Chemistry BC2001x: General Chemistry I

Lecture 16: Tuesday November 10, 2009

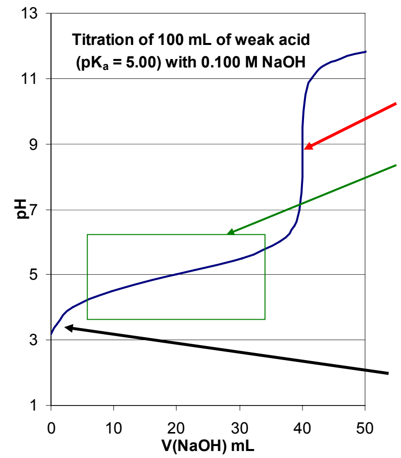
Topics: Diprotic acid titrations; distribution diagrams

Pick up

(1) Acid-base distribution diagrams
This topic is not covered in Chang.

(2) Graded Problem Set 7

Titration of a weak acid with strong base



Review from last lecture:

Adding base so pH rises throughout

at Ve = 40.0 mL: very steep change

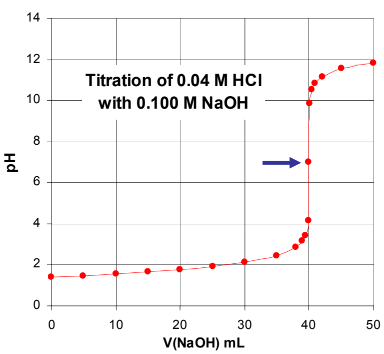
Buffer region: 10% to 90% of V_e:
pH rises slowly.

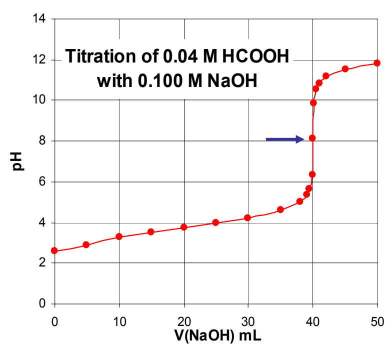
Halfway to equivalence, pH = pK_a

Equivalence point has pH > 7:
weak acid HA has been converted to conjugate weak base A^-.

(When the acid is quite weak, there is a small steeper rise in pH at the very beginning.)

Comparison of strong/weak titration curves



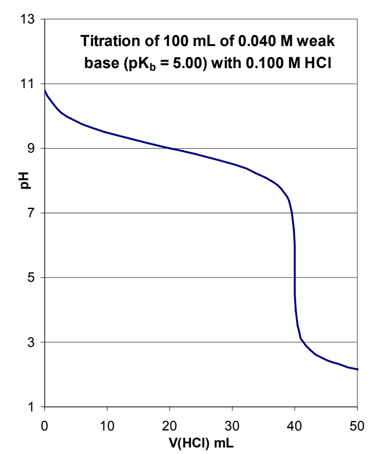


Both have very steep jump at V_e. pH at V_e differs (> 7 for weak).

Identical after V_e.

Before V_e: weak acid has larger pH throughout, somewhat steeper rise in buffer region. Sometimes a brief steeper climb at the beginning.

Titration of a weak base with strong acid



Adding acid: pH falls throughout

at V_e = 40.0 mL: steep change

Halfway to equivalence, pH = pK_a

(pK_b = 5 so pK_a = 14 - 5 = 9)

Equivalence point has pH < 7:
weak base B has been converted to conjugate weak acid HB^+.

Calculations very similar to those for weak acid; see problem set 8.

Distribution diagrams: monoprotic acid

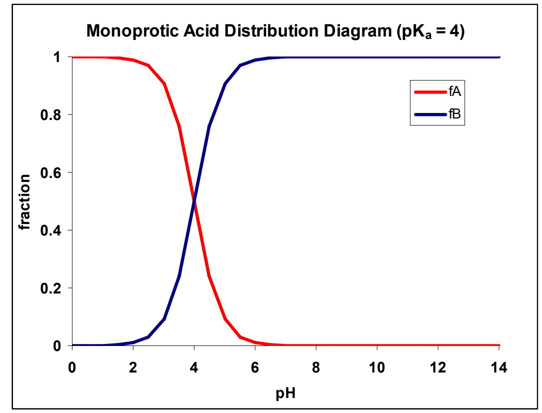
Let f_B = fraction in basic form (A^-)
and f_A = fraction in acidic form (HA)
$f_B = [A^-]/\{[A^-]+[HA]\}$
$1/f_B = \{[A^-]+[HA]\}/[A^-] = 1 + [HA]/[A^-]$
$K_a = [H^+][A^-]/[HA] \rightarrow [HA]/[A^-] = [H^+]/K_a$
$1/f_B = 1 + [H^+]/K_a = \{K_a + [H^+]\}/K_a$

$$f_B = K_a/\{K_a + [H^+]\}$$

$$f_A = (1 - f_B) = [H^+]/\{K_a + [H^+]\}$$

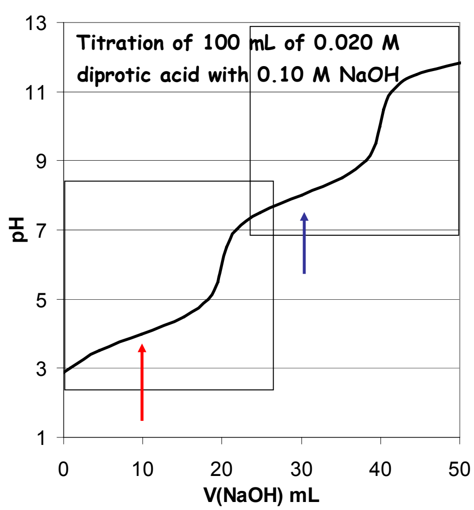
For a given K_a, we will plot f_A and f_B vs. pH
(Do not memorize these equations!)
(Observe: only pH and K_a, not concentration of the weak acid or base, enter into calculations of f's!)

Distribution diagrams: monoprotic acid



The shapes are the same for all weak acids;
the curves simply shift left/right so they cross at pH = pK_a

Diprotic acid titration: qualitative facts



CASE I:

Big difference in K_a's:

pK_{a1} = 4.00 and pK_{a2} = 8.00

$K_{a1}/K_{a2} = 10^4$ = 10,000

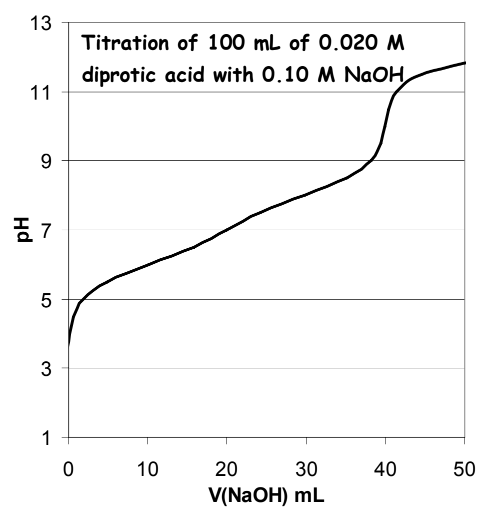
pH rises steeply both at V_{1e} (20 mL) and V_{2e} (40 mL)

looks like sequential monoprotic titration curves

Halfway to V_{1e} pH = pK_{a1}

Halfway between V_{1e} and V_{2e}, pH = pK_{a2}

Diprotic acid titrations



CASE II: less difference

pK_{a1} = 6.00 and pK_{a2} = 8.00

K_{a1}/K_{a2} = 100

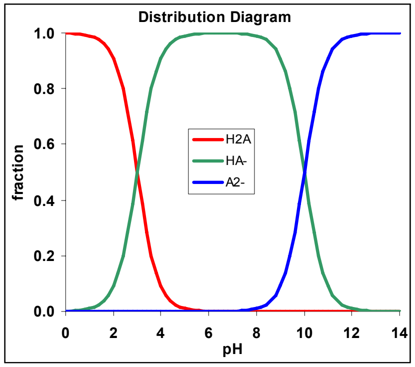
pH rises steeply at V_{2e} but not at V_{1e}

The two stages of hydrolysis are overlapping:

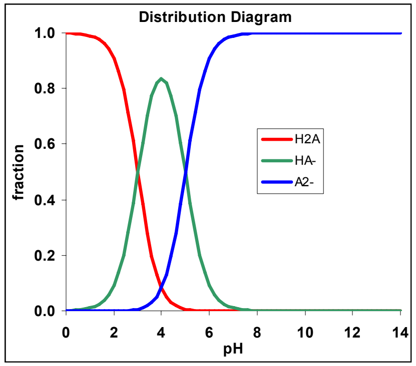
$H_2A \rightarrow H^+ + HA^-$ step incomplete when

$HA^- \rightarrow H^+ + A^{2-}$ begins to occur.

Distribution diagrams: diprotic acids

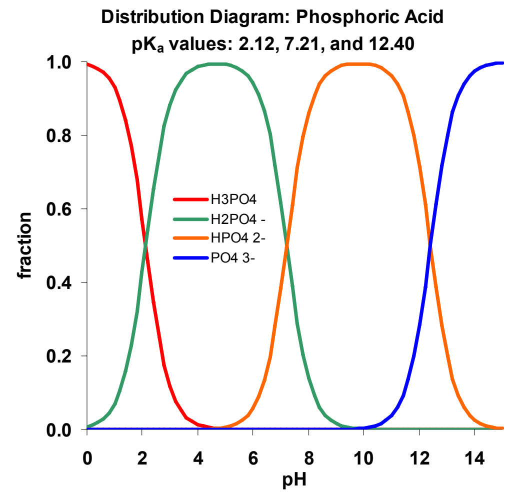


pK_{a1} = 3 and pK_{a2} = 10



pK_{a1} = 3 and pK_{a2} = 5

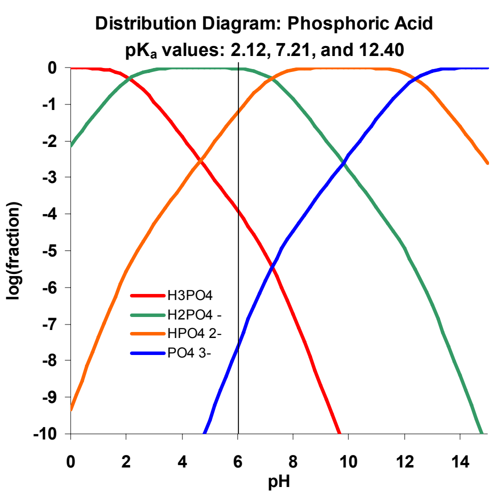
Distribution diagram: triprotic acid H_3PO_4



pH	dominant form
< 2.1	H_3PO_4
2.1 – 7.2	$H_2PO_4^-$
7.2 – 12.5	HPO_4^{2-}
> 12.4	PO_4^{3-}

In commonly used "phosphate buffers" with pH around 7, the two important species are $H_2PO_4^-$ and HPO_4^{2-}, whose ratio is governed by K_{a2}. [H_3PO_4] and [PO_4^{3-}] are negligible, so K_{a1} and K_{a3} have no effect on the pH.

Distribution diagram: triprotic acid H_3PO_4



logarithmic version (look at y-axis) (to see smaller values):

at pH = 6:

most is $H_2PO_4^-$

between 1 & 10% HPO_4^{2-}

about 0.01% H_3PO_4

10^{-6} % PO_4^{3-}

Distribution diagrams

Not used for calculations, but show clearly how and why we can make useful approximations with acid/base solutions.

Simply by considering the pK_a's of the acid, and the pH of the solution, we can say which species are present in large amount, and which are negligible.

For weak monoprotic acid, if pH is 2 units less that pK_a or less, 99+% will be in form HA, less than 1% A^-.

For a diprotic acid, if pH << pK_{a2}, to find pH or H^+, we can ignore A^{2-}, and focus only on the species involved in K_{a1}, H_2A and HA^-

For a diprotic acid, if pH >> pK_{a1}, to find pH or H^+, we can ignore H_2A, and focus only on the species involved in K_{a2}, HA^- and A^{2-}

For phosphoric acid with pH between about 4 and 10, both H_3PO_4 and PO_4^{3-} are negligible. The pH can be found considering $H_2PO_4^-$ and HPO_4^{2-} only, and the K between them: K_{a2}.