CHEM 116 – Honors and Majors General and Analytical Chemistry I

3 Exams, 9 Quizzes, 10 Labs, 12 Weeks HWK - 865 points (1245 in course)

EIII: AVE = 95 (63%) Range: 36 - 146

EII: AVE = 106 (71%)

EI: AVE = 87 (58%)

Q1	6.0	Q5	6.6	Q8	6.4
Q3	4.2	Q6	6.2	Q9	8.3
Q4	7.8	Q7	6.1	Q10	4.9

E1	19.4	E7	13.0	4-4	15.9
E2	17.3	SP	17.7	E8	14.8
L3	18.4	L5	17.9	10.5	
E5	16.3				

class average 71.2%

GPA 3.1

Class Averages

EXAM	288	64%
QZ	57	63%
LAB	150	75%
HWK	102	82%

Course Grade Estimate

A	75%
B	65%
C	50%
D	40%

Polyprotic Acids and Bases – Intermediate Form

Consider a diprotic acid

$$H_2A(aq) + H_2O(l) \iff H_3O^+(aq) + HA^-(aq)$$ **base**

acid $$HA^-(aq) + H_2O(l) \iff H_3O^+(aq) + A^{2-}(aq)$$

If H_2A is a weak acid its conjugate base, HA^- is amphoteric. It can act as an acid (second equation) or as a base (reverse of first reaction). What is the pH of a solution of HA^- such as NaHA?

Exact Treatment (H pp. 216 - 218) for NaHA

species: H_2A, HA^-, A^{2-}, H^+, OH^-, Na^+ => need 6 equations

charge balance: $[H^+] + [Na^+] = [HA^-] + 2[A^{2-}] + [OH^-]$

material balance: $M_{NaHA} = [Na^+] = [H_2A] + [HA^-] + [A^{2-}]$

equilibria: $K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$ $\quad K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$ $\quad K_w = [H^+][OH^-]$

One can show that

$$[H^+]^2 = \frac{K_{a1}K_{a2}[HA^-] + K_{a1}K_w}{K_{a1} + [HA^-]}$$

exact relation

Polyprotic Acids and Bases – Intermediate Form

$$[H^+]^2 = \frac{K_{a1}K_{a2}[HA^-] + K_{a1}K_w}{K_{a1} + [HA^-]}$$

1. when the major species is HA^- => $[HA^-] = M_{HA^-}$ (F_{HA^-})

$$\approx \frac{K_{a1}K_{a2}M_{NaHA} + K_{a1}K_w}{K_{a1} + M_{NaHA}} = \frac{K_{a1}(K_{a2}M_{NaHA} + K_w)}{K_{a1} + M_{NaHA}}$$

2. often $K_w \ll K_{a2}M_{NaHA}$

$$\approx \frac{K_{a1}K_{a2}M_{NaHA}}{K_{a1} + M_{NaHA}}$$

3. and $K_{a1} \ll M_{NaHA}$ this often needs to be checked

$$\approx \frac{K_{a1}K_{a2}M_{NaHA}}{M_{NaHA}} = K_{a1}K_{a2}$$

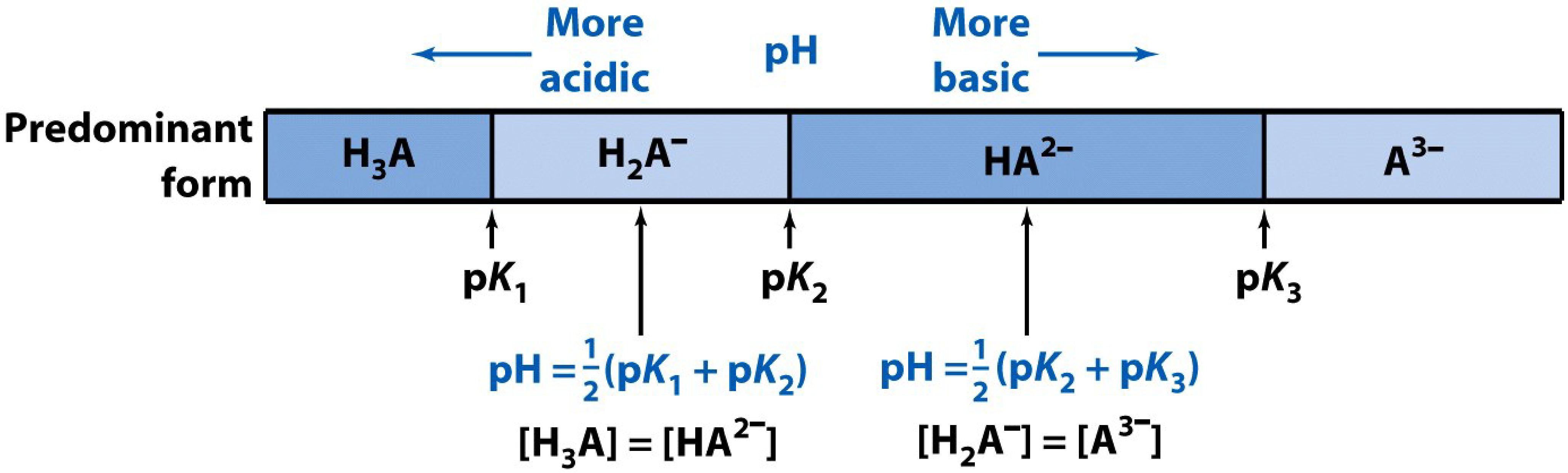
or

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

REVIEW FROM FRIDAY

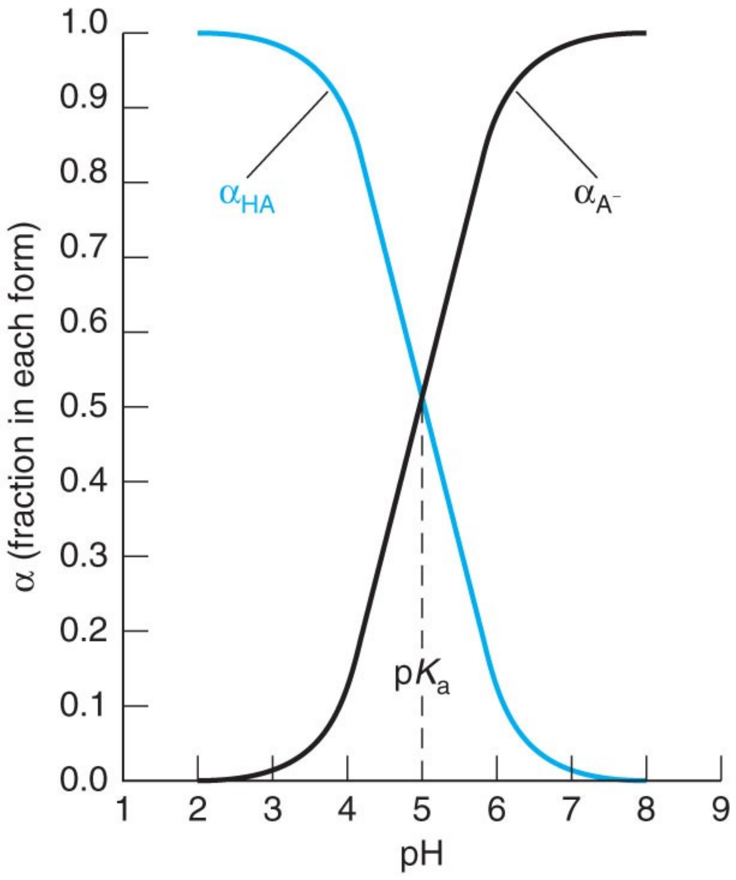
Polyprotic Acids and Bases – Predominant Species

$$pH = pK_a + \log_{10} \frac{[B]}{[A]}$$

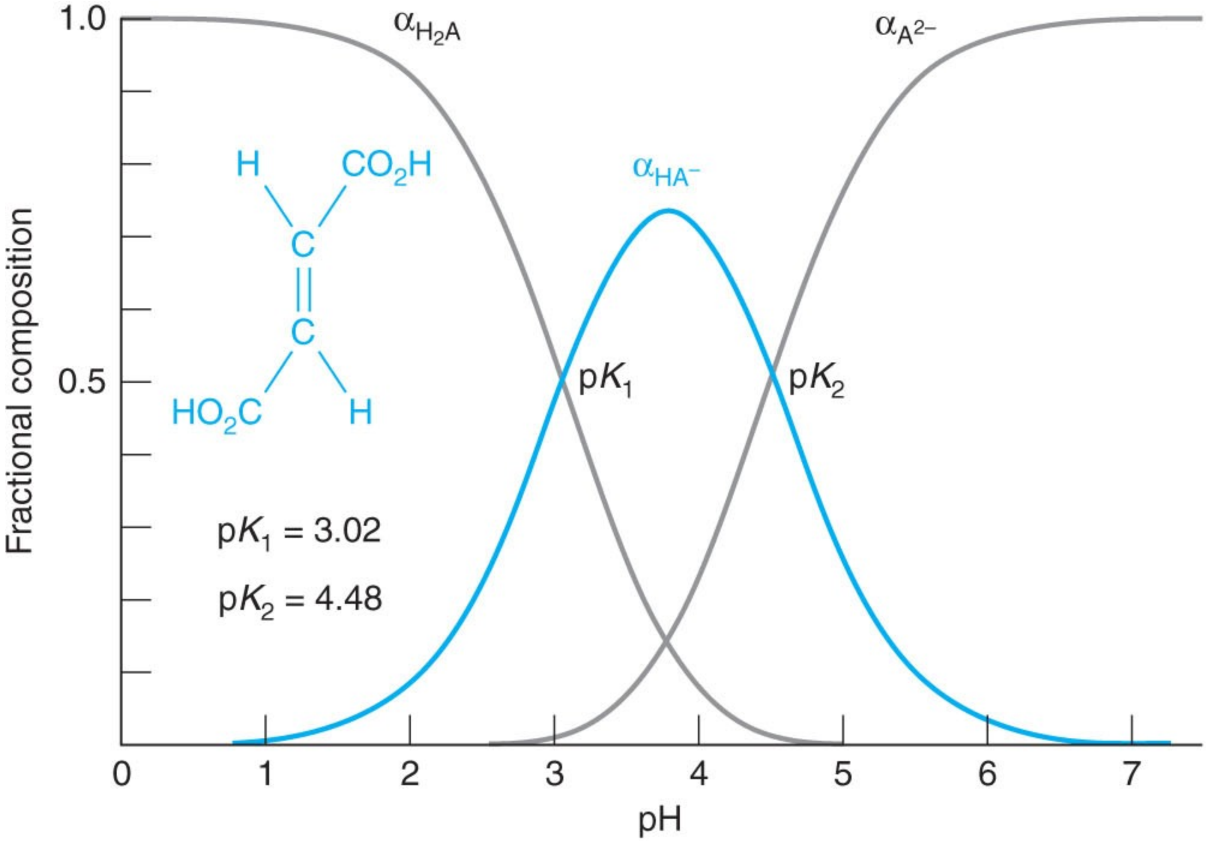


H_3PO_4	2.148	7.197	12.374

Fractional Composition Diagrams, α versus pH



monoprotic acid, HA



diprotic acid, H_2A

Titrations

H Ch 11

FIND EQUIVALENCE POINT FIRST

CORRECT MOLARITY AS TITRANT IS ADDED

11-1 Strong Acid/Base
11-2 Weak Acid with Strong Base
11-3 Weak Base with Strong Acid
11-4 Polyprotic Titrations

no quiz next week

homework for week 14,15 due dates next Wednesday and Friday

lab notebooks due next Wednesday in discussion

Acid-Base Titrations

"Learn to recognize buffers! They lurk in every corner of acid-base chemistry."

Acid-Base Titrations

Solution of a base of known concentration is added to an acid of unknown concentration (or acid of known concentration added to a base of unknown concentration)

titrant
titration curve
equivalence point half-equivalence point

pH > 7 titrating weak acid
pH = 7 titrating strong acid or base
pH < 7 titrating weak base

endpoint

Acid-Base Titrations - Strong

strong acid or strong base titration overview

classic Arrhenius neutralization reaction characterized by

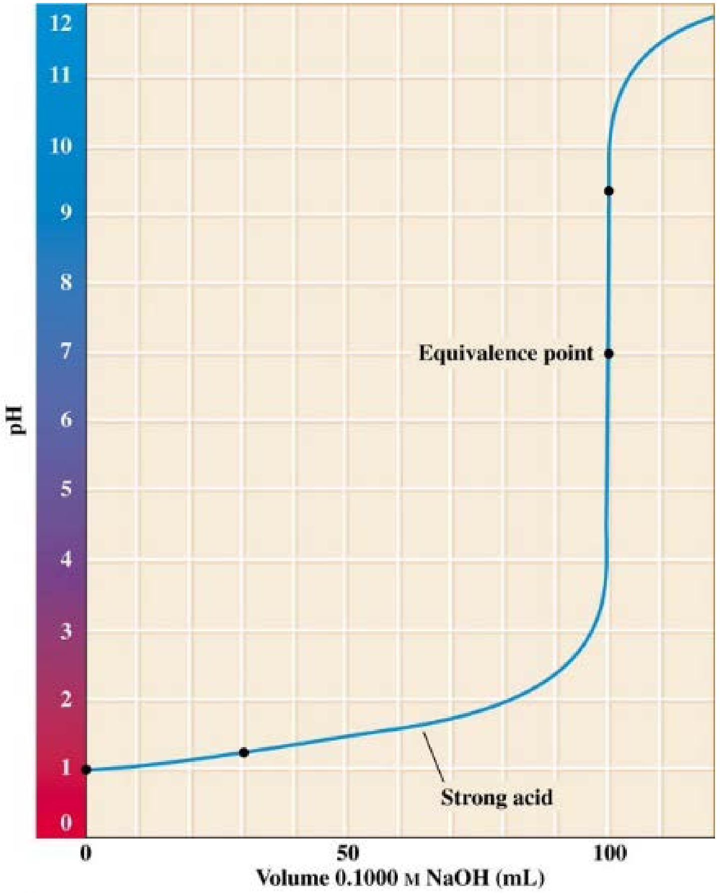
strong acid (base):

strong base (acid) titrant:

total ionic equation:

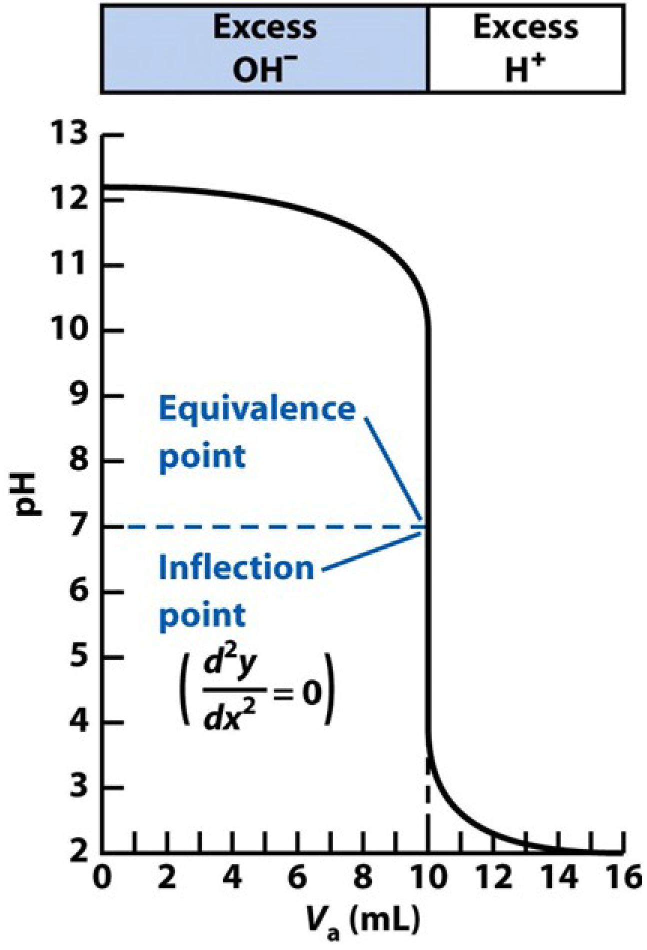
net ionic equation (what is *K*?):

titration curve – one inflection point (equivalence point)



Strong Base Titrations

EX 1. Determine the pH for titration of 50.00 mL of 0.02000 M KOH with 0.1000 M HBr.



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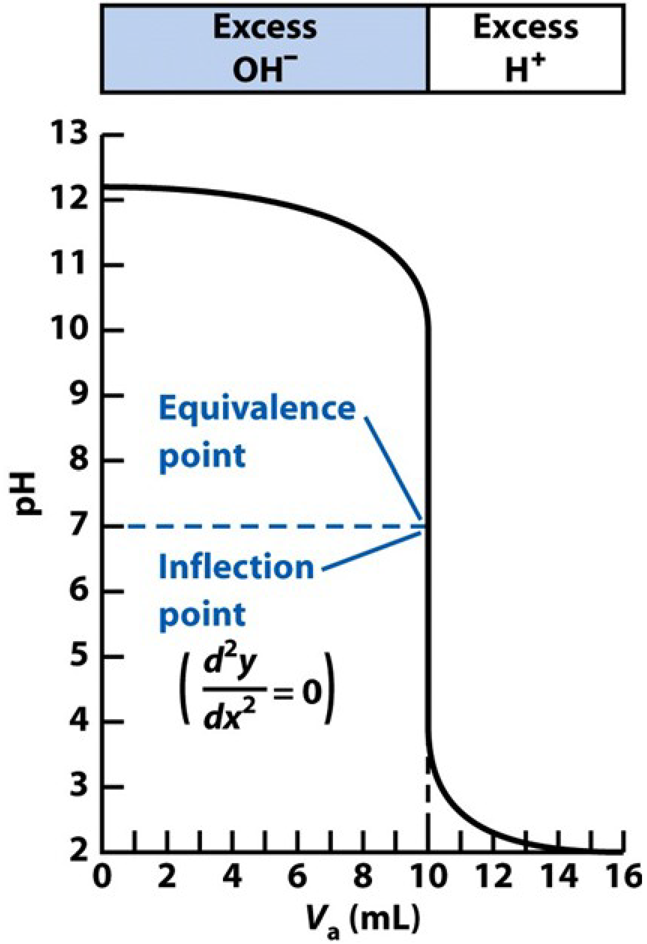

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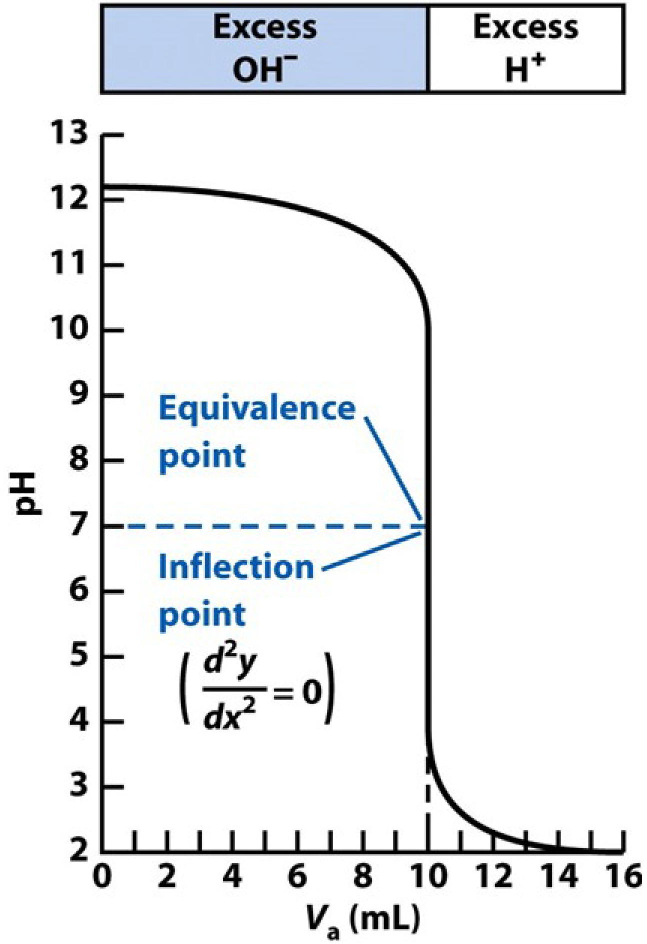

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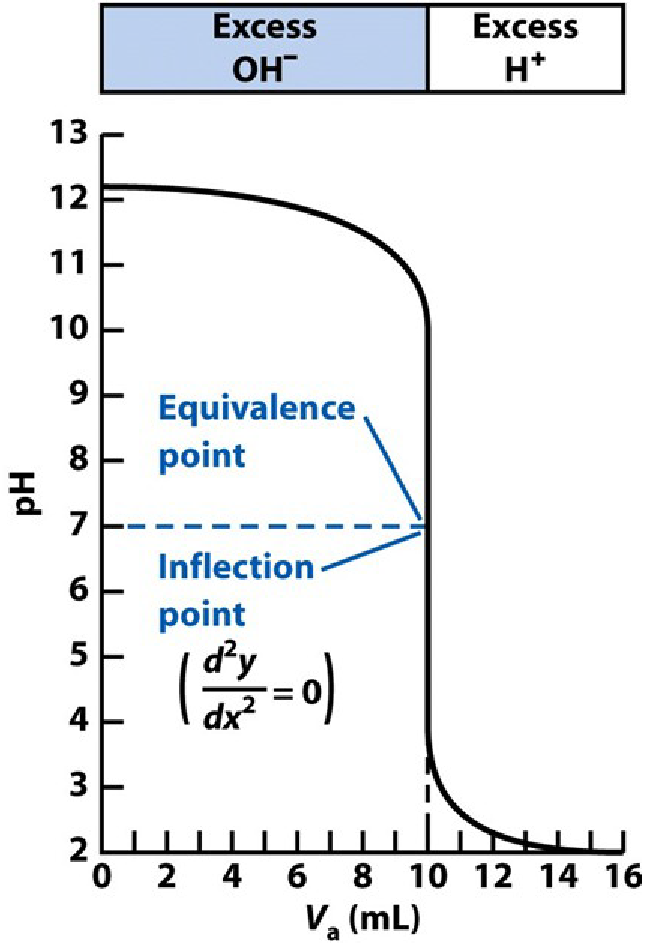

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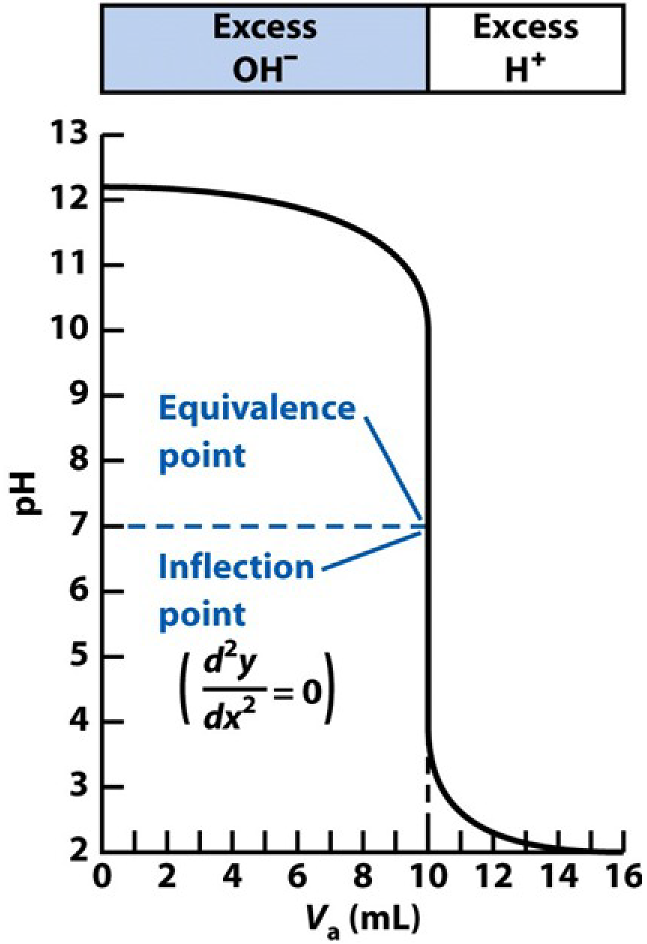
pH = 13.9956 + log (0.02000) = 12.2966 => **12.297**



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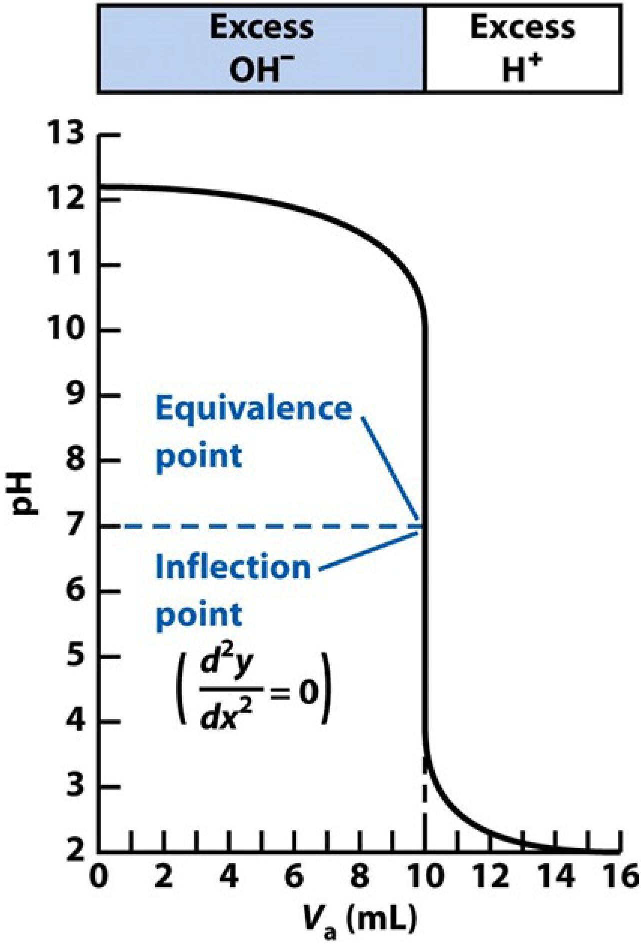

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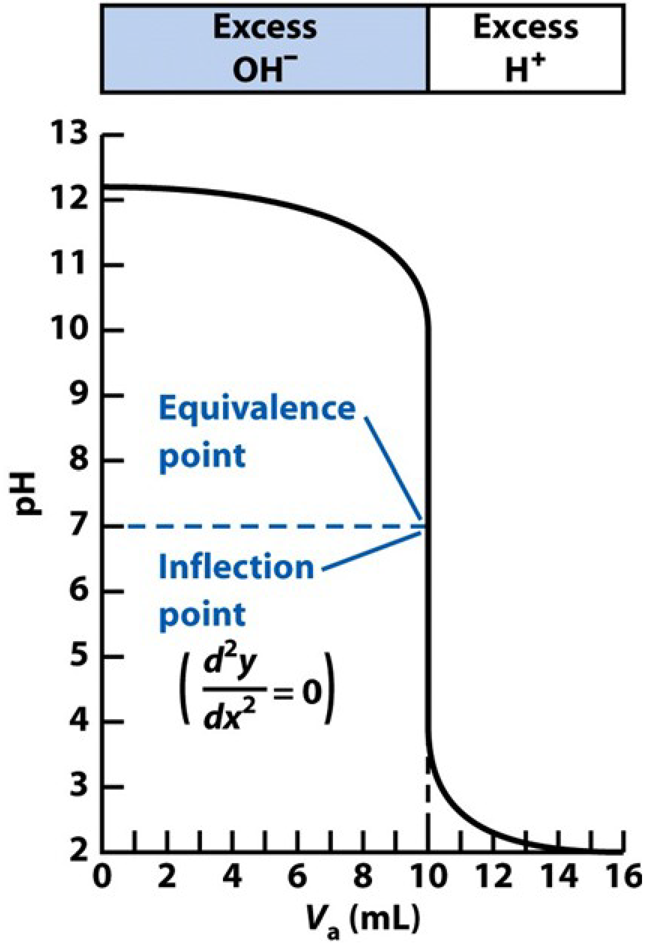
pH = 13.9956 + log {[50(0.02) - 3(0.1)] / 53} = **12.116**



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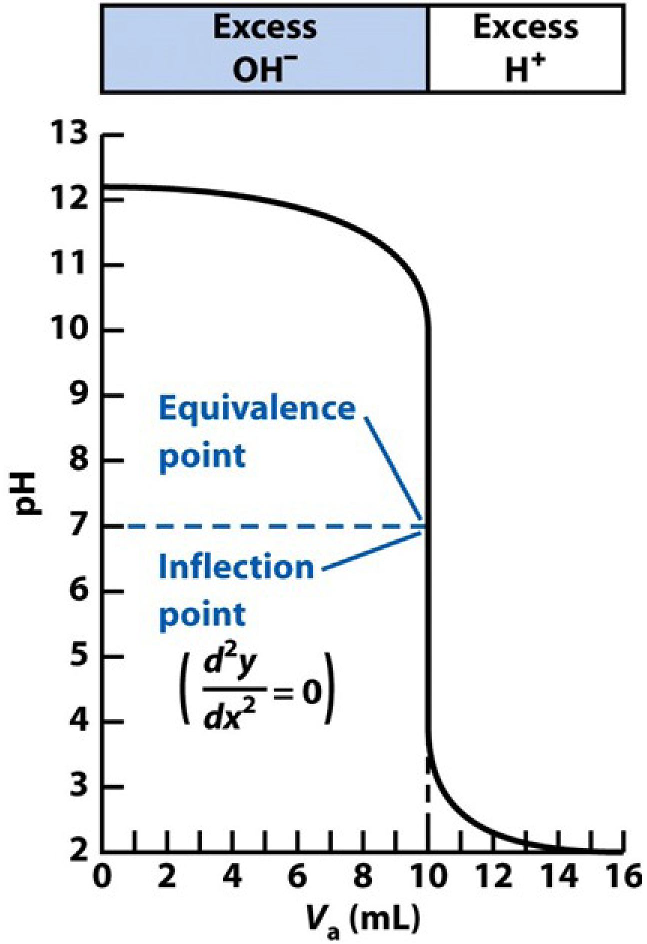

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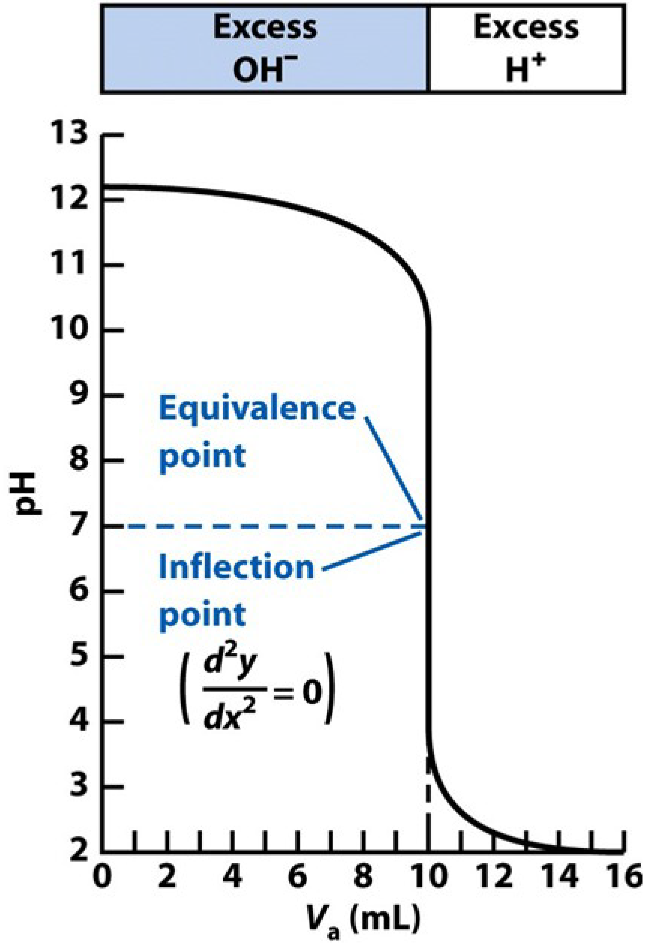
$K_w = [H^+]^2 \Rightarrow [H^+] = \sqrt{K_w} \Rightarrow pH = ½\, pK_w = 13.9956/2 =$ **6.998**



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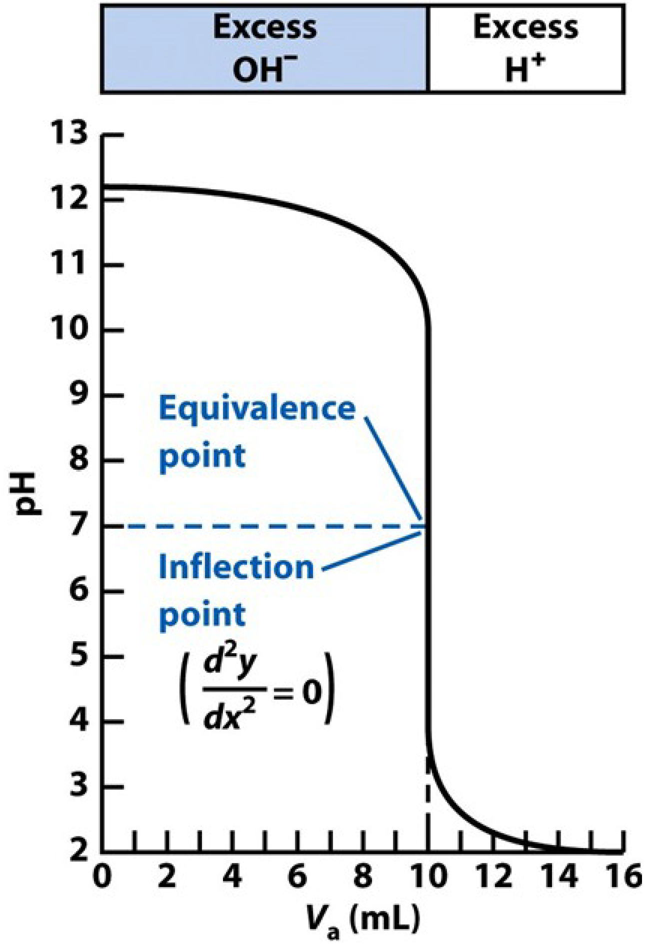
d) when 10.50 mL of HBr is added excess H^+



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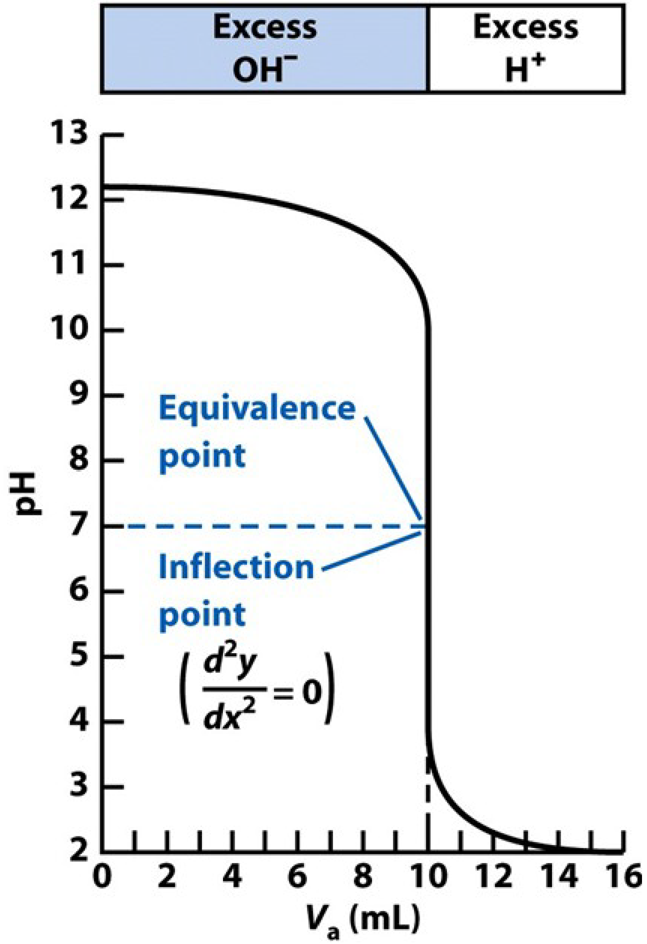
d) when 10.50 mL of HBr is added excess H^+

pH = -log {[(10.5)(0.1) - 50(0.02)] / **60.5**} = 3.0827 => **3.083**

pH = pK_w – pOH, pK_w = -log (1.01×10^{-14}) = 13.9956



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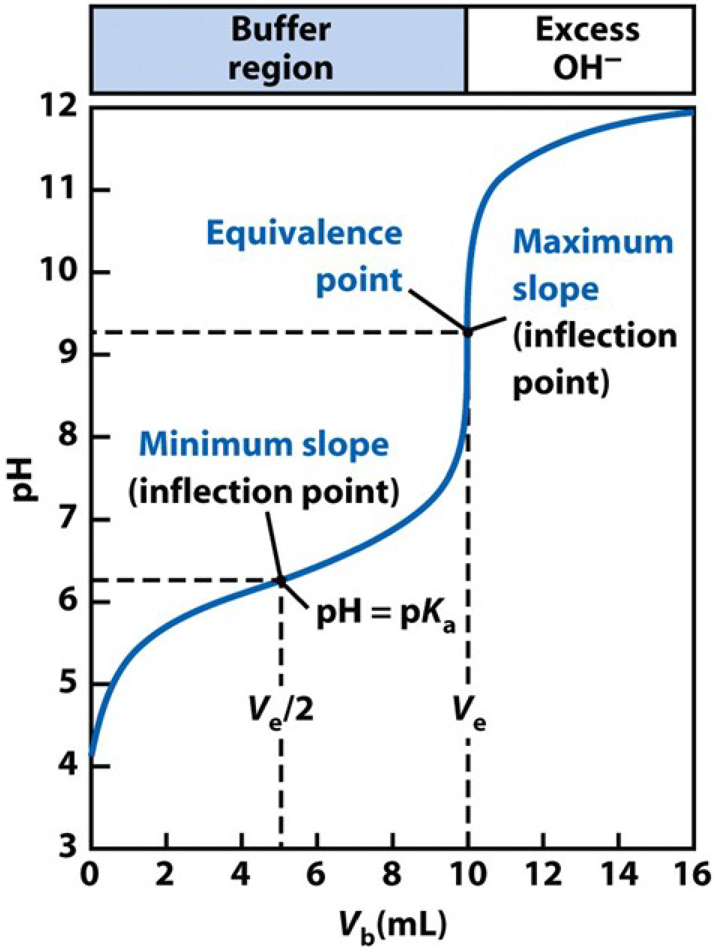

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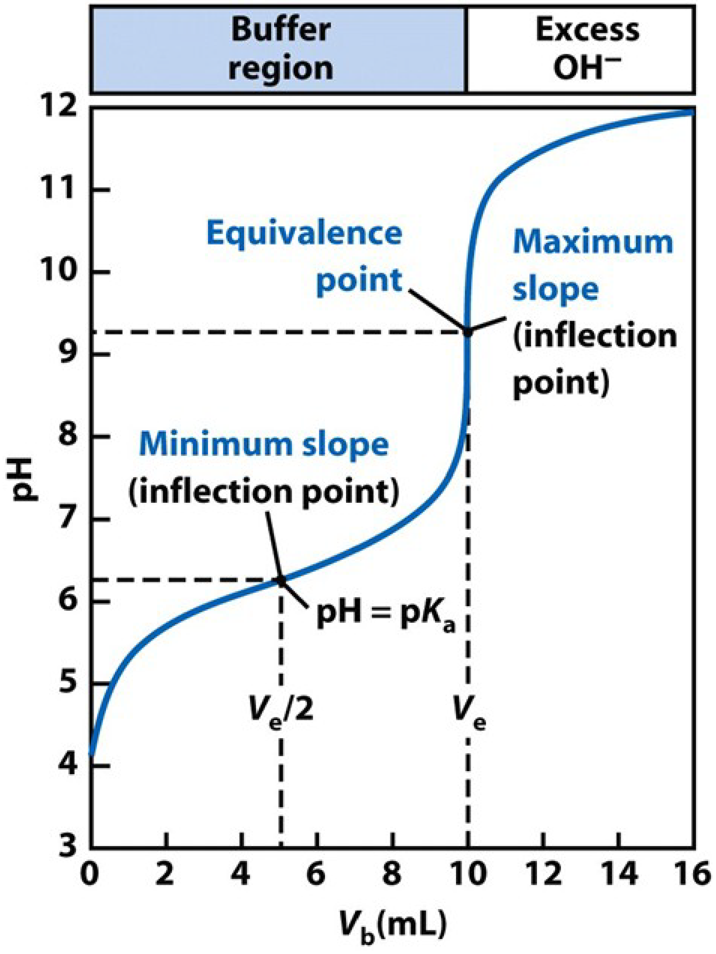

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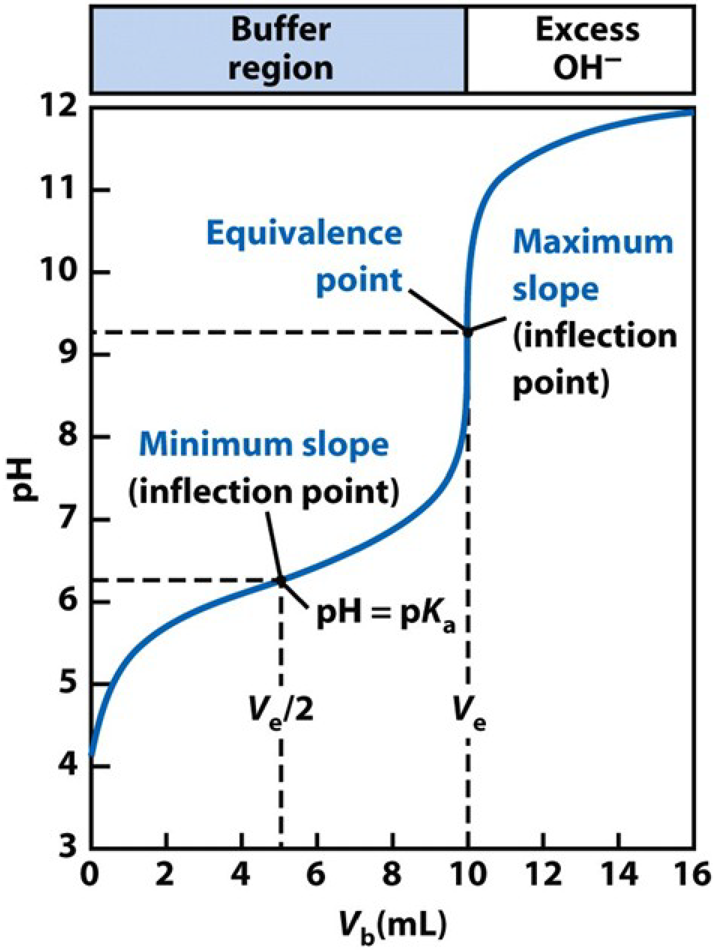

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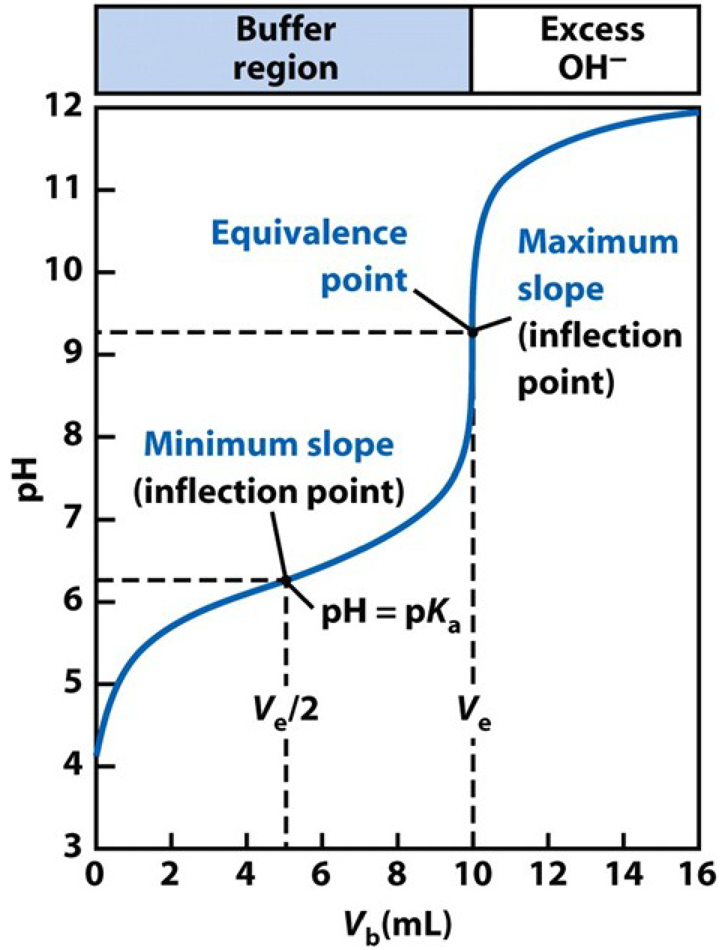

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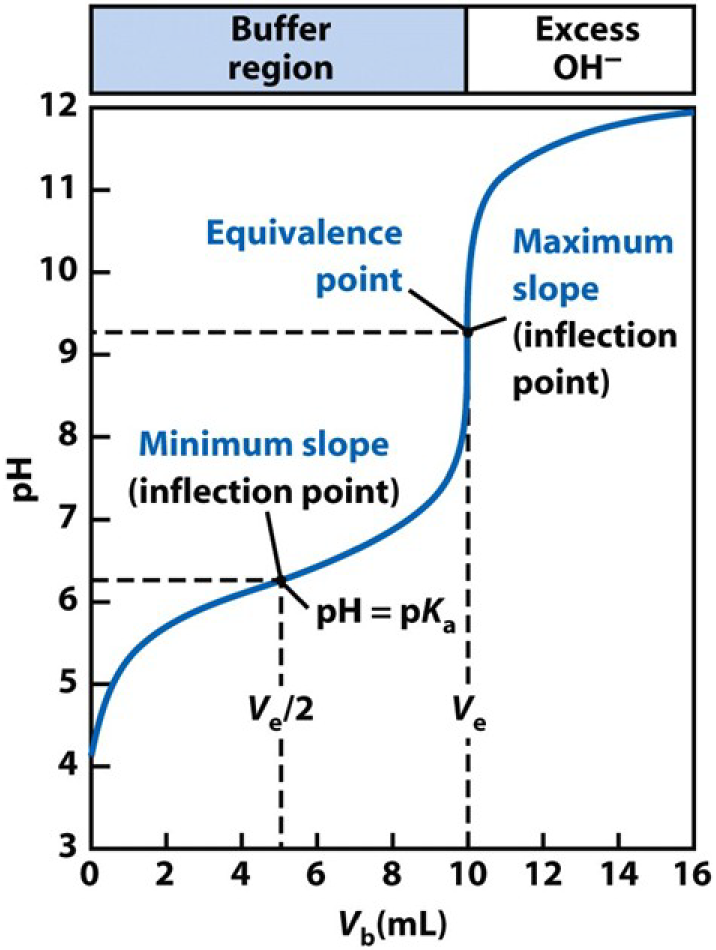

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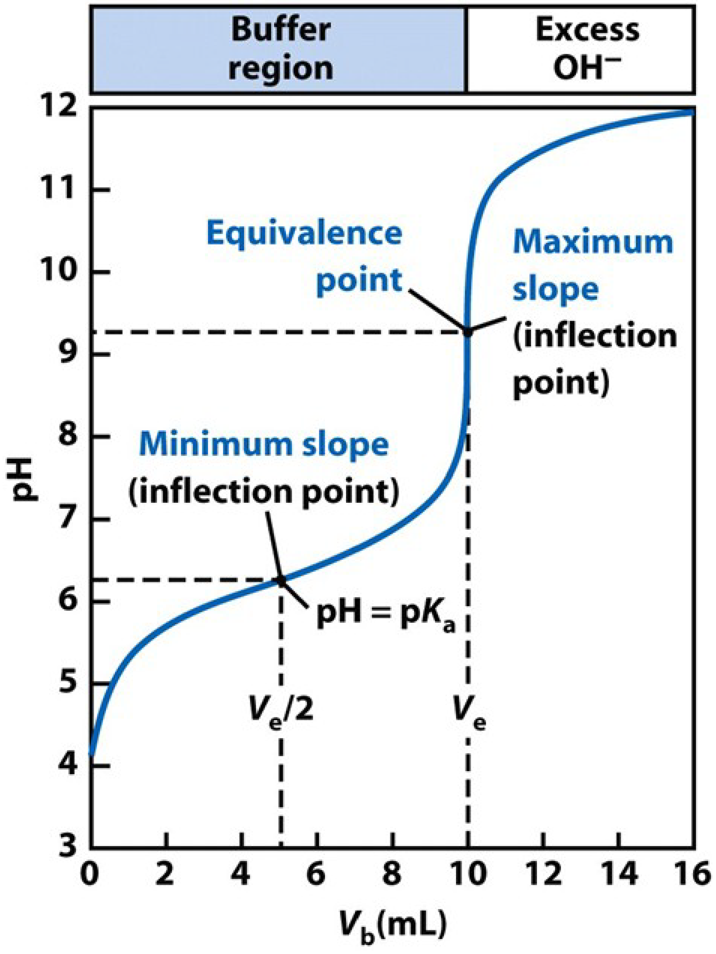
b) when 3.00 mL of NaOH is added buffer, $pH = pK_a + \log [A^-]/[HA]$

$pH = 6.27 + \log \{3(0.1) / [50(0.02) - 3(0.1)]\} =$ **5.90**



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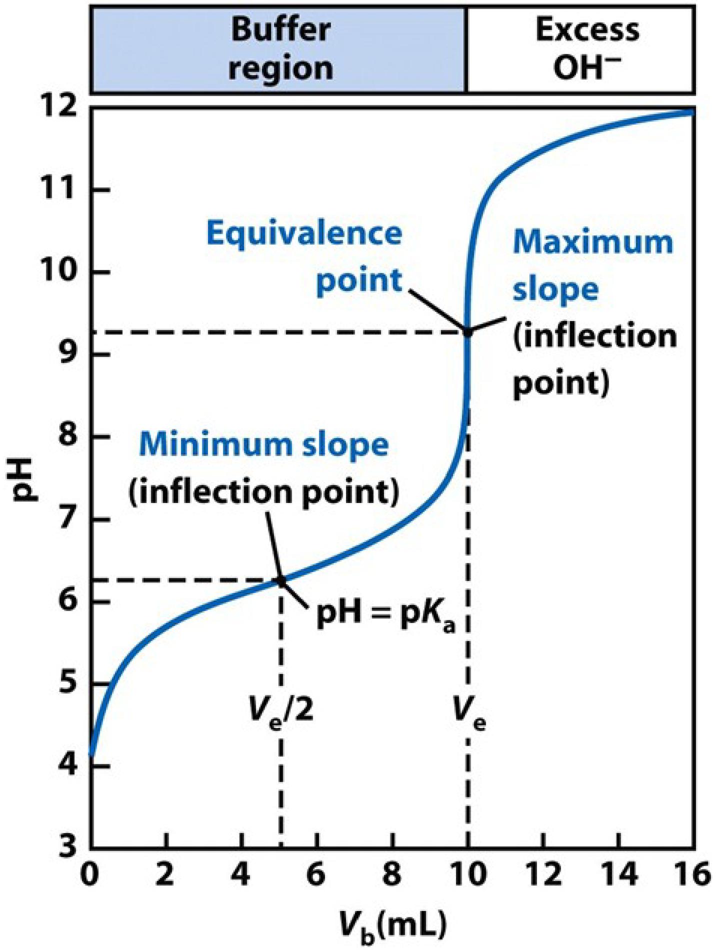

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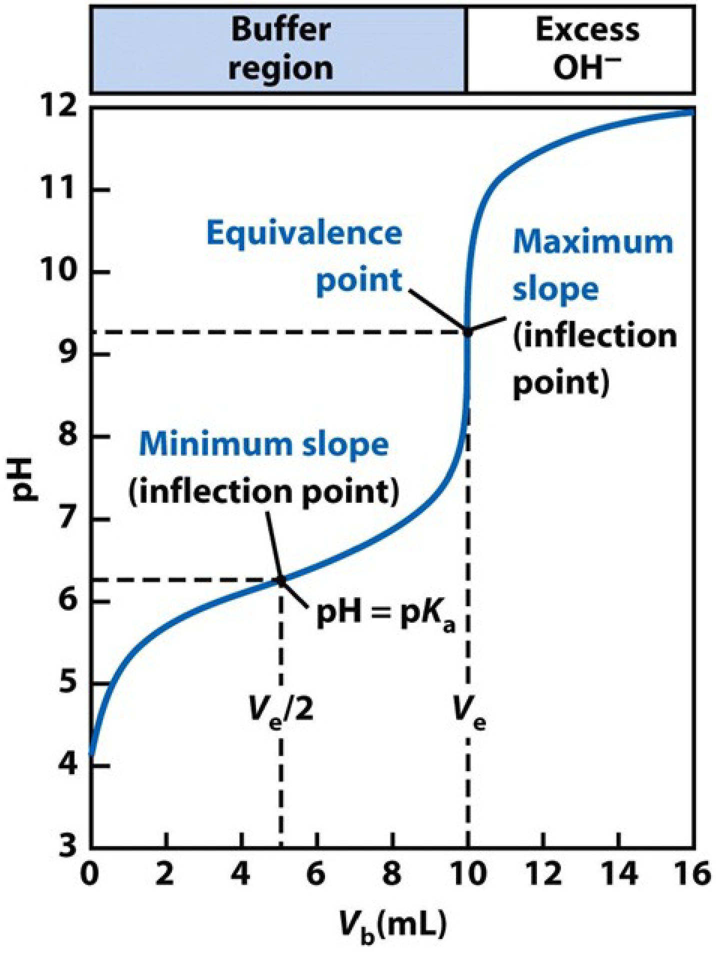
$K_b = K_w/K_a = x^2/[0.02(50/60)-x]$, $[OH^-] = 1.76 \times 10^{-5}$, pH = **9.25**



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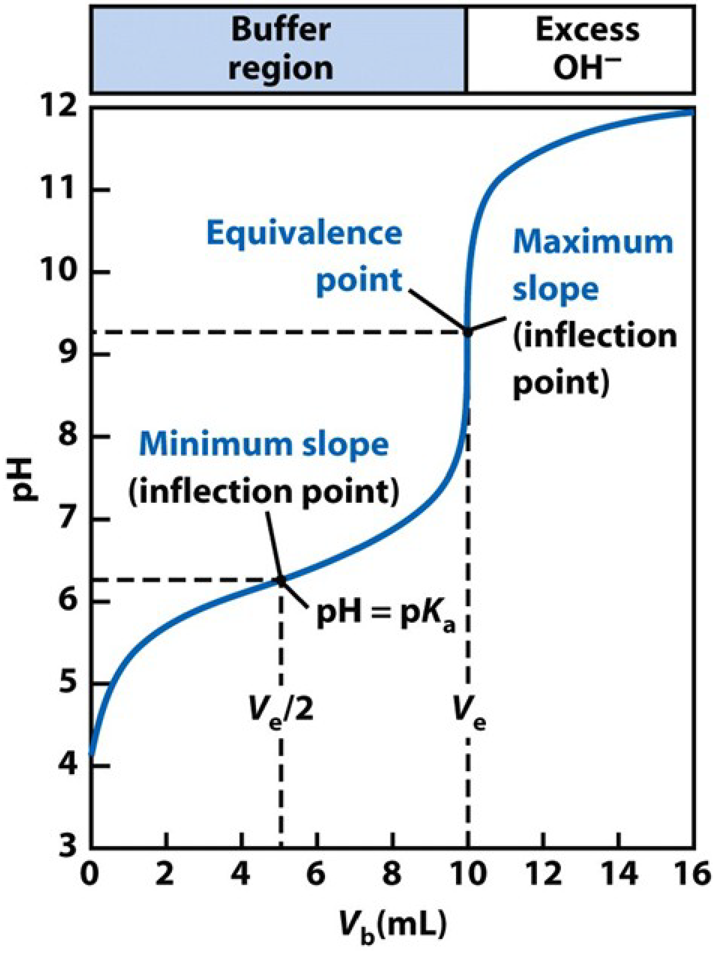
d) when 10.10 mL of NaOH is added excess OH^-



Weak Acid Titrations

EX 2. 50.00 mL 0.02000 M MES [2-(*N*-morpholino)ethane-sulfonic acid, p*Ka* = 6.27] titrated with 0.1000 M NaOH.

EQ PT: $n_{OH^-} = (MV)_{OH^-} = n_{H^+} = (MV)_{H^+} \Rightarrow V_e = V_{OH^-} = (50)(0.02)/0.1 =$ **10.00 mL**

a) before any base is added weak acid: $K = x^2/(F-x)$

$K_a = 10^{-6.27} = x^2 / (0.02 - x) \Rightarrow [H^+] = 1.04 \times 10^{-4} \Rightarrow pH =$ **3.98**

b) when 3.00 mL of NaOH is added buffer, $pH = pK_a + \log [A^-]/[HA]$

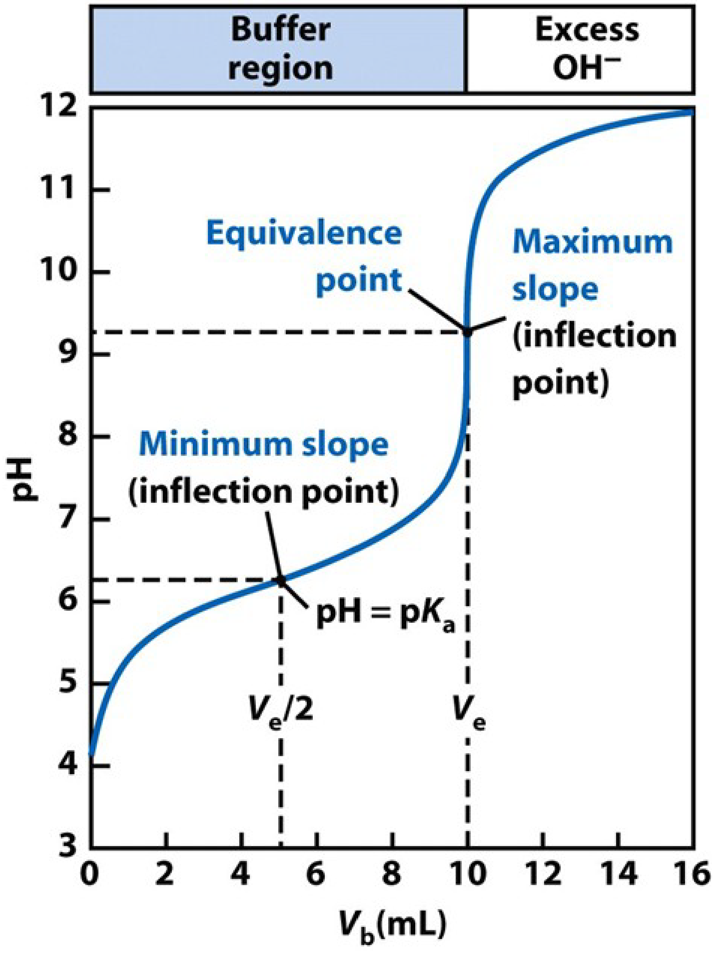
pH = 6.27 + log {3(0.1) / [50(0.02) - 3(0.1)]} = **5.90**

c) at the equivalence point $[OH^-] = [HA] \rightarrow A^-$, weak base: $K = x^2/(F-x)$

$K_b = K_w/K_a = x^2/[0.02(50/60)-x]$, $[OH^-] = 1.76 \times 10^{-5}$, pH = **9.25**

d) when 10.10 mL of NaOH is added excess OH^-

pH = 13.9956 + log {[(10.1)(0.1) - 50(0.02)] / 60.1} = **10.22**



Acid-Base Titrations - Weak

weak acid (base) titrated with strong base (acid):

weak acid (base):

strong base (acid) titrant:

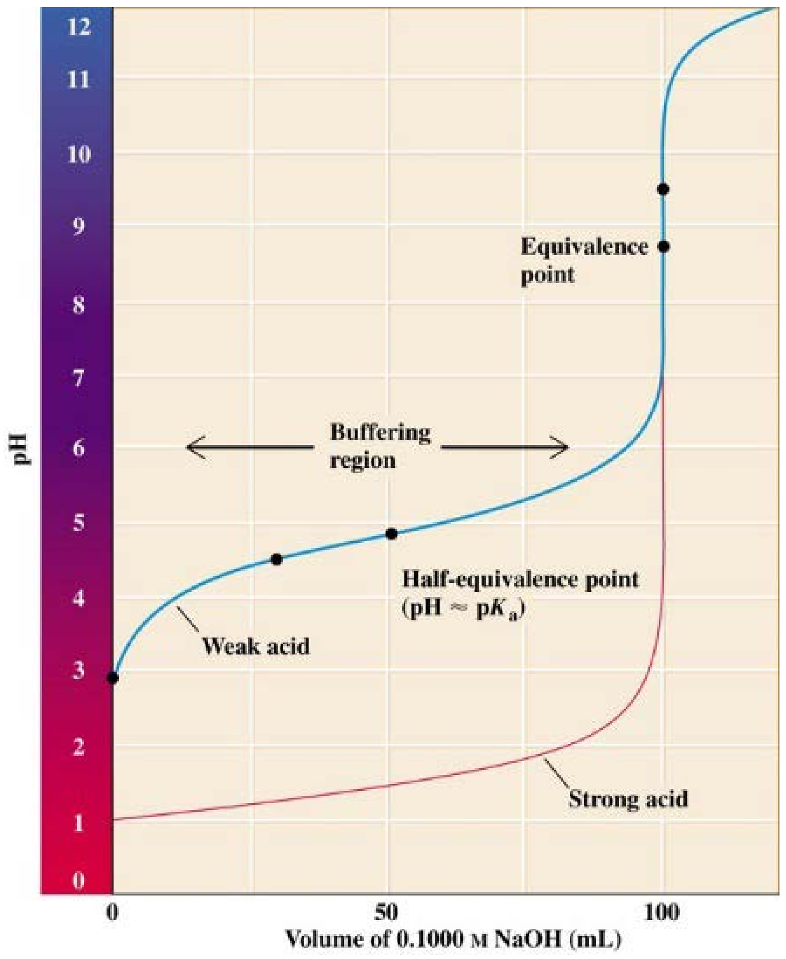
total ionic equation:

net ionic equation (what is *K*?):

titration curve - two inflection points

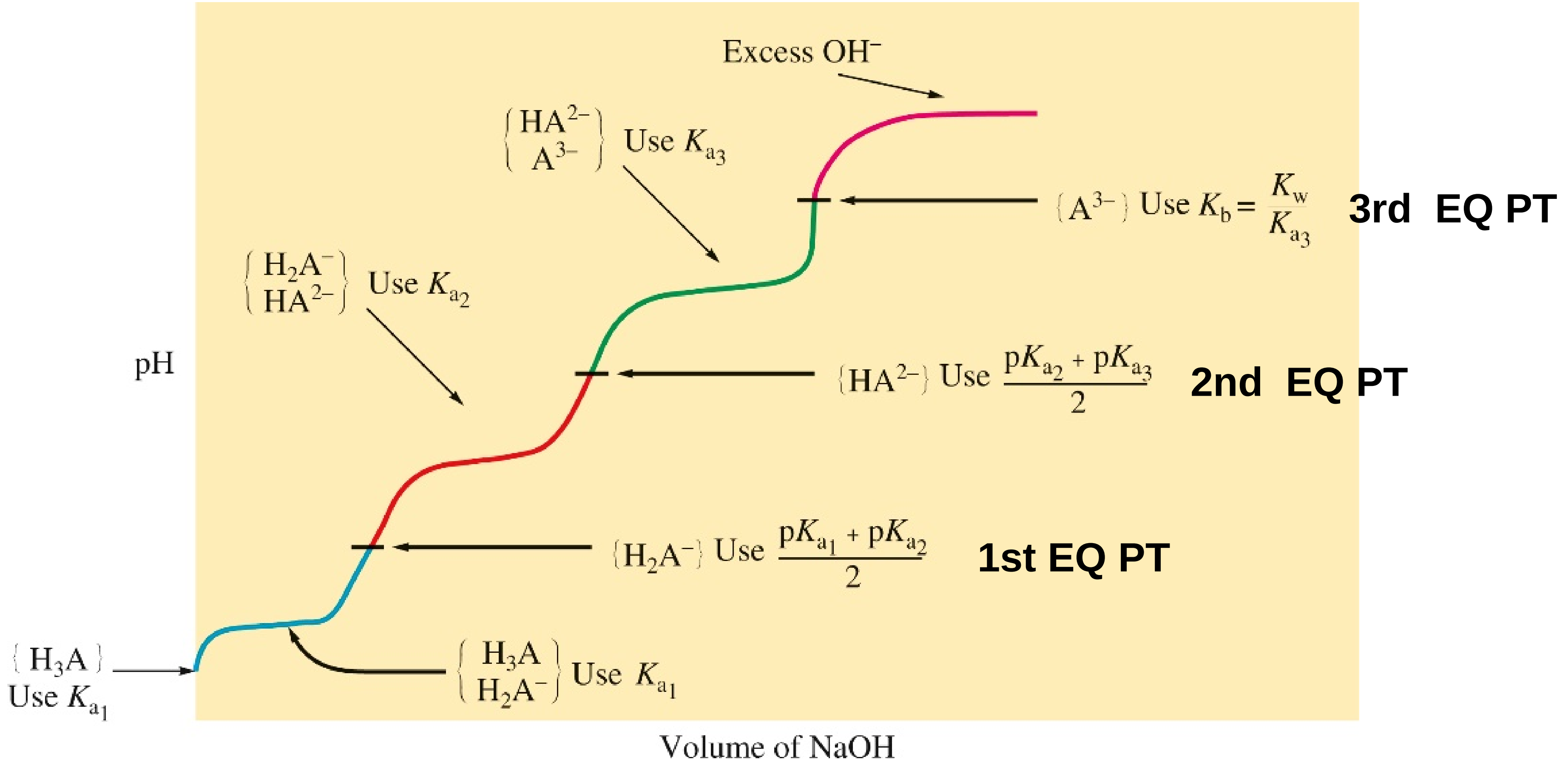
half-equivalence point (perfect 1/1 buffer)

equivalence point sol'n identical to conjugate base (acid) dissolved in water)



Polyprotic Titrations (Mostly Treated as a Buffer)

$$H_3A \rightarrow H_2A^- \rightarrow HA^{2-} \rightarrow A^{3-}$$



Levelling Effect

Acidity Constants in Water at 25°C

Acid	Formula	Conjugate Base	K_a	pK_a
Hydriodic	HI	I^-	$\approx 10^{11}$	≈ -11
Hydrobromic	HBr	Br^-	$\approx 10^{9}$	≈ -9
Perchloric	$HClO_4$	ClO_4^-	$\approx 10^{7}$	≈ -7
Hydrochloric	HCl	Cl^-	$\approx 10^{7}$	≈ -7
Chloric	$HClO_3$	ClO_3^-	$\approx 10^{3}$	≈ -3
Sulfuric (1)	H_2SO_4	HSO_4^-	$\approx 10^{2}$	≈ -2
Nitric	HNO_3	NO_3^-	≈ 20	≈ -1.3
Hydronium ion	H_3O^+	H_2O	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	6.6×10^{-1}	0.18
Iodic	HIO_3	IO_3^-	1.6×10^{-1}	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	5.9×10^{-2}	1.23
Sulfurous (1)	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.82
Sulfuric (2)	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Chlorous	$HClO_2$	ClO_2^-	1.1×10^{-2}	1.96
Sulfurous (2)	HSO_3^-	SO_3^{2-}	1.0×10^{-7}	7.00
Arsenic (2)	$H_2AsO_4^-$	$HAsO_4^{2-}$	9.3×10^{-8}	7.03
Hydrosulfuric	H_2S	HS^-	9.1×10^{-8}	7.04
Phosphoric (2)	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Hypochlorous	$HClO$	ClO^-	3.0×10^{-8}	7.52
Hydrocyanic	HCN	CN^-	6.2×10^{-10}	9.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Carbonic (2)	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Methylammonium ion	$CH_3NH_3^+$	CH_3NH_2	2.3×10^{-11}	10.64
Arsenic (3)	$HAsO_4^{2-}$	AsO_4^{3-}	3.0×10^{-12}	11.52
Hydrogen peroxide	H_2O_2	HO_2^-	2.4×10^{-12}	11.62
Phosphoric (3)	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.66
Water	H_2O	OH^-	1.0×10^{-14}	14.00
Hydrogen sulfide ion	HS^-	S^{2-}	1.0×10^{-19}	19.00
Hydrogen	H_2	H^-	1.0×10^{-33}	33.00
Ammonia	NH_3	NH_2^-	1.0×10^{-38}	38.00
Hydroxide ion	OH^-	O^{2-}		

acids stronger than H_3O^+

conjugate bases stronger than OH^-