

# CHEM 116 – Honors and Majors General and Analytical Chemistry I

3 Exams, 9 Quizzes, 10 Labs, 13 Weeks HWK - 875 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

## Class Averages

EXAM    288    64%

QZ        57     63%

LAB      165    83%

HWK     109    81%

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 15.2

E5 16.3

## Course Grade Estimate

A    75%

B    65%

C    50%

D    40%

**class average 71.2%**

**GPA 3.1**

# Titration

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H Ch 11

**FIND EQUIVALENCE POINT FIRST**

**CORRECT MOLARITY AS TITRANT IS ADDED**

- 10-1 The Intermediate Form**
- 11-4 Polyprotic (basic) Titrations**

**homework for week 14,15  
due dates this Wednesday  
and Friday**

**lab notebooks due on  
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

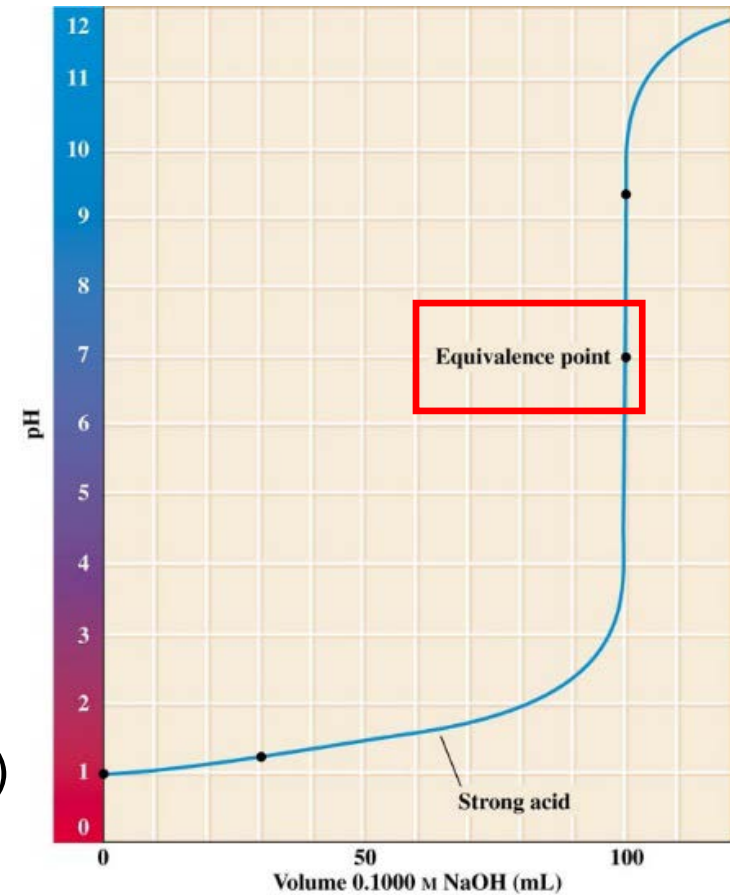
strong acid (base):

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.

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

a) before any acid is added **strong base**

$$\text{pH} = 13.9956 + \log(0.02000) = 12.2966 \Rightarrow \mathbf{12.297}$$

b) when 3.00 mL of HBr is added **excess OH<sup>-</sup>**

$$\text{pH} = 13.9956 + \log \{ [50(0.02) - 3(0.1)] / \mathbf{53} \} = \mathbf{12.116}$$

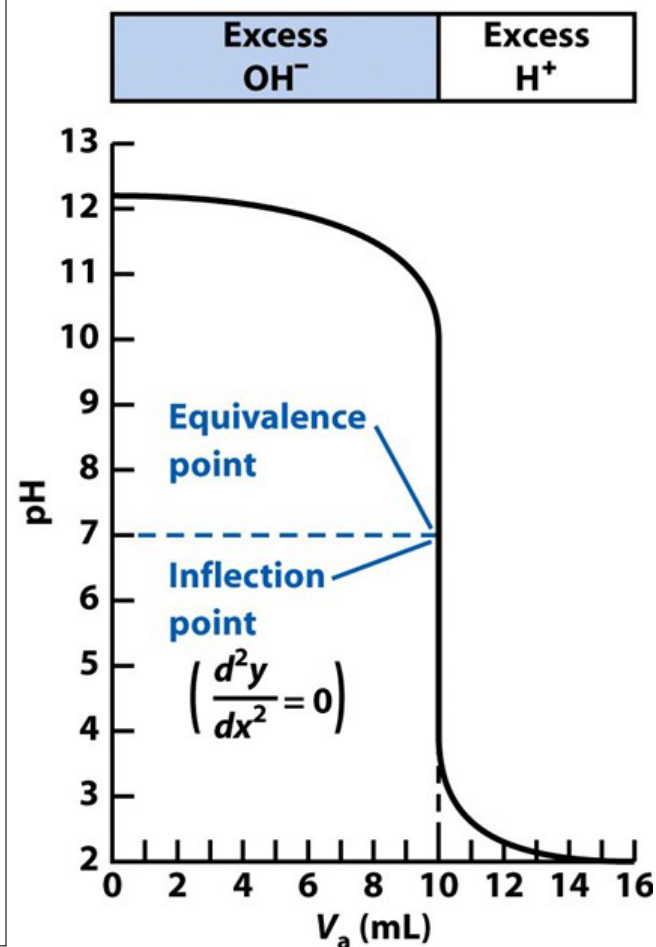
c) at the equivalence point **[H<sup>+</sup>] = [OH<sup>-</sup>]**

$$K_w = [\text{H}^+]^2 \Rightarrow [\text{H}^+] = \sqrt{K_w} \Rightarrow \text{pH} = \frac{1}{2} \text{p}K_w = 13.9956/2 = \mathbf{6.998}$$

d) when 10.50 mL of HBr is added **excess H<sup>+</sup>**

$$\text{pH} = -\log \{ [ (10.5)(0.1) - 50(0.02) ] / \mathbf{60.5} \} = 3.0827 \Rightarrow \mathbf{3.083}$$

$$\text{pH} = \text{p}K_w - \text{pOH}, \quad \text{p}K_w = -\log(1.01 \times 10^{-14}) = 13.9956$$



# Acid-Base Titrations - Weak

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

weak acid (base):

strong base (acid) titrant:

total ionic equation:

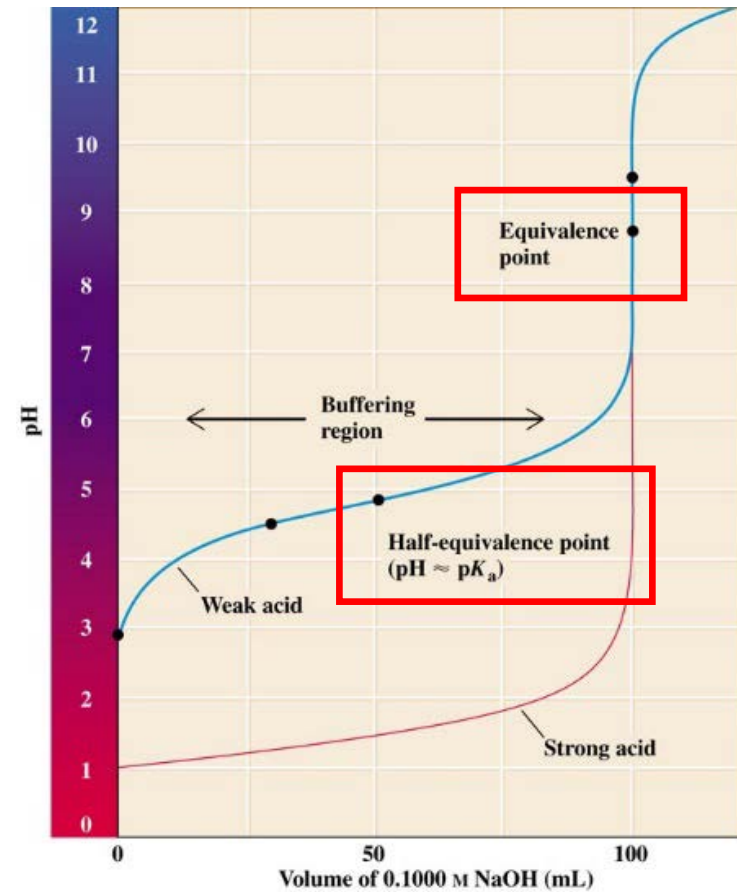
net ionic equation (what is  $K$ ):

titration curve - **two inflection points**

**half-equivalence point** (perfect 1/1 buffer)

**equivalence point**, solution identical to conjugate

base (acid) dissolved in water



# Weak Acid Titrations

**EX 2.** 50.00 mL 0.02000 M MES [2-(*N*-morpholino)ethanesulfonic acid,  $pK_a = 6.27$ ] 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:  $K = x^2/(F-x)$

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

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

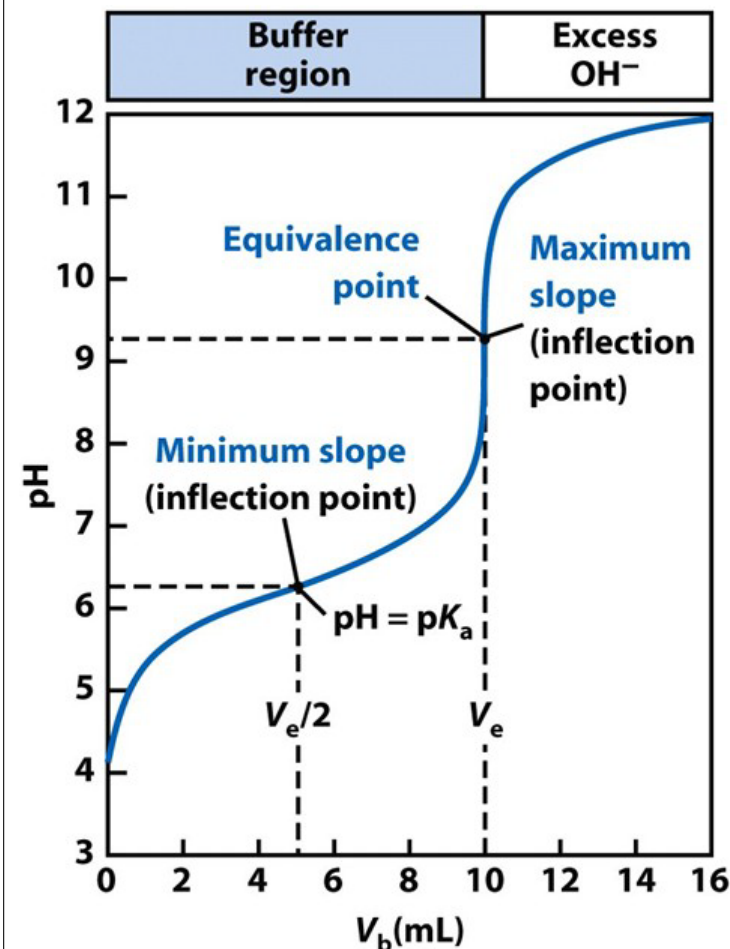
$$\text{pH} = 6.27 + \log \{3(0.1) / [50(0.02) - 3(0.1)]\} = 5.90$$

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

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

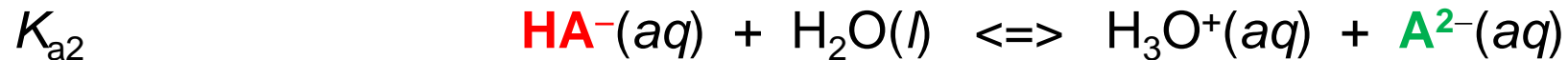
d) when 10.10 mL of NaOH is added excess  $OH^-$

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

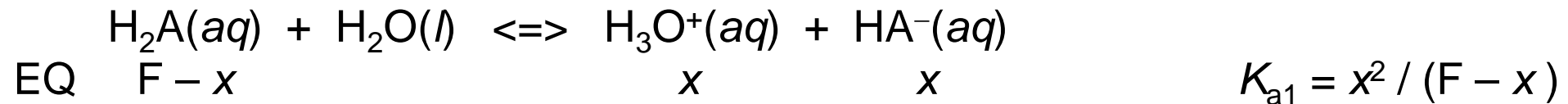


# Review Polyprotic Acids – Intermediate Form

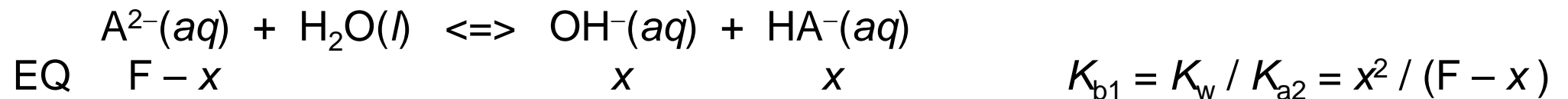
To determine the pH of  $H_2A$  or the salts  $NaHA$  or  $Na_2A$  which are all part of a diprotic system



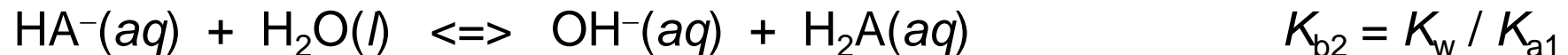
1) A solution of  $H_2A$ , with formal concentration  $F$ , is treated as if it were a monoprotic acid.



2) A solution of a salt containing the basic anion  $A^{2-}$ , with formal concentration  $F$ , is treated as if it were a monobasic base.



3) The species  $HA^-$  (as in a solution of  $NaHA$ ) is an **intermediate form** as it can behave as an acid ( $K_{a2}$  expression) or as a base (use square root formula)





# The Intermediate Form

A systematic approach can account for both the acidity and basicity of the intermediate form. It can be shown (we will accept Harris's derivation) that, with  $K_1 = K_{a1}$  and  $K_2 = K_{a2}$

$$[\text{H}^+] = \sqrt{\frac{K_1 K_2 [\text{HA}^-] + K_1 K_w}{K_1 + [\text{HA}^-]}}$$

If one started with NaHA ( $\text{Na}^+$  and  $\text{HA}^-$  in solution) the principal species in solution would be  $\text{HA}^-$  since  $K_{a2}$  and  $K_{b2}$  are very small. So the equilibrium  $[\text{HA}^-]$  can be replaced by F.

$$[\text{H}^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

Due to the small value of  $K_w$  it is often true that  $K_w \ll K_2 F$  so the term with  $K_w$  can be ignored

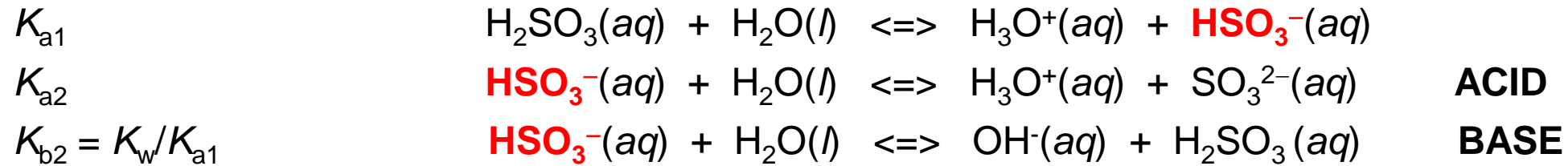
$$[\text{H}^+] \approx \sqrt{\frac{K_1 K_2 F}{K_1 + F}}$$

If  $\text{H}_2\text{A}$  is not too strong of an acid or F is not too dilute so that  $K_1 \ll F$  then

$$[\text{H}^+] \approx \sqrt{K_1 K_2} \quad \text{or} \quad \text{pH} \approx \frac{1}{2}(\text{p}K_1 + \text{p}K_2)$$

# An Application

**EX 3.** What is the pH of a 0.050 F aqueous solution of NaHSO<sub>3</sub>? For sulfurous acid  $K_{a1} = 0.0139$ ,  $K_{a2} = 6.73 \times 10^{-8}$  ( $pK_{a1} = 1.8569$ ,  $pK_{a2} = 7.1719$ )



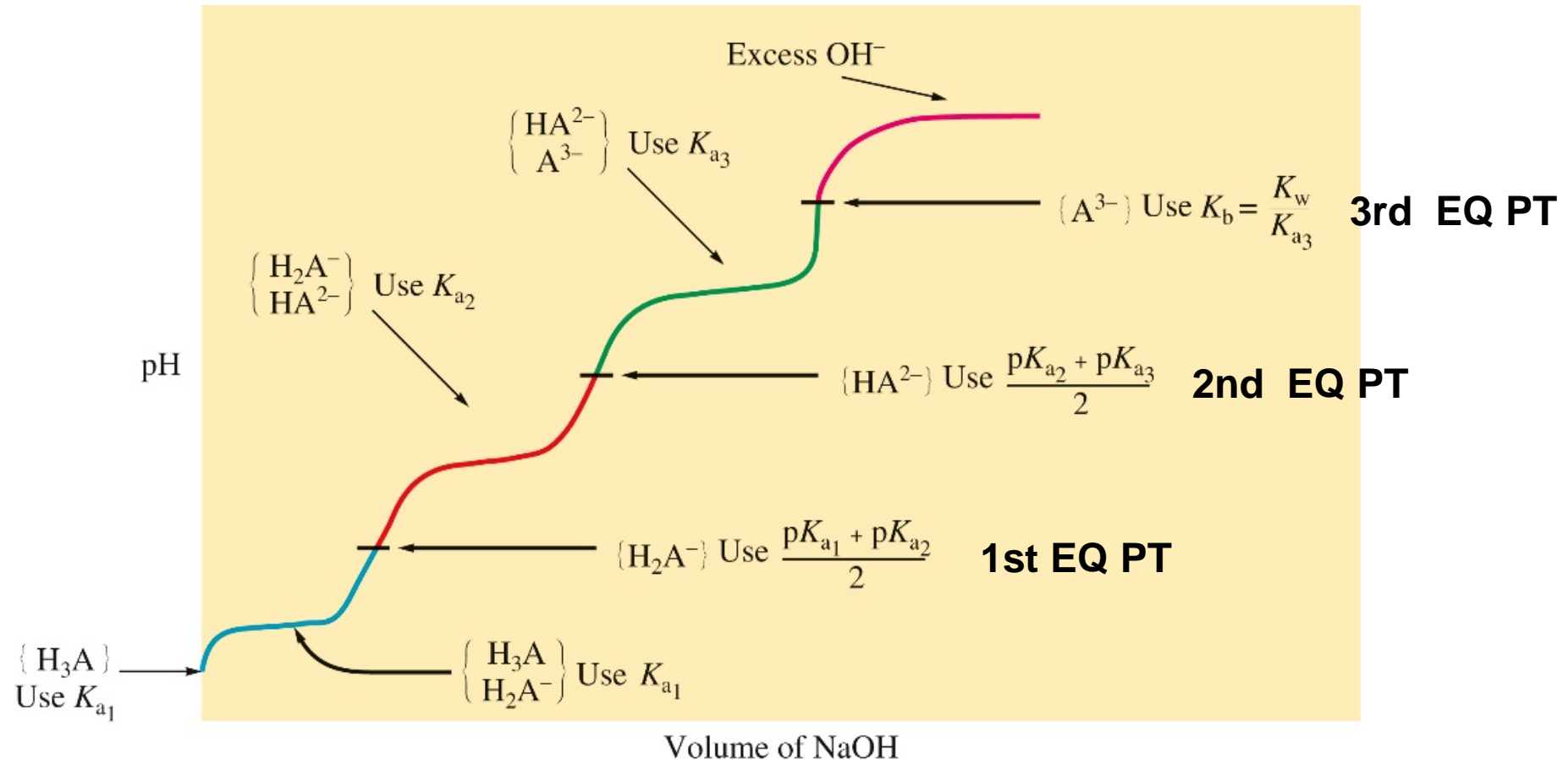
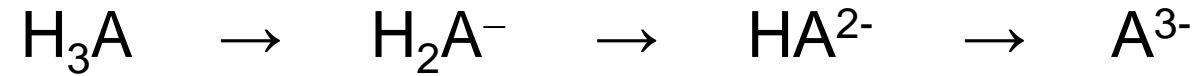
$$[\text{H}^+] = \sqrt{\frac{K_1 K_2 [\text{HA}^-] + K_1 K_w}{K_1 + [\text{HA}^-]}} = \sqrt{\frac{(0.0139)(6.73 \times 10^{-8})(0.05) + (0.0139)(1.01 \times 10^{-14})}{0.0139 + 0.05}} = 2.705 \times 10^{-5}$$

$\Rightarrow$  **pH = 4.57**

shortcut:  $\text{pH} = \frac{1}{2} (pK_{a1} + pK_{a2}) = \frac{1}{2} (1.8569 + 7.1719) = 4.51$

as a monoprotic:  $K_{a2} = x^2 / (0.05 - x) \Rightarrow x = [\text{H}^+] = 5.797 \times 10^{-5} \Rightarrow \text{pH} = 4.24$  (NG cannot ignore base)

# Polyprotic Titrations (Mostly Treated as a Buffer)



# Polybasic Titration

**EX 4.** 10.00 mL 0.100 M base  $pK_{b1} = 4.00$ ,  $pK_{b2} = 9.00$  titrated with 0.100 M HCl. ( $pK_{a1} = 5.00$ ,  $pK_{a2} = 10.00$ )



EQ PT:  $n_{\text{H}^+} = (\text{MV})_{\text{H}^+} = n_{\text{OH}^-} = (\text{MV})_{\text{OH}^-} \Rightarrow V_e = (10)(0.1)/0.1 = \mathbf{10.00 \text{ mL}}$ ,  $2V_e = \mathbf{20.00 \text{ mL}}$

a) before any acid is added (point A) weak base:  $K_{b1} = x^2 / (F - x)$   
 $10^{-4} = x^2 / (0.1 - x) \Rightarrow x = [\text{OH}^-] = 3.112 \times 10^{-3} \Rightarrow \text{pH} = \mathbf{11.49}$

b) when 1.5 mL of HCl is added  $\text{:B:} / \text{:BH}^+$  buffer  
 $\text{pH} = pK_{a2} + \log [\text{:B:}] / [\text{:BH}^+] = 10 + \log \{ [10(0.1) - 1.5(0.1)] / 1.5(0.1) \} = \mathbf{10.75}$

c) when 10.0 mL of HCl is added (point C) 1st EQ PT,  $\text{:B:} \rightarrow \text{:BH}^+$ , intermediate form  
 $\text{pH} = \frac{1}{2} (pK_{a1} + pK_{a2}) = \frac{1}{2} (5 + 10) = \mathbf{7.50}$

# Polybasic Titration

**EX 4.** 10.00 mL 0.100 M base  $pK_{b1} = 4.00$ ,  $pK_{b2} = 9.00$  titrated with 0.100 M HCl. ( $pK_{a1} = 5.00$ ,  $pK_{a2} = 10.00$ )



**EQ PT: 10.00 mL,  $2V_e = 20.00$  mL**

d) when 15.0 mL of HCl is added **2nd  $\frac{1}{2}$  EQ PT, 1/1 buffer of  $\text{:BH}^+/\text{BH}_2^{2+}$**

$$\text{pH} = pK_{a1} + \log 1 = \mathbf{5.00}$$

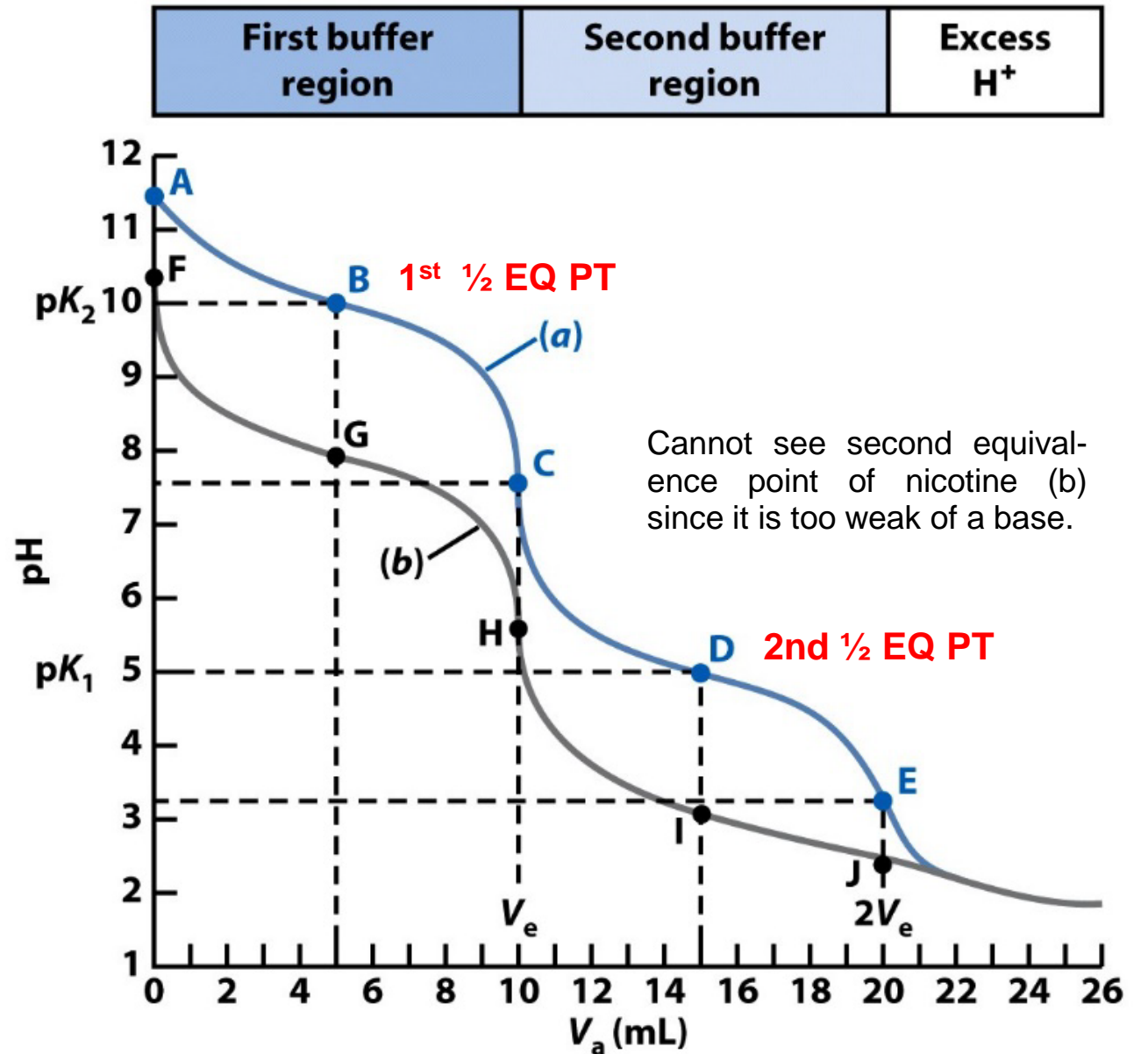
e) when 20.0 mL of HCl is added (point E) **2nd EQ PT,  $\text{:BH}^+ \rightarrow \text{BH}_2^{2+}$ , weak acid:  $K_{a1} = x^2 / (F - x)$**

$$10^{-5} = x^2 / [0.1(10/30) - x] \Rightarrow x = [\text{H}^+] = 5.723 \times 10^{-4} \Rightarrow \text{pH} = \mathbf{3.24}$$

f) when 25.0 mL of HCl is added **excess strong acid**

$$\text{pH} = -\log [(25 - 20)(0.1) / (25 + 10)] = \mathbf{1.85}$$

# Polybasic Titration



# Leveling Effect

Acidity Constants in Water at 25°C				
Acid	Formula	Conjugate Base	$K_a$	$pK_a$
Hydriodic	HI	$I^-$	$\approx 10^{11}$	$\approx -11$
Hydrobromic	HBr	$Br^-$	$\approx 10^9$	$\approx -9$
Perchloric	$HClO_4$	$ClO_4^-$	$\approx 10^7$	$\approx -7$
Hydrochloric	HCl	$Cl^-$	$\approx 10^7$	$\approx -7$
Chloric	$HClO_3$	$ClO_3^-$	$\approx 10^3$	$\approx -3$
Sulfuric (1)	$H_2SO_4$	$HSO_4^-$	$\approx 10^2$	$\approx -2$
Nitric	$HNO_3$	$NO_3^-$	$\approx 20$	$\approx -1.3$
Hydronium ion	$H_3O^+$	$H_2O$	1	0.0
Urea acidium ion	$(NH_2)CONH_3^+$	$(NH_2)_2CO$ (urea)	$6.6 \times 10^{-1}$	0.18
Iodic	$HIO_3$	$IO_3^-$	$1.6 \times 10^{-1}$	0.80
Oxalic (1)	$H_2C_2O_4$	$HC_2O_4^-$	$5.9 \times 10^{-2}$	1.23
Sulfurous (1)	$H_2SO_3$	$HSO_3^-$	$1.5 \times 10^{-2}$	1.82
Sulfuric (2)	$HSO_4^-$	$SO_4^{2-}$	$1.2 \times 10^{-2}$	1.92
Chlorous	$HClO_2$	$ClO_2^-$	$1.1 \times 10^{-2}$	1.96

acids stronger  
than  $H_3O^+$

Sulfurous (2)	$HSO_3^-$	$SO_3^{2-}$	$1.0 \times 10^{-7}$	7.00
Arsenic (2)	$H_2AsO_4^-$	$HA_2O_4^{2-}$	$9.3 \times 10^{-8}$	7.03
Hydrosulfuric	$H_2S$	$HS^-$	$9.1 \times 10^{-8}$	7.04
Phosphoric (2)	$H_2PO_4^-$	$HPO_4^{2-}$	$6.2 \times 10^{-8}$	7.21
Hypochlorous	HClO	$ClO^-$	$3.0 \times 10^{-8}$	7.52
Hydrocyanic	HCN	$CN^-$	$6.2 \times 10^{-10}$	9.21
Ammonium ion	$NH_4^+$	$NH_3$	$5.6 \times 10^{-10}$	9.25
Carbonic (2)	$HCO_3^-$	$CO_3^{2-}$	$4.8 \times 10^{-11}$	10.32
Methylammonium ion	$CH_3NH_3^+$	$CH_3NH_2$	$2.3 \times 10^{-11}$	10.64
Arsenic (3)	$HA_2O_4^{2-}$	$AsO_4^{3-}$	$3.0 \times 10^{-12}$	11.52
Hydrogen peroxide	$H_2O_2$	$HO_2^-$	$2.4 \times 10^{-12}$	11.62
Phosphoric (3)	$HPO_4^{2-}$	$PO_4^{3-}$	$2.2 \times 10^{-13}$	12.66
Water	$H_2O$	$OH^-$	$1.0 \times 10^{-14}$	14.00
Hydrogen sulfide ion	$HS^-$	$S^{2-}$	$1.0 \times 10^{-19}$	19.00
Hydrogen	$H_2$	$H^-$	$1.0 \times 10^{-33}$	33.00
Ammonia	$NH_3$	$NH_2^-$	$1.0 \times 10^{-38}$	38.00
Hydroxide ion	$OH^-$	$O^{2-}$		

bases stronger  
than  $OH^-$