Mono-protic Acids and Mono-basic Bases

Acid is a substance which increase $[H_3O^+]$ in water.

Strong acids (SA) dissociate nearly completely in solutions, and SAs consumes basic groups nearly completely.

Base is a substance which decrease $[H_3O^+]$ in water.

Strong bases (SB) consume acidic hydrogens nearly completely.

Conjugate base of a strong acid is of negligible basicity.
Conjugate acid of a strong base is of negligible acidity.

Strong Acids and Bases:

Solute dissociation complete.
$pH = -\log a_{H+} \cong -\log c_{H+}$

for low μ solutions and $[SA]_0 = [H^+] = c_{H+}$ or $[SB]_0 = [OH^-]$ ($\geq 10^{-6}$M).

However if solutes concentrations (SA/SB) $\leq 10^{-6}$M,
requires systematic equilibrium calculations to calculate c_{H+}
if solute (SA/SB); 10^{-8}M - 10^{-6}M.

What is the pH of 10^{-8} M KOH or HCl?

Behavior of a compound as an acid/base is generally dependent on the environment.

$KOH \longrightarrow K^+ + OH^-$

$H_2O = H^+ + OH^-$

Setting up CBE, MBE and water dissociation equilibria;

$[H^+] + [K^+] = [OH^-]$
$[K^+] = 1\times10^{-8}$
$[H^+][OH^-] = K_w$

Concentration of $H^+ = x$
$x(x + 1\times10^{-8}) = K_w$
$x = 9.512\times10^{-8} \Rightarrow pH = 7.02$

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

$H_2O = H^+ + OH^-$

Setting up CBE, MBE and water dissociation equilibria;

$[H^+] = [Cl^-] + [OH^-]$
$[Cl^-] = 1\times10^{-8}$
$[H^+][OH^-] = K_w$

Concentration of $H^+ = x$
$x(x - 1\times10^{-8}) = K_w$
$x = 1.051\times10^{-7} \Rightarrow pH = 6.978$

Formal Concentration (Formality):

Molarity of a substance if it did not change its chemical form when dissolved.

Acetic acid; CH_3COOH 1mol/L = 1F

In reality, fraction of the acetic acid in solution dissociates,

$$CH_3COOH = CH_3COO^- + H^+$$
$$F\text{-}x \qquad x \qquad x$$

Thus the actual molarity of UNDISSOCIATED acetic acid is less that F mol/L.

Weak Acids and Bases:

Strengths of weak acids/bases shown by their K values.
(few strong acids encountered)

acid dissociation K_a:

$HA + H_2O \rightleftharpoons A^- + H_3O^+$
$F\text{-}x \qquad x \qquad x$

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

$$x^2 - K_a(F - x) = 0$$
$$x^2 - K_aF = 0 \qquad x << F$$
$$\boxed{[H^+] = x = \sqrt{K_aF}}$$

stronger WA HA ~ weaker A^-
(acid) (conj. Base)

$-\log K_a = pK_a$

Base constant K_b;

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

$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

$-\log K_b = pK_b$

$K_{a,HA}K_{b,A^-} = K_w$

$K_aK_b = K_w$

For aqueous solutions;

$2\,H_2O \rightleftharpoons OH^- + H_3O^+$

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

$$\boxed{\begin{aligned} K_{a,HA}K_{b,A^-} &= K_w \\ K_aK_b &= K_w \end{aligned}}$$

Conjugate bases of WA are weak bases, the strength of which related to the acid strength of WA.

Composition of A^- (salt; NaA) solutions:

$A^- + H_2O = HA + OH^-$

F initial concentration

(F - x) x x equilibrium concentration

$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{x^2}{F - x}$$ solve for x;

$x^2 - K_b(F - x) = 0$

$x^2 - K_bF = 0$ $x << F$

$$\boxed{[OH^-] = x = \sqrt{K_bF}}$$

$$[H^+] = \frac{K_w}{\sqrt{K_bF}}$$

Composition of fully protonated HA solutions:

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

F initial concentration

(F - x) x x equilibrium concentration

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{F - x}$$ solve for x;

Fractional dissociation of HA α_i:

$$\alpha_A = \frac{[A^-]}{[HA]+[A^-]} = \frac{x}{F_{HA}} = \frac{[A^-]}{F} = \alpha_1$$ Fractional compositions

$$\alpha_{HA} = \frac{[HA]}{[HA]+[A^-]} = \frac{[HA]}{F} = \frac{F_{HA} - x}{F_{HA}} = 1 - \frac{x}{F_{HA}} = 1 - \alpha_A = \alpha_0$$

$1 - \alpha_1 = \alpha_0$ $[HA] = \alpha_0 F_{HA}$

$\alpha_1 + \alpha_0 = 1$ $[A^{-1}] = \alpha_1 F_{HA}$

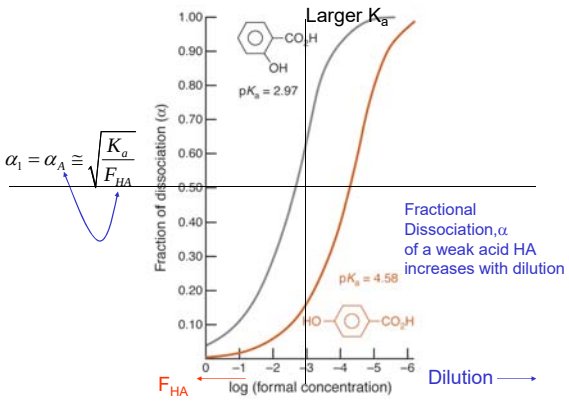
Note: F = Total concentration of all species containing the moiety A.

$$\alpha_A = \frac{[A^-]}{[HA]+[A^-]} = \frac{x}{F_{HA}} = \frac{[A^-]}{F} = \alpha_1$$

$$K_a = \frac{x^2}{F_{HA} - x} \Rightarrow x \cong \sqrt{K_aF_{HA}}$$

Fractional composition $\alpha_A = \frac{\sqrt{K_aF_{HA}}}{F_{HA}} = \sqrt{\frac{K_a}{F_{HA}}}$

Although the use of the approximations greatly simplifies the algebra, care must be exercised in its use. Approximations are valid if the approximation yields a value for $x \leq 0.05 \times$formal concentration.



Fractional Association of Base B (or A^- from NaA):

$B + H_2O = BH^+ + OH^-$

F-x x x

$$\alpha_B = \frac{[B]}{[BH^+]+[B]} = \frac{[B]}{F_B}$$

Fractional compositions

$$\alpha_{BH} = \frac{[BH^+]}{[BH^+]+[B]} = \frac{[BH^+]}{F_B}$$

Buffers

A mixture of a ($HA + A^-$) or ($B + BH^+$) forms a (pH) **buffer**.

A buffer solution is a solution which resists pH changes due to the addition of *small* amounts acids or bases.

Such small additions do change the pH of the buffer, but only by a very small amount.

Buffer action:

Mixture of ($HA + A^-$) or ($B + BH^+$) will consume any *small* (foreign) amount of OH^- or H^+ added to it, thereby maintain the $[H^+]$ *nearly constantly*.

Approximate calculation of buffer pH:

Consider acid dissociation, expressed as;

$$pH = pK_{a,HA} + \log\frac{[A]}{[HA]} \leftarrow \frac{[base]}{[acid]}$$

(pK_a of HA)

HA refers to the weak acid, it can be BH^+.

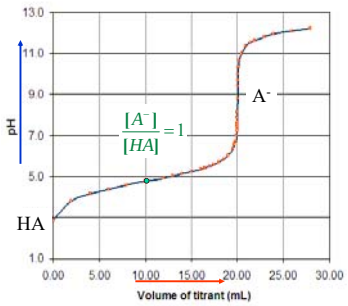
$$pH = pK_w - pK_{b,B} + \log\frac{[B]}{[BH^+]} \leftarrow \frac{[base]}{[acid]}$$

(pK_a of BH^+)

Henderson-Hasselbach Equation

$$pH = pK_{a,HA} + \log\frac{[A]}{[HA]}$$

(pK_a of HA)

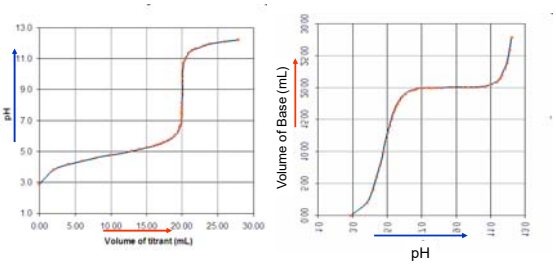


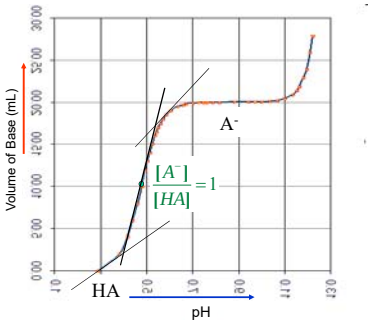
Buffer capacity β:

The ability of a buffer solution to resist 'foreign' acids/bases: depends on the number of molecules of HA and A^- or B and BH^+ in the mixture *and* the ratio $[A^-]/[HA]$ or $[B]/[BH^+]$.

β Increases as the above ratio(s) reaches unity.

β highest at [HA]=[A-]





$$\beta = \frac{dC_{OH^-}}{dpH} = -\frac{dC_{H^+}}{dpH}$$

Buffer capacity β:

The ability of a buffer solution to *resist* 'additional' acids/bases: depends on the number of molecules of HA and A^- or B and BH^+ in the mixture and the ratio $[A^-]/[HA]$ or $[B]/[BH^+]$.

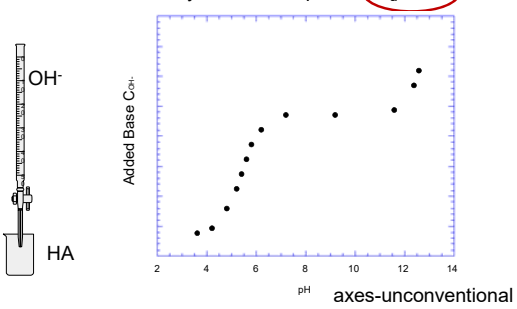
β Increases as the above ratio(s) reaches unity.

Buffer capacity - Definition: The number of *mmol* of a strong acid/base required to cause a unit change in pH per *mL* of buffer solution.

$$\beta = \frac{dC_{OH^-}}{dpH} = -\frac{dC_{H^+}}{dpH}$$

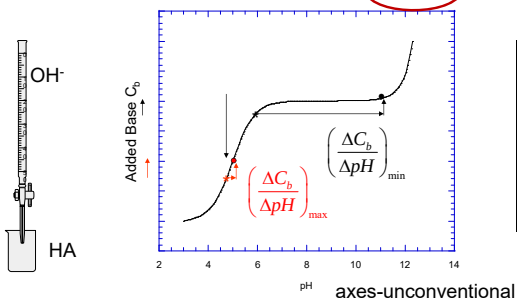
β highest at $[HA]=[A^-]$

For an HA/A^- buffer system; Example for pK_a=5.00



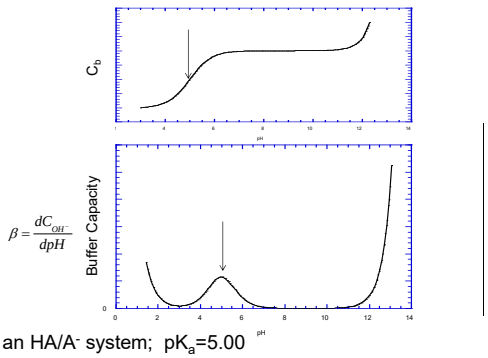
axes-unconventional

For an HA/A^- buffer system; Example for pK_a=5.00



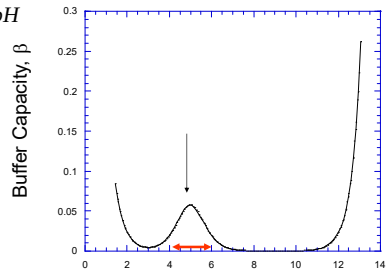
axes-unconventional

The *variation* of pH of a buffer @ pH ~ pK is the *lowest*.



For an HA/A^- system; pK_a=5.00

$$\beta = \frac{dC_{OH^-}}{dpH}$$



For an HA/A$^-$ system; pK_a=5.00

Useful (rule of thumb) buffer range of a buffer of WA is $pK_a \pm 1$.

Buffer capacity is highest at pH = pK and at that point [HA]=[A] and are large.

When pH = pK for a mixture of a conjugate pair concentrations are equal.

To make a high capacity buffer of pH ≅ X, pick a system where pK ≅ pH desired of the buffer and the conjugate pair concentrations are high and equal.

Buffer Preparation:

Buffers can be prepared by (a) adding a strong base (OH^-) to a weak acid (HA) or by (b) adding a strong acid (H^+) to a weak base.

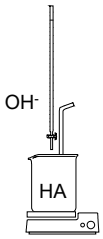
Either procedure will produce mixture of a weak acid and it's conjugate base mixture.

See text.

Note: $pH = pK_{a,HA} + \log\frac{[A]}{[HA]}$ approximation !!

pK_a of HA

and K_a = f(T)



To prepare a buffer of desired pH choose a WA with pK_a close to the desired buffer pH and adjust the pH adding strong acid/base as needed.

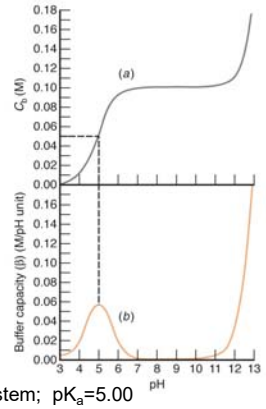
Useful (rule of thumb) buffer range of a buffer of WA is $pK_a \pm 1$.

amounts to $0.1 < [A]/[HA] < 10$; @ [A]/[HA] ≅ 1, best

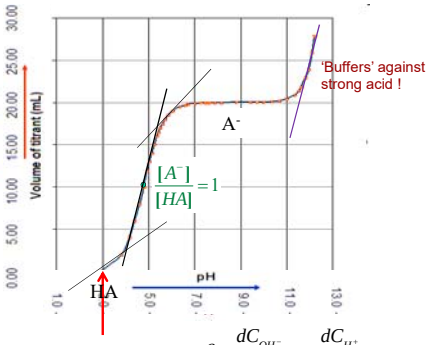
For $0.1 > [A]/[HA] > 10$ 'the resistance to' would be only to base and acid additions, respectively – not a 'buffer' !!.

Note: Buffer pH depends on temperature and ionic strength μ.

At high concentrations of acids and bases or extreme pH values the analytical concentrations of species are significantly different from formal concentrations. Thus HHE loses it's validity in such regions.



For an HA/A$^-$ system; pK_a=5.00



$$\beta = \frac{dC_{OH^-}}{dpH} = -\frac{dC_{H^+}}{dpH}$$

Table 10-2 Structures and pK_a values for commonly used buffers[a, b]

Name	Structure	pK_a (~25°C)	Formula mass
Phosphoric acid	H_3PO_4	2.15 (pK_1)	97.995
Piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) (PIPES)	$^-O_3SCH_2CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_2SO_3^-$	2.67 (pK_1)	302.370
Citric acid	$HO_2CCH_2\overset{OH}{\overset{\vert}{C}}(CO_2H)CH_2CO_2H$	3.13 (pK_1)	192.124
Piperazine-*N*,*N*′-bis(3-propanesulfonic acid) (PIPPS)	$^-O_3SCH_2CH_2CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_2CH_2SO_3^-$	3.79 (pK_1)	330.424
Piperazine-*N*,*N*′-bis(4-butanesulfonic acid) (PIPBS)	$^-O_3SCH_2CH_2CH_2CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_2CH_2CH_2SO_3^-$	4.29 (pK_1)	358.477
N,*N*′-Diethylpiperazine dihydrochloride (DEPP·2HCl)	$CH_3CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_3 \cdot 2Cl^-$	4.48 (pK_1)	207.100
Citric acid	$H_3(\text{citrate})^+$	4.76 (pK_2)	192.124
Acetic acid	CH_3CO_2H	4.76	60.052
N,*N*′-Diethylethylenediamine-*N*,*N*′-bis(3-propanesulfonic (DESPEN)	$^-O_3SCH_2CH_2CH_2\overset{+}{N}HCH_2CH_2H\overset{+}{N}CH_2CH_2CH_2SO_3^-$ (CH_2CH_3 on both N)	5.62 (pK_1)	360.493
2-(*N*-Morpholino)ethanesulfonic acid (MES)	$O\langle\overset{+}{N}HCH_2CH_2SO_3^-$	6.15	195.238

Table 10-2 (continued) Structures and pK_a values for commonly used buffers[a, b]

Name	Structure	pK_a (~25°C)	Formula mass
Citric acid	$H(\text{citrate})^{2-}$	6.40 (pK_3)	192.124
N,*N*,*N*′,*N*′-Tetraethylethylenediamine dihydrochloride (TEEN·2HCl)	$(CH_3CH_2)_2\overset{+}{N}HCH_2CH_2H\overset{+}{N}(CH_2CH_3)_2 \cdot 2Cl^-$	6.58 (pK_1)	245.232
N-2-Acetamidoiminodiacetic acid (ADA)	$H_2\overset{O}{\overset{\Vert}{N}}CH_2\overset{+}{N}H(CH_2CO_2^-)(CH_2CO_2H)$	6.60	190.154
1,3-Bis[tris(hydroxymethyl)methylamino]propane hydrochloride (BIS-TRIS propane·HCl)	$(HOCH_2)_3C\overset{+}{N}H_2(CH_2)_3NHC(CH_2OH)_3 \cdot Cl^-$	6.80	318.795
Piperazine-*N*,*N*′-bis(2-ethanesulfonic acid) (PIPES)	$^-O_3SCH_2CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_2SO_3^-$	6.80 (pK_2)	302.370
N-2-Acetamido-2-aminoethanesulfonic acid (ACES)	$H_2\overset{O}{\overset{\Vert}{N}}CH_2\overset{+}{N}H_2CH_2CH_2SO_3^-$	6.85	182.199
3-(*N*-Morpholino)-2-hydroxypropanesulfonic acid (MOPSO)	$O\langle\overset{+}{N}HCH_2\overset{OH}{\overset{\vert}{C}}HCH_2SO_3^-$	6.93	225.264

a. The protonated form of each molecule is shown. Acidic hydrogen atoms are shown in bold type. Several buffers in this table are widely used in biomedical research because of their relatively weak binding of metal ions and physiologic inertness (C. L. Bering, *J. Chem. Ed.* **1987**, *64*, 803). However, the buffers ADA, BICINE, ACES, and TES have greater metal-binding ability than formerly thought (R. Nakon and C. R. Krishnamoorthy, *Science* **1983**, *221*, 749). Lutidine buffers for the pH range 3 to 8 with limited metal-binding power have been described by U. Bips, H. Elias, M. Haurüder, G. Kleinhans, S. Pfeifer, and K. J. Wannowius, *Inorg. Chem.* **1983**, *22*, 3862.

b. Temperature and ionic strength dependence of pK_a can be found for the following buffers in the following references: HEPES—D. Feng, W. F. Koch, and Y. C. Wu, *Anal. Chem.* **1989**, *61*, 1400; MOPSO—Y. C. Wu, P. A. Berezansky, D. Feng, and W. F. Koch, *Anal. Chem.* **1993**, *65*, 1084; ACES and CHES—R. N. Roy, J. Bice, J. Greer, J. A. Carlsten, J. Smithson, W. S. Good, C. P. Moore, L. N. Roy, and K. M. Kuhler, *J. Chem. Eng. Data* **1997**, *42*, 41; TEMN, TEEN, DEPP, DESPEN, PIPES, PIPPS, PIPBS, MES, MOPS, and MOBS—A. Kandegedara and D. B. Rorabacher, *Anal. Chem.* **1999**, *71*, 3140. This last set of buffers was specifically developed for low metal-binding ability (Q. Yu, A. Kandegedara, Y. Xu, and D. B. Rorabacher, *Anal. Biochem.* **1997**, *253*, 50).

Table 10-2 (continued) Structures and pK_a values for commonly used buffers[a, b]

Name	Structure	pK_a (~25°C)	Formula mass
N,*N*-Bis(2-hydroxyethyl)glycine (BICINE)	$(HOCH_2CH_2)_2\overset{+}{N}HCH_2CO_2^-$	8.35	163.172
Glycylglycine	$H_3\overset{+}{N}CH_2\overset{O}{\overset{\Vert}{C}}NHCH_2CO_2^-$	8.40	132.118
Piperazine-*N*,*N*′-bis(4-butanesulfonic acid) (PIPBS)	$^-O_3SCH_2CH_2CH_2CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_2CH_2CH_2SO_3^-$	8.55 (pK_2)	358.477
N,*N*′-Diethylpiperazine dihydrochloride (DEPP·2HCl)	$CH_3CH_2\overset{+}{N}H\ H\overset{+}{N}CH_2CH_3 \cdot 2Cl^-$	8.58 (pK_2)	207.100
N,*N*′-Diethylethylenediamine-*N*,*N*′-bis(3-propanesulfonic (DESPEN)	$^-O_3SCH_2CH_2CH_2\overset{+}{N}HCH_2CH_2H\overset{+}{N}CH_2CH_2CH_2SO_3^-$ (CH_2CH_3 on both N)	9.06 (pK_2)	360.493
Boric acid	$B(OH)_3$	9.24 (pK_1)	61.833
Cyclohexylaminoethanesulfonic acid (CHES)	$\langle\overset{+}{N}H_2CH_2CH_2SO_3^-$	9.39	207.292
N,*N*,*N*′,*N*′-Tetraethylethylenediamine dihydrochloride (TEEN·2HCl)	$(CH_3CH_2)_2\overset{+}{N}HCH_2CH_2H\overset{+}{N}(CH_2CH_3)_2 \cdot 2Cl^-$	9.88 (pK_2)	245.232
3-(Cyclohexylamino)propanesulfonic acid (CAPS)	$\langle\overset{+}{N}H_2CH_2CH_2CH_2SO_3^-$	10.40	221.318
N,*N*,*N*′,*N*′-Tetraethylmethylenediamine dihydrochloride (TEMN·2HCl)	$(CH_3CH_2)_2\overset{+}{N}HCH_2H\overset{+}{N}(CH_2CH_3)_2 \cdot 2Cl^-$	11.01 (pK_2)	231.206
Phosphoric acid	HPO_4^{2-}	12.15 (pK_3)	97.995
Boric acid	$OB(OH)_2^-$	12.74 (pK_2)	61.833

Calculation of α_{HA} and α_A of a HA/A equilibrium system

In any aqueous solution containing HA, the ion A^- has to be present, and vice versa. The concentration and therefore the fractional composition is dependent on the $[H^+]$ in the solution. In general, calculation of concentrations and fractions require the solution of a set of equations that relate the concentrations.

$$\longrightarrow \quad HA = H^+ + A^- \qquad K_a$$

$$\longrightarrow \quad H_2O = H^+ + OH^- \qquad K_w$$

In general use the expressions for K's above, with mass balance and charge balance equations to solve for actual $[H^+]$, $[OH^-]$, $[HA]$ and $[A^-]$, with F_{HA} calculate α values.

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

$$[HA] = \frac{[H^+]F}{[H^+]+K_a} \quad \textit{by rearrangement}$$

$$\alpha_{HA} = \frac{[HA]}{[HA]+[A^-]} = \frac{[HA]}{F} = \boxed{\frac{[H^+]}{[H^+]+K_a}}$$

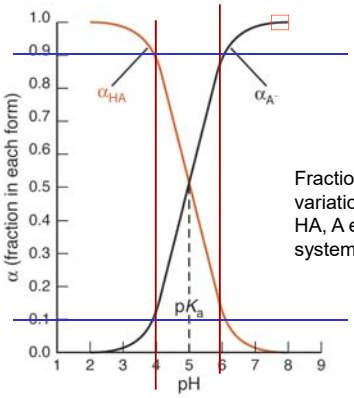
similar approach $\alpha_A = \dfrac{[A^-]}{[HA]+[A^-]} = \dfrac{[A^-]}{F} = \boxed{\dfrac{K_a}{[H^+]+K_a}}$

next page

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

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

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



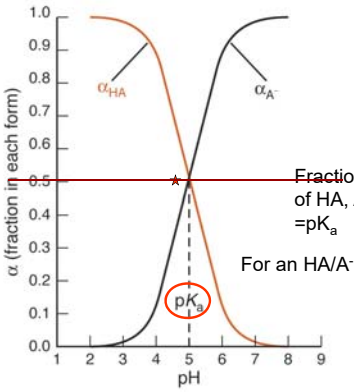
Fractional composition variation with pH of HA, A equilibrium system

α_i plots shows the fraction of any given protic species in solution.

For a buffer of pH 8, from HA/A^- system; pK_a= 5, the species represented by the fractional composition curve is present predominantly the A^- protic form.

If a buffer has a pH=4, then the species represented by the curves is present as ~10 % A^- and ~90% HA.

No matter which form of HA we add, so long as the buffer controls the pH, the composition is dictated by the pH and the α_i plots.



Fractional composition of HA, A equal at pH $=pK_a$

For an HA/A^- system; pK_a=5.00