Determining the pK Value of a Titratable Group: Single or Multiple End-points

Use graphic (http://www.drcarman.info/biol251/aatrshn.jpg) with text – note color-coded circled numbers – for all determinations.

Single End-point Determination (E.g., HOAc)

To determine a single pK value (e.g., a weak acid such as HOAc as in CHEM 121), begin with the far left sets of images (top and bottom, far left) that use the yellow background numbers.

Step 1) Determine the value in mL at the endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 5 mL.

Steps 2 & 3) Split the difference between the 5 mL and the origin (0 mL; step 2), which is 2.5 mL (step 3).

Step 4) Read up to the pH curve (red curve) at 2.5 mL.

Step 5) Draw a parallel line to the left onto the pH curve.

Step 6) Where the line intersects is the pK value. This can be quite cumbersome.

Excel's **advantages** are illustrated in the bottom left image.

Steps 1-4) Still perform these steps in your head (or on paper as need be).

Steps 5-6) Skip!

Step 7) Click inside the chart area to "turn on" the graph in Excel and move your cursor over the 2.5 mL line ON the pH curve (red line).

Step 8) A pop-up (or down) window will appear with the corresponding pH value in it which is your pK value.

NOT SHOWN: insert a text box and key in your pK value. If this was HOAc, this would be the pK_{a1}. If it were an amino acid this would be your pK_{COOH}.

Multiple End-point Determinations
(E.g., Any Amino Acid or Mineral Acid with $\geq$ 2 Titratable Protons)

To determine the **first pK value** (e.g., an amino acid as in BIOL 223 and 251 and CHEM 220), begin with the far left sets of images (top and bottom, far left) that use the yellow background numbers.

Step 1) Determine the value in mL at the endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 5 mL.

Steps 2 & 3) Split the difference between the 5 mL and the origin (0 mL; step 2), which is 2.5 mL (step 3).

Step 4) Read up to the pH curve (red curve) at 2.5 mL.

Step 5) Draw a parallel line to the left onto the pH curve.

Step 6) Where the line intersects is the pK value. This can be quite cumbersome.

Excel's **advantages** are illustrated in the bottom left image.

Steps 1-4) Still perform these steps in your head (or on paper as need be).

Steps 5-6) Skip!

Step 7) Click inside the chart area to "turn on" the graph in Excel and move your cursor over the 2.5 mL line ON the pH curve (red line).

Step 8) A pop-up (or down) window will appear with the corresponding pH value in it which is your pK value.

NOT SHOWN: insert a text box and key in your pK value. This is the pK_{COOH}.

To determine the **second pK value** (e.g., an amino acid as in BIOL 223 and 251 and CHEM 220), begin with the middle sets of images (top and bottom) that use the blue background numbers.

Step 1) Determine the value in mL at the FIRST endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 5 mL.

Step 2) Determine the value in mL at the SECOND endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 11 mL.

Steps 3 & 4) Split the difference between the 5 mL and the 11 mL (step 3), which is 3 mL (step 4).

Step 5) Read up to the pH curve (red curve) at 8 mL.

Step 6) Draw a parallel line to the left onto the pH curve.

Step 7) Where the line intersects is the pK value. This can be quite cumbersome.

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Steps 1-5) Still perform these steps in your head (or on paper as need be).

Steps 6-7) Skip!

Step 8) Click inside the chart area to "turn on" the graph in Excel and move your cursor over the 8 mL line ON the pH curve (red line).

Step 9) A pop-up (or down) window will appear with the corresponding pH value in it which is your pK value.

NOT SHOWN: insert a text box and key in your pK value. **Excepting** histidine, glutamate and aspartate, this is the pK_{NH2}. If this was histidine, this would be the pK_R (imidazole ring); if it were glutamate or aspartate, this would the the pK_R (carboxylate group).

To determine the **third pK value** (e.g., an amino acid as in BIOL 223 and 251 and CHEM 220), begin with the far right sets of images (top and bottom, far right) that use the green background numbers.

Step 1) Determine the value in mL at the SECOND endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 11 mL.

Step 2) Determine the value in mL at the THIRD endpoint using the first derivative curve (dpH/dV scale; blue line). In the example, that value is 15.75 mL.

Steps 3 & 4) Split the difference between the 11 mL and the 15.75 mL (step 3), which is 2.375 mL (step 4).

Step 5) Read up to the pH curve (red curve) at 13.375 mL.

Step 6) Draw a parallel line to the left onto the pH curve.

Step 7) Where the line intersects is the pK value. This can be quite cumbersome.

Excel's **advantages** are illustrated in the bottom left image.

Steps 1-5) Still perform these steps in your head (or on paper as need be).

Steps 6-7) Skip!

Step 8) Click inside the chart area to "turn on" the graph in Excel and move your cursor over the 13 mL line ON the pH curve (red line).

Step 9) A pop-up (or down) window will appear with the corresponding pH value in it which has a pH value at 13 mL (11.56 in this example).

Step 10) Repeat Step 8 on the 13.5 mL line. A pop-up (or down) window will appear with the corresponding pH value in it which has a pH value at 13.5 mL (11.66 in this example).

NOTE: We used the two volume values (13 mL and 13.5 mL) because we did NOT titrate to 0.25 mL volumes, hence, we split the difference at/between the two readings.

Step 11) Add up the two pH values and divide their sum by 2. This is your 3d pK value (11.61 in this example).

NOT SHOWN: insert a text box and key in your pK value. For histidine, glutamate and aspartate, this is the pK_{NH2}. If this was the titration of arginine, this would be the pK_R (guanidino group); if it were the titration of lysine, this would be the pK_R (ε-amine).