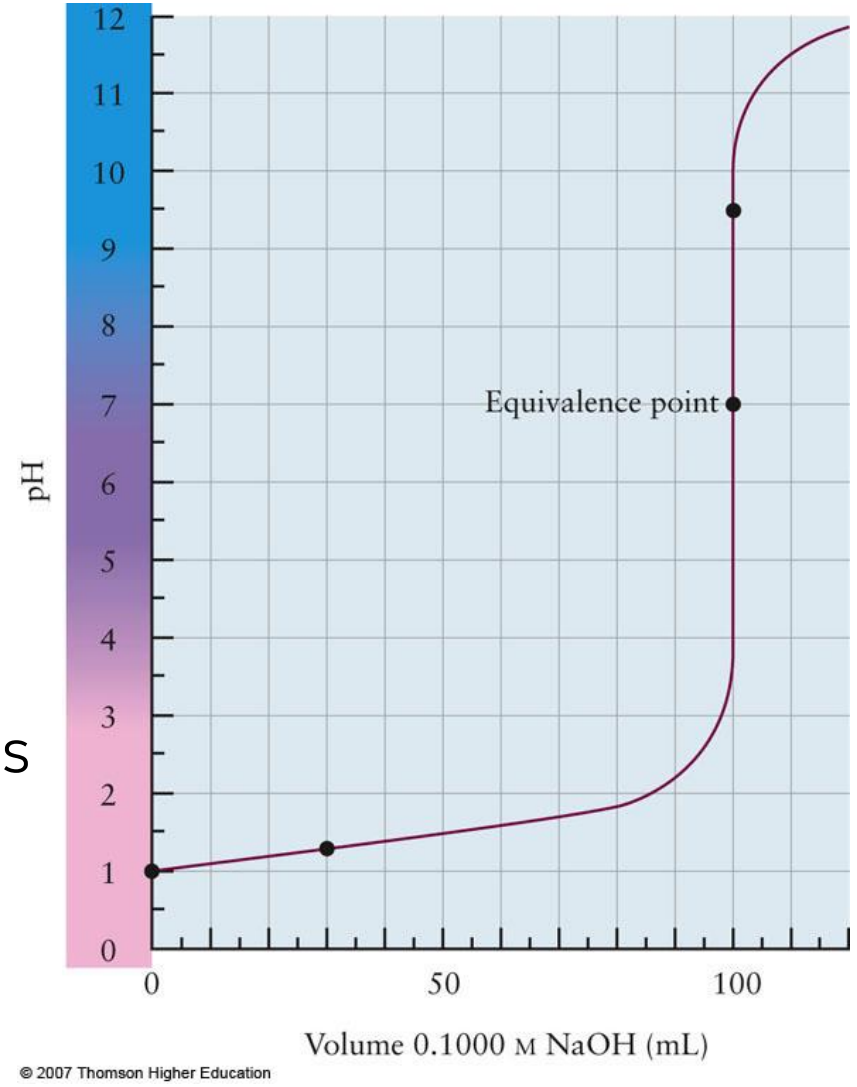
  [H+]=

  pH=

- With V_b = 100 mL = V_e
  - Equivalence point.
  - At equivalent point, the pH is neutral
    pH= 7.0

- With V_b = 100.05 mL,
  - 100 mL * 0.1 M of NaOH is consumed by the acid-base reaction.
  - Only OH- 0.05 mL * 0.1 M remains
  - 100.05 mL dilutes the solution

  [OH-] =



© 2007 Thomson Higher Education

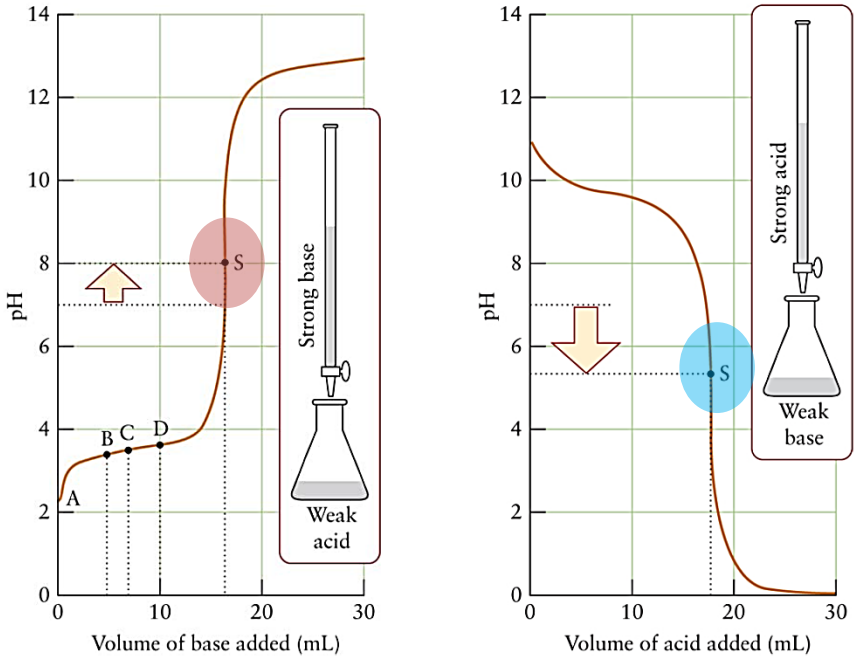
12.3. S.A.-W.B. and W.A.-S.B. Titrations

- Weak Acid – **Strong Base** Titration

: A strong base dominates the weak acid and the pH at the stoichiometric point is **greater than 7.**

- Why?

Ex) $HCOOH\ (aq) + NaOH\ (aq) \rightarrow HCOONa\ (aq) + H_2O\ (l)$



Weak acid (analyte) + Strong base (titrant)

- CH_3CO_2H (acetic acid) + NaOH

  0.1 M / 100 mL 0.1 M / V_b mL

- $\underline{V_b = 0\ mL}$

  HAc ←→ H^+ + Ac-:

  Ka = 1.78×10^{-5} = (x) (x) / (0.1-x) = x^2 / 0.1, → pH = 2.88

- $\underline{V_b < V_e}$

  $HAc + OH^- \rightarrow Ac^- + H_2O$

  $C_aV_a - C_bV_b$ C_bV_b

  HAc: weak acid

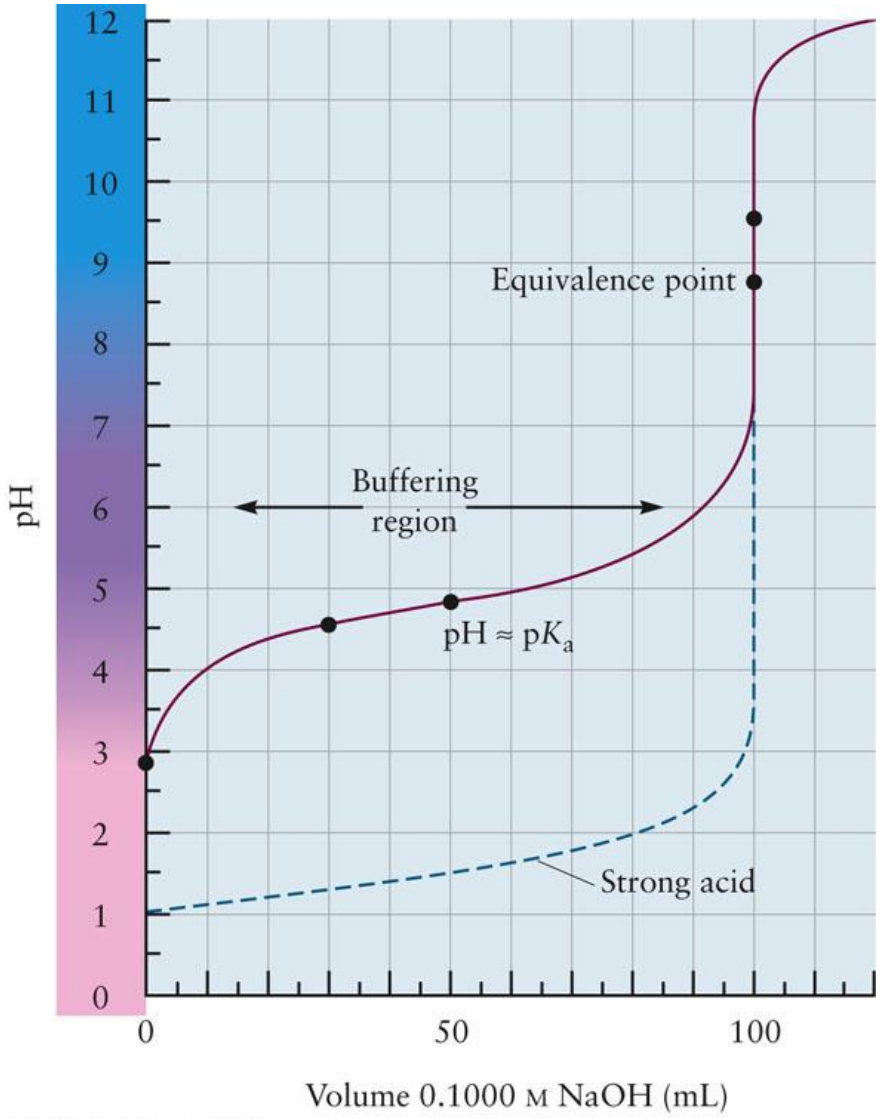
  Ac-: conj. Base of weak acid

  → Buffer !!!

  $pH = pKa + \log([Ac^-]/[HAc])$

  $= pKa + \log(C_bV_b / (C_aV_a - C_bV_b))$

At mid-point, Vb = $1/2V_e$, pH = pKa.



© 2007 Thomson Higher Education

At eq. point,

Most of the HAc is converted to Ac-.

However, Ac- has some **basicity** and it wants to return to HAc.

$$Ac^- + H_2O \leftrightarrow HAc + OH^-$$

0.1 M* 100 mL/200 mL-x x x

Equivalence point is basic.

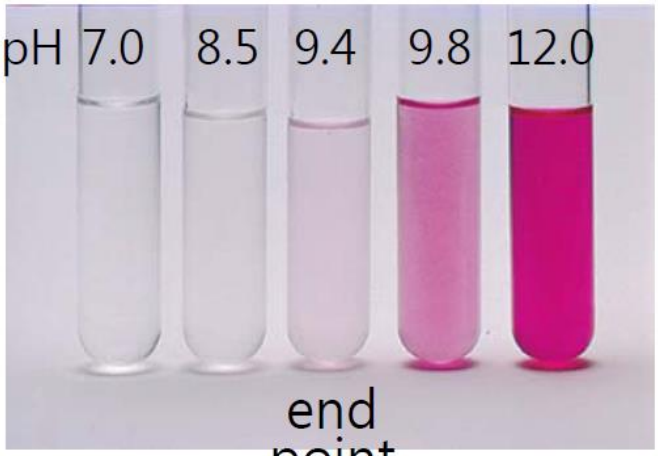
Example Estimate the pH at the stoichiometric point of the titration of 25.00 mL of 0.100 M HCOOH (aq) with 0.150 M NaOH (aq).

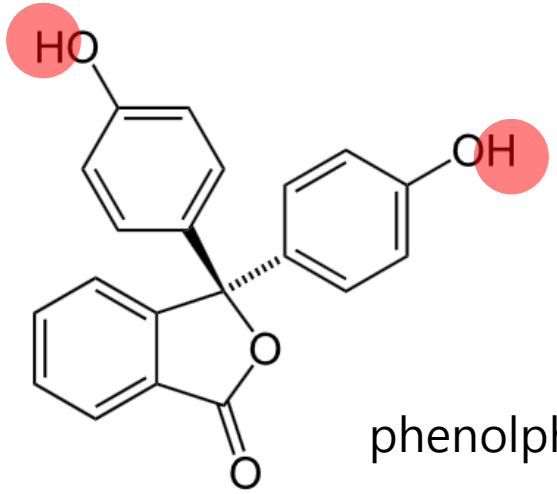
Use $K_a = 1.8 \times 10^{-4}$ for formic acid.

$$HCOOH\ (aq) + NaOH\ (aq) \leftrightarrow Na^+\ (aq) + H_2O\ (l) + HCO^-\ (aq)$$

$$HCO^-\ (aq) + H_2O\ (l) \leftrightarrow HCOOH\ (aq) + OH^-\ (aq)$$

= What is the pH of the HCO^{2-} solution that is generated from the acid-base titration ?

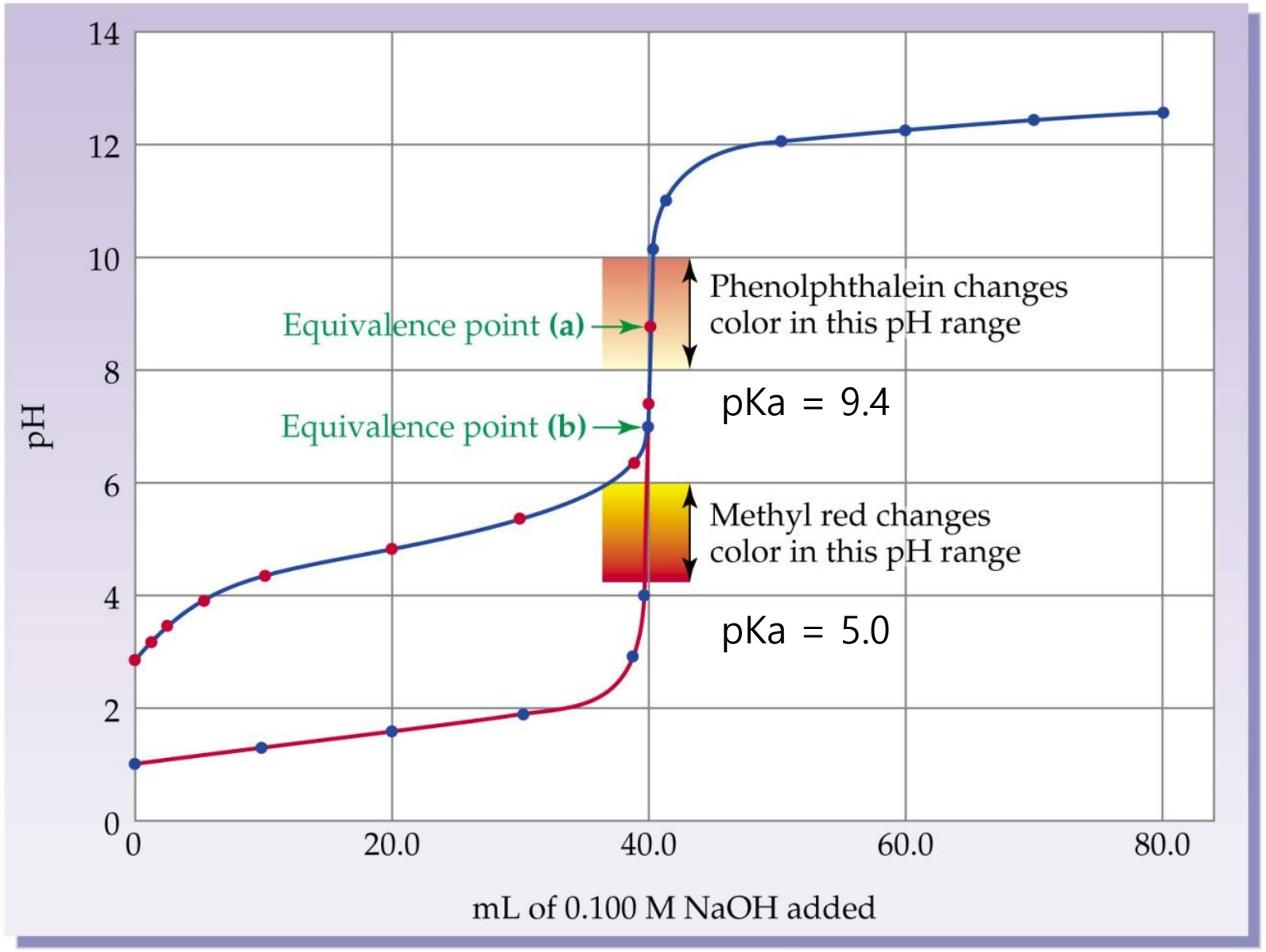


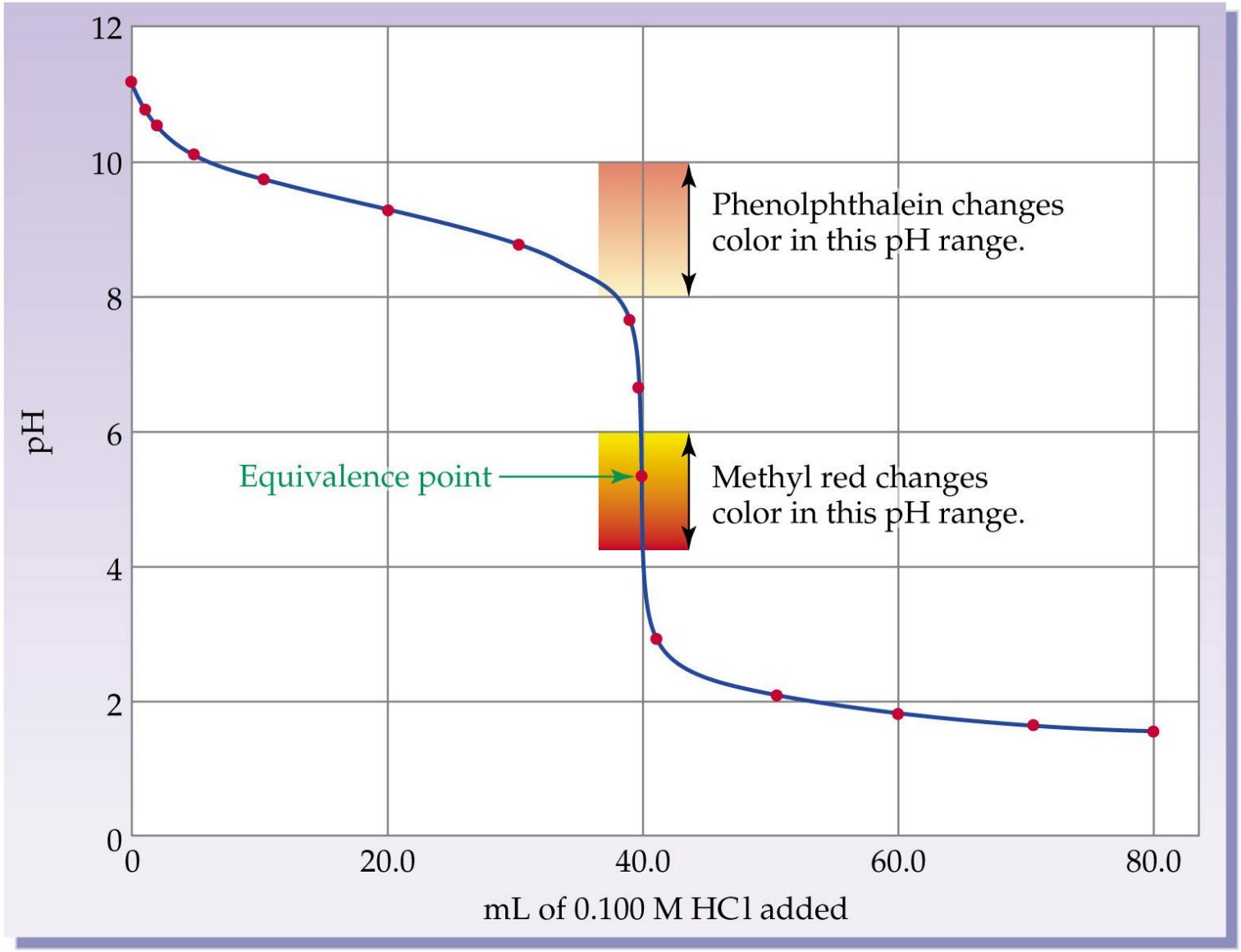


phenolphthalein

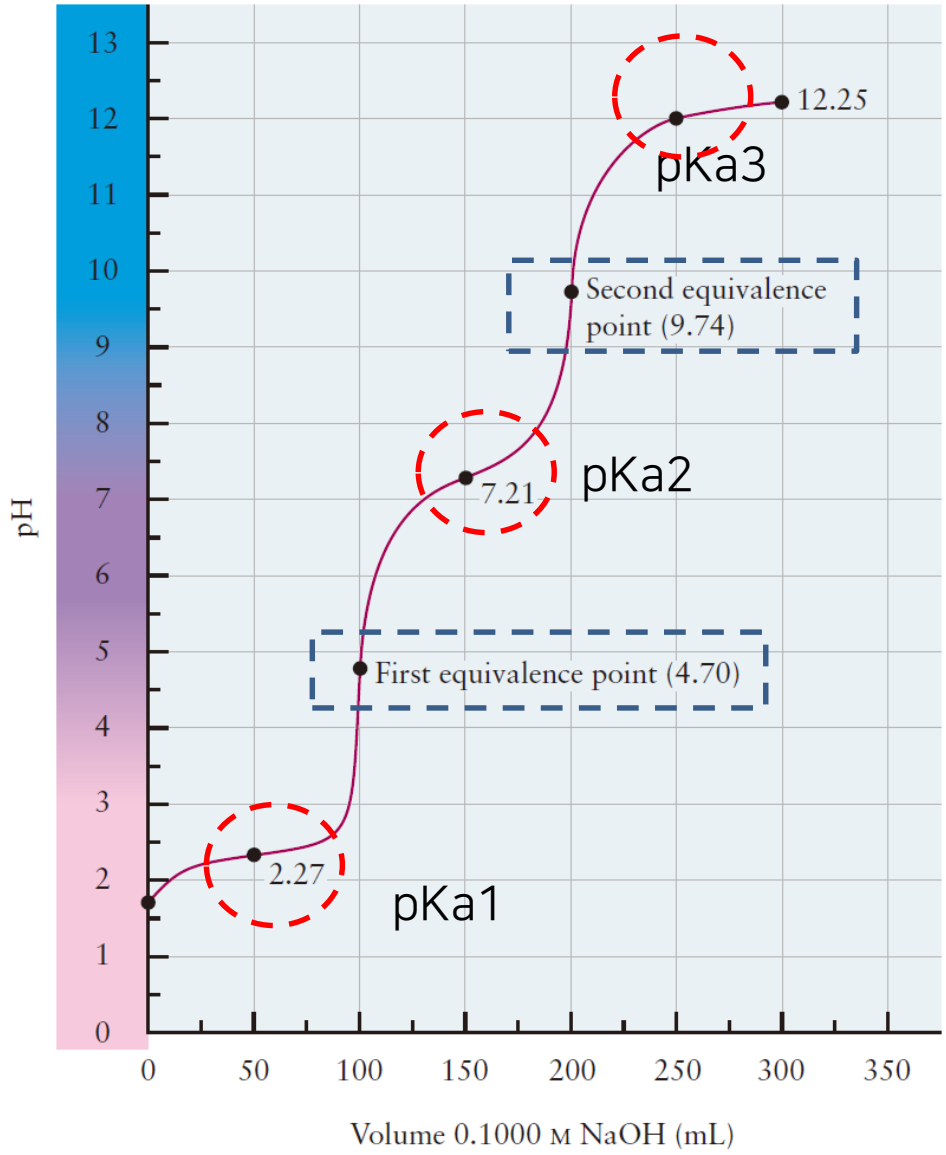
Indicator	pK_{In}	pH range of color change	Color of acid form		Color of base form
thymol blue	1.7	1.2 to 2.8	red		yellow
methyl orange	3.4	3.2 to 4.4	red		yellow
bromophenol blue	3.9	3.0 to 4.6	yellow		blue
bromocresol green	4.7	3.8 to 5.4	yellow		blue
methyl red	5.0	4.8 to 6.0	red		yellow
litmus	6.5	5.0 to 8.0	red		blue
bromothymol blue	7.1	6.0 to 7.6	yellow		blue
phenol red	7.9	6.6 to 8.0	yellow		red
thymol blue	8.9	8.0 to 9.6	yellow		blue
phenolphthalein	9.4	8.2 to 10.0	colorless		pink
alizarin yellow R	11.2	10.1 to 12.0	yellow		red
alizarin	11.7	11.0 to 12.4	red		purple

*The colors of the acid and base forms are only a symbolic representation of the actual colors.


14
12
10
8
6
4
2
0
pH
0
20.0
40.0
60.0
80.0
mL of 0.100 M NaOH added
Equivalence point (a)
Equivalence point (b)
Phenolphthalein changes color in this pH range
pKa = 9.4
Methyl red changes color in this pH range
pKa = 5.0


12
10
8
6
4
2
0
pH
0
20.0
40.0
60.0
80.0
mL of 0.100 M HCl added
Phenolphthalein changes color in this pH range.
Equivalence point
Methyl red changes color in this pH range.

12.4. Titration of a Polyprotic Acid



100.0 mL of 0.100 M H_3PO_4 is titrated with 0.100 M NaOH.

$$HPO_4^{2-}(aq) + OH^-(aq) \rightarrow PO_4^{3-}(aq) + H_2O(l)$$

$$H_2PO_4^-(aq) + OH^-(aq) \rightarrow HPO_4^{2-}(aq) + H_2O(l)$$

$$H_3PO_4(aq) + OH^-(aq) \rightarrow H_2PO_4^-(aq) + H_2O(l)$$